TRIS(1,3-DIHYDROXY-2-PROPYL)AMINE, A PLANAR TRIALKYLAMINE:

SYNTHESIS, STRUCTURE, AND PROPERTIES.

A POTENTIAL PRECURSOR TO HYPERVALENT NITROGEN

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DISSERTATION ABSTRACT

TRIS(1,3-DIHYDROXY-2-PROPYL)AMINE, A PLANAR TRIALKYLAMINE: SYNTHESIS, STRUCTURE, AND PROPERTIES. A POTENTIAL PRECURSOR TO HYPERVALENT NITROGEN

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The hindered amine tris(1,3-dihydroxy-2-propyl)amine, **36**, is a potential precursor to possible examples of nitrogen hypervalency. There are no simple, effective, and general methods to synthesize hindered tertiary amines. Extending previous work in our laboratory on $Rh_2(OAc)_4$-catalyzed insertions of carbenoids into N-H bonds, we achieved a synthesis of **36** in five steps and 49% overall yield. Starting from commercially available dihydroxyacetone dimer, our synthesis makes **36** available in multigram quantities.

Some properties and structure of **36** have been studied. The *p*K_a of **36** was found to be 3.08 ± 0.03, a low value for a tertiary amine. The X-ray crystal structure of **36** showed the nitrogen is essentially planar (sum of C-N-C angles 359.05(7) °), and the average C-N bond length (1.454 Å) was shorter than normal. An explanation of this bond contraction is offered. The oxidation potential $E_{1/2}^{ox}$ of **36** measured by cyclic voltammetry was found to be 0.88 V. The oxidation was reversible; oxidations of ordinary tertiary amines are usually irreversible. The X-ray crystal structure of **36**·HCl revealed a severely flattened tetrahedral geometry about nitrogen (average H-N-C angle 102.3 °).

The reaction of **36** with boric acid led to a "one- boron" compound, **67** (2,8,9-tris(hydroxymethyl)-5-bora-1-aza-4,6,11-trioxytricyclo[3.3.3.$0^{1,5}$]undecane) and a "two-boron" compound, **69** (1,7-dibora-11-aza-2,6,8,14,15,17-hexaoxytetracyclo-[8.4.2.$2.^{7,12}0^{4,11}$]octadecane). The X-ray crystal structure of **67** showed a dative bond between nitrogen and boron (1.6875(13) Å). Compound **69** is very hydrolytically unstable, but the X-ray crystal structure of a complex of **69** with pyridine confirmed the presence in **69** of two borons.

The reaction of **36** with Z-Si$(OEt)_3$ (Z = Me, Ph) led to analogous "one-silicon" and "two-silicon" compounds. The X-ray crystal structures of both two-silicon compounds revealed a nearly symmetrical SiNSi array (Z = Me) and an unsymmetrical one (Z = Ph).

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INTRODUCTION

The Octet Rule which was provided by Lewis[1] and Langmuir[2] has been considered a central dogma governing chemical bonding in organic molecules for a long time. The Octet Rule means molecular electron bonds are most stable when the atoms achieve a noble gas configuration. However, it is clear that this rule has its limitations. For example, PCl_5 has ten electrons about the phosphorus. More surprisingly, XeF_4 and XeF_2 were synthesized by Claassen, Selig, and Malm[3] in 1962. According to the Octet Rule, the rare-gas atoms should be inert due to their full valence shells. The Octet Rule has never been able to provide a good theoretical treatment for such compounds. Obviously a new theory to explain these compounds was needed.

1.1 Hypervalent bond

In 1969, J. I. Musher[4] established the concept of hypervalent molecules: they are ions or molecules having elements bearing more electrons than the octet (nine or more) within a valence shell. He also suggested there were two methods to form hypervalent bonds: (1) make up a dsp^3 or d^2sp^3 orbital by hybridization using higher-lying d orbitals or (2) make up highly ionic orbitals revising (modifying) the basic idea of Lewis that a bond is formed by a localized pair of two electrons.

The expansion of the octet has traditionally been explained by participation of d orbitals in hybridization. Smith and coworkers[5] used the experimentally determined bond lengths of XeF_2 and XeF_4 to support covalent models with ten electrons in the xenon valence shell of XeF_2, and twelve electrons in the xenon valence shell of XeF_4. In explanation of the bonding schemes, they used the then-popular theory of an sp^3d hybridized configuration for XeF_2, and sp^3d^2 hybridized configuration for XeF_4. d-Orbitals cannot be utilized to hold extra electrons if the energy gap between n(sp) and n(d) is too large. The second row elements (*i.e.* Li – Ne) have high-energy d orbitals, therefore traditionally hypervalency has been thought possible only for third row elements (*i.e.* Na – Ar) and beyond.

In 1951, Pimentel[6] and, independently, Rundle[7] set up the basis for new developments in this area by proposing the idea of a three-center four-electron (3c-4e) bond, employing molecular orbital theory. However, the idea of a 3c-4e bond was widely ignored initially. It gradually came to be used only when d orbital hybridization apparently could not be supported. So Pimentel and Spratley[8] refuted the conclusions that Smith and coworkers had drawn about covalent models for XeF_2 and XeF_4, and they insisted that the bonding scheme involved the 3c-4e interaction. Later, Musher[4] further developed the theory of hypervalent bonding that Pimentel had proposed in 1951, and introduced hybrid orbital wave functions, atomic "geminals," for this type of bond. Schleyer and Reed[9] investigated the bonding of hypervalent molecules theoretically and reached the conclusion that employing dsp^3 or $d^2sp^3$is not at all correct and rather misleading. Through this and the efforts of Kutzelnigg and coworkers,[10] the idea of a 3c-4e bond has become supported and is now generally accepted.

1.1.1 Three-center four-electron ("hypervalent") bond

A 3c-4e bond is formed from three adjacent p-type atomic orbitals arranged in a line with lobes lying along the internuclear axis. These overlap in a σ-fashion to form three molecular orbitals (see Figure 1.1). Two electrons are in a bonding molecular orbital and two are in a nonbonding orbital. "According to the fundamental description of a 3c-4e bond, one pair of bonding electrons is delocalized to the two ligands (substituents), resulting in the charge distribution of almost –0.5 charge on each ligand and almost +1.0 charge on the central atom."[11] In order to experimentally construct a 3c-4e bond in penta-coordinate hypervalent molecules, four ways were proposed by Akiba[11,18] (Scheme 1). (1) Add two free radicals from ligands to combine with an unshared pair of electrons in the central atom's p-orbital. (2) Add two unshared pairs of electrons to coordinate to a central atom's vacant p-orbital. (3) Add a pair of unshared electrons of one ligand to the σ^* orbital of a Z–X bond in a cationic molecule. (4) Add a pair of unshared electrons of one ligand to the σ^* orbital of a Z–X bond of a neutral molecule (*e.g.*, silicon compounds).

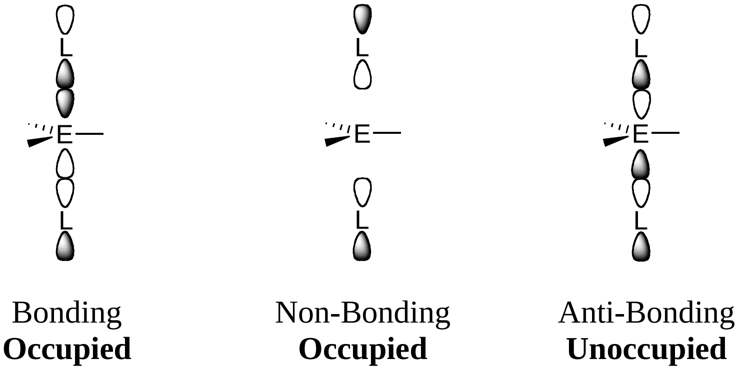
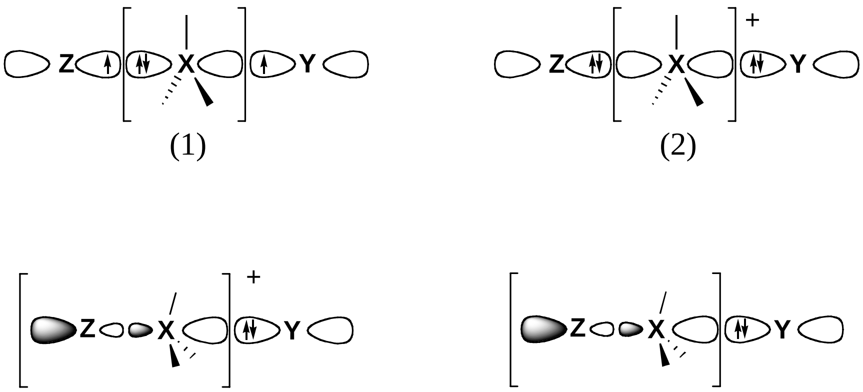


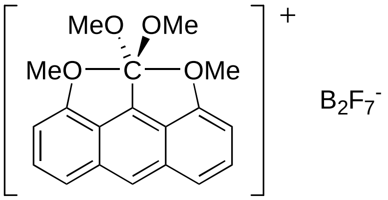
Figure 1.1. The three-center four-electron bonding scheme for elements E and L


(1) (2) (3) (4)

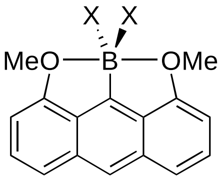
Scheme 1 Modes of creation of a 3c-4e bond in pentacoordinate hypervalent molecules

When X is carbon, method (4) is similar to the transition state of the S_N2 reaction.Therefore sometimes hypervalent compounds are referred to as "frozen transition states."

For example, pentacoordinate hypervalent carbon compound **1**[16] and boron compound **2**[17] correspond to method (2) above.



1



2

Compared to a normal covalent bond (*i.e.* a 2c-2e bond) in which no electrons occupy any nonbonding or antibonding orbitals, in a 3c-4e bond the nonbonding molecular orbital is the highest occupied molecular orbital (HOMO). A 3c-4e bond is referred to as an electron-rich, orbital-deficient bond. A hypervalent bond will be weak and long in comparison with a normal covalent bond. As implied in the hypervalent bonding scheme of Figure 1.1, appreciable electron density is strongly localized on the axial ligands. The apical bond is much more polarized than the equatorial ones. Thus the axial ligands should be electron–withdrawing groups while the central atom must be comparatively electropositive for the purpose of stabilizing the electron density distribution. Some calculated data and experimental evidence on phosphorus hypervalent compounds (PH_xF_{5-x},[14] PCl_xF_{5-x}[15]) supported this aspect of hypervalent bonding theory. In all of these phosphoranes the axial positions were occupied with fluorines in preference to hydrogens or chlorines.

The 3c-4e bond model was first applied to trihalide ions (X_3^-, XY_2^-, and XYZ^-) and bifluoride ion (HF_2^-) by Rundle.[7] It was able to explain that the trihalide ions were linear and the bonds were slightly longer and presumably slightly weaker than the corresponding ordinary halogen-halogen bonds. For example, the I–I bond length (1.16 Å) of I_3^- is longer by 10% than that of diiodine (1.06 Å). In 1985, Martin[12] and coworkers used the 3c-4e molecular orbital model for F_3^-, which should be a quite unstable hypervalent compound. The three-center bonding scheme for the trifluoride anion is shown in Figure 1.2(a). The σ–delocalized orbitals involving σ overlap of p–orbitals are analogous to the three-center bonding in the allyl anion (Fig. 1.2(b)). Three-center bonding like that shown in Figure 1.2(a) is sometimes called a "σ-allyl" system. The structure of F_3^- was calculated at two levels (DZP (a polarized double-ζ set)/ACCD (approximate coupled clusters with double substitutions) and TZP (a polarized triple-ζ)/ACCD). In both cases the structure of F_3^- was found to be linear with equivalent bonds. At the DZP/ACCD level, the F–F bond length was calculated to be 1.711 Å, while at the TZP/ACCD level it was 1.701Å, which was about 0.3 Å longer than that of F_2 (F–F: 1.412 Å). The bonding in F_3^-

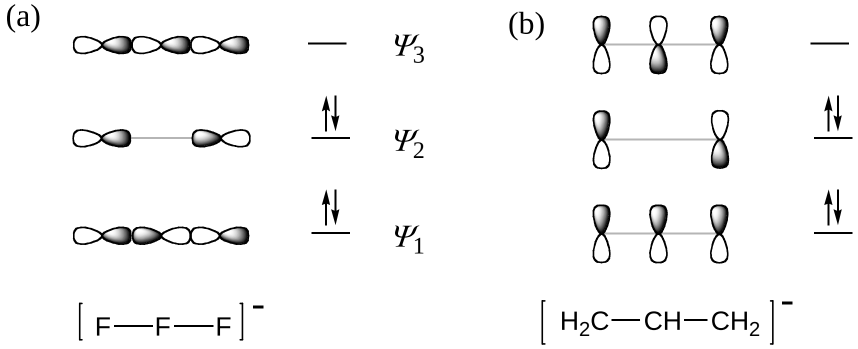


Figure 1.2 (a) Linear 3c-4e σ bonding scheme for F_3^- (b) 3c-4e π-bonding for the allyl anion.

could be described as a 3c-4e bond involving only p-orbitals. In agreement with this is the ACCD charge distribution in the ion (F_3^-), which puts a –0.51 charge on each apical fluorine and a +0.03 charge on the central fluorine.

Normally hypervalent molecules have a trigonal bipyramidal (TBP) or pseudo TBP geometry[13] that employs two types of bonding: hypervalent bonding for the two axial ligands, and normal covalent bonding to the equatorial ligands. The molecular structure of PF_5 in Figure 1.3 is an example of true TBP geometry. It is composed of three P–F bonds in the equatorial plane and one axial 3c-4e bond. The apical (or axial) bond (1.577 Å) is longer and weaker than the equatorial bond (1.534 Å).

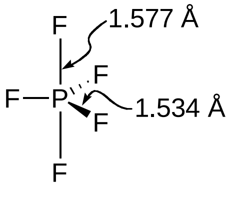


Figure 1.3 Trigonal bipyramidal molecular structure of PF_5

But the term *pseudo TBP* is most employed to describe hypervalent species because most hypervalent species have a distorted TBP geometry. This may be the result of one or more ligands being different than the others, or one or more ligands being replaced by a lone pair of electrons. This is illustrated in Figure 1.4.

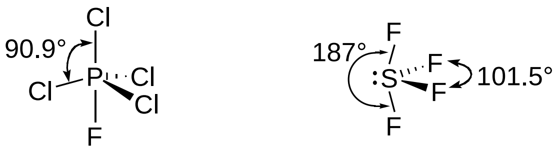
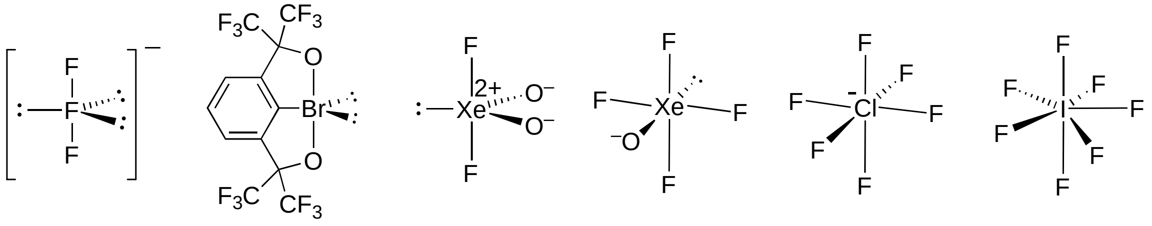


Figure 1.4 Pseudo-TBP molecular structure of PCl_4F[20] and SF_4[19]

The N–X–L designation[21] is a convenient notation system to describe the structure of hypervalent species: N represents the number of electrons associated with the valence shell of the central atom, X is the symbol of the central atom (Groups 1,2 13–18), L is the number of ligands directly bonding the central atom X. In general, hypervalent compounds are those compounds with N > 8, *i.e.* the octet is expanded. According to the N–X–L designation, multiple bonds are counted as polarized single bonds no matter the actual character of the bonds. Following are some examples to illustrate the N-X-L system. (Figure 1.5).



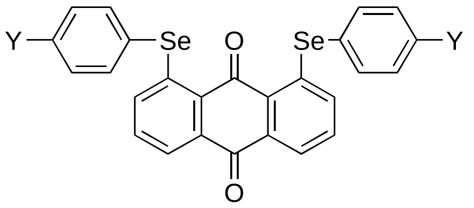
10-F-2[12] 10-Br-3[22] 10-Xe-4[23] 12-Xe-5[24] 14-Cl-6[25] 14-I-7[26]

Figure 1.5 Examples of the N-X-L designation system

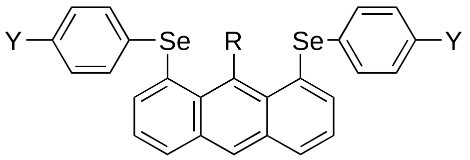
1.1.2 Extended hypervalent bond (5c–6e bond)

In 1988, Farnham[27] and coworkers reported that tris(dialkylamino)sulfonium perfluoro-2-methyl-2-pentyl carbanion reacted with perfluoroalkyl iodides (R_fI) to give a novel structure of the form $[R_f\text{–I–F–I–}R_f]^-$. The crystal structure analysis and high–level *ab initio* calculation proved that bonding in this form was a five–center, six–electron hypervalent σ bond with fluorine at the central position, not an ion–dipole complex. In the calculations of Farnham *et al.* on this 5c–6e bond, the negative charge was localized at the central and terminal positions. In order to stabilize a 5c–6e bond, the central and terminal positions should be occupied by the more electronegative elements, with less electronegative elements at the other two positions. In the 3c–4e bond only the terminal positions should be occupied by electronegative elements and the central position by more electropositive atoms. The electronic density distribution of the 5c–6e bond differs from that of the 3c–4e bond. So Farnham *et al.* called the 5c–6e bond an extended hypervalent σ bond. In 1989, Dixon[28] *et al.* gave other examples of 5c–6e hypervalent bonding, *i.e.* $[Xe_2F_3]^+$ ($[\text{F-Xe-F-Xe-F}]^+$) and $XeIF_3$ (F-Xe-F-I-F). The electronic structures of $[Xe_2F_3]^+$ and Xe_2IF_3 were calculated by using *ab initio* molecular orbital theory with polarized, split-valence basis sets.

Anthraquinone **3** and 9–methoxyanthracene **4** were synthesized by Nakanishi[29] and coworkers. The structures of **3** and **4** were determined by X-ray crystallography, which revealed the linear alignment of five C—Se···O···Se—C atoms in **3a** and **4a**. The Se-O distances in **3a** and **4a** are 2.673–2.688 Å and 2.731–2.744 Å respectively, which are about 25% shorter than the sum of van der Waals radii of the atoms. This evidence strongly supported the extended hypervalent $[\sigma^*(C_i\text{—}Se)\cdots n_p(O)\cdots\sigma^*(Se\text{—}C_i)]$ 5c–6e



3a Y = H
3b Y = Cl



4a (R = OMe, Y = H)
4b (R = H, Y = H)
4c (R = H, Y = Cl)

interactions in **3a** and **4a**. They suggested that 5c–6e bond should be constructed by the combination of the two hypervalent $n_p(O)\cdots\sigma^*(\ Se\text{—}C_i)$ 3c–4e interactions through the central $n_p(O)$. The quantum chemical calculations performed on **3a, 4a** and **4b** suggested that the origin of the linear alignment of the five C—Se···O···Se—C atoms in **3a** and **4a** was stabilization due to 5c-6e extended hypervalent 5c–6e bonding. An approximate molecular orbital model which summarizes Nakanishi's ideas is shown in Figure 1.6.[29]

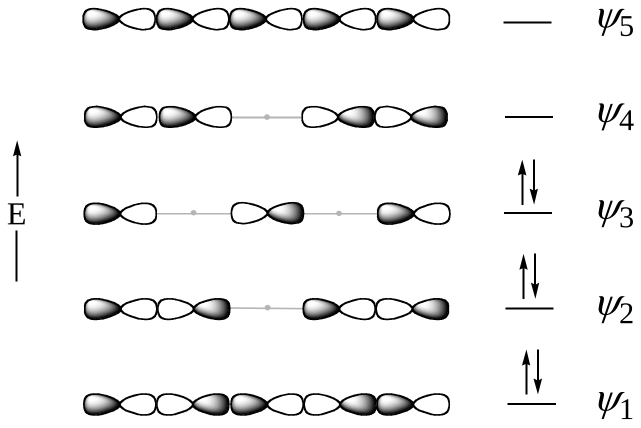


Figure 1.6 Approximate molecular orbital model of the 5c-6e bond

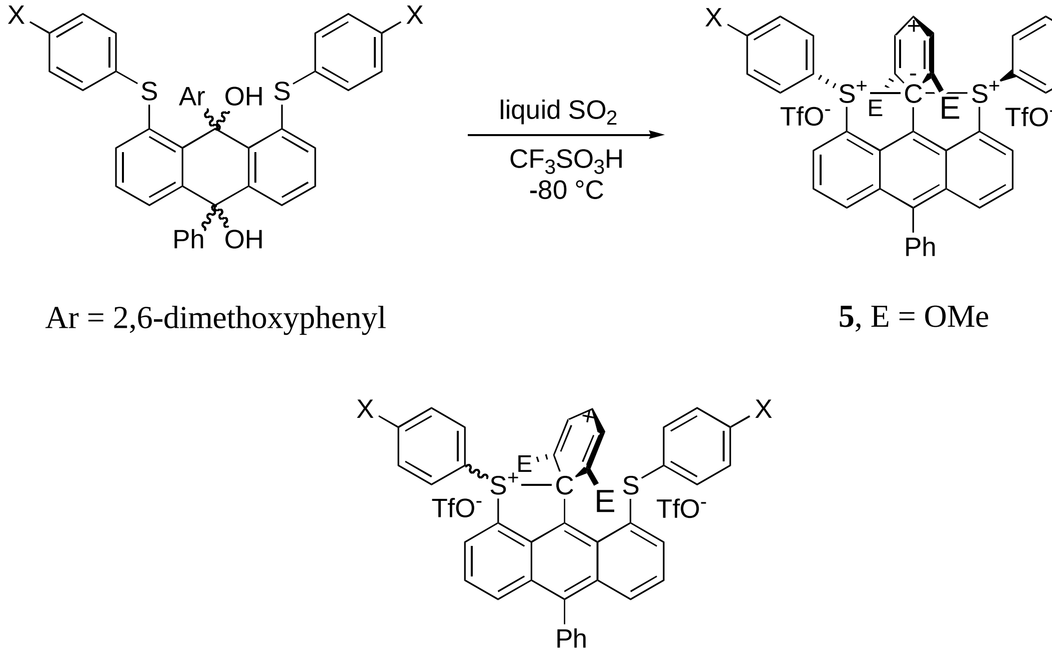
1.2 Hypervalent compounds based on second row elements

Since Claassen, Selig, and Malm[3] synthesized the xenon fluorides in 1962, there have been many papers published dealing with either the synthesis of new hypervalent species, the calculated and experimental geometries of hypervalent compounds, or descriptions of hypervalent bonding schemes. Especially in the past twenty years, many different hypervalent compounds of elements from the third row or below were synthesized and studied.[11] However, by contrast, just a few hypervalent compounds based on *second* row elements were synthesized or even detected. Only hypervalent compounds of boron, carbon, and fluorine have been reported, and there exist only a few examples of these compounds.

The first 10-F-2 hypervalent fluorine species was reported by Ault and Andrew[30] in 1976. It was the highly unstable trifluoride anion F_3^- generated by simultaneous deposition of an Ar/F_2 mixture with CsF, RbF or KF. All three alkali metal trifluorides ($M^+F_3^-$) were detected at low temperature by Raman and infrared spectroscopy.

The chemists most successful at synthesizing and characterizing second row hypervalent species of carbon and boron are J. C. Martin and Kin-ya Akiba. They have prepared and characterized a series of compounds with boron and carbon hypervalent centers.

In 1979, Forbus and Martin[31] used the reaction in Figure 1.7 to prepare the first directly observable pentavalent carbon species (10–C–5), an analogue to the transition state in the Walden inversion mechanism. ^1H NMR spectroscopy and, in the case of X = F, ^{19}F NMR spectroscopy were used to confirm that the structure of **5** was the symmetrical trigonal bipyramidal geometry, not an unsymmetrical 8–C–4 species, such as **6**.



Ar = 2,6-dimethoxyphenyl

5, E = OMe

6, E = OMe

Figure 1.7 The synthesis of 10-C-5 compound **5**[31]

Whereas very useful trianionic OCO pincer ligands (Figure 1.8) have been used to synthesize hypervalent phosphorus, sulfur, and iodine species,[32] application of these ligands to prepare hypervalent species from second row elements hasn't been reported.

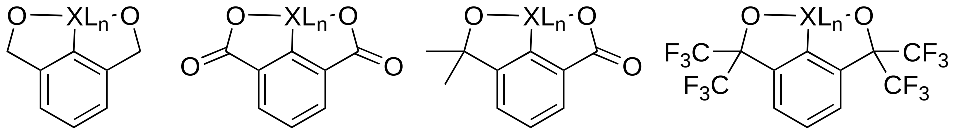
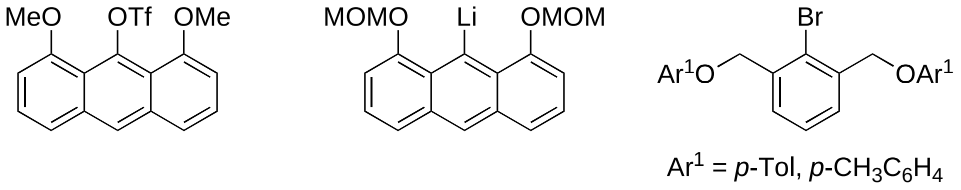


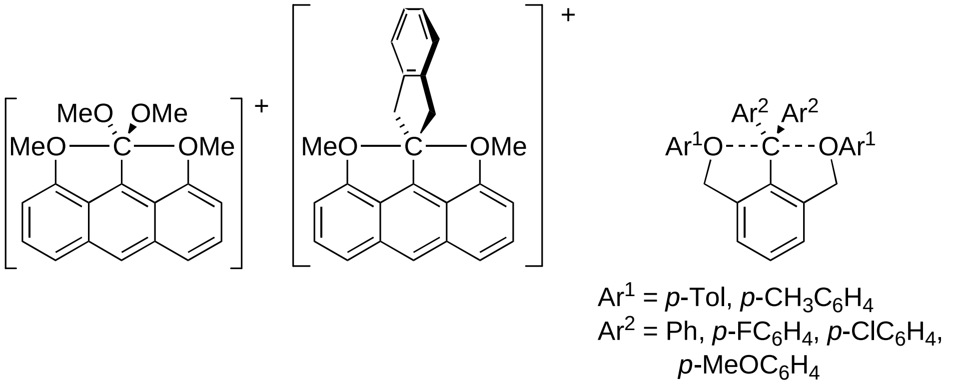
Figure 1.8 Hypervalent compounds with O-C-O pincer ligands[33]

Recently, Kin-ya Akiba and coworkers designed new kinds of ligands (Figure 1.9) for synthesis of a series of hypervalent carbon compounds (Figure 1.10) and boron species.[34] NMR spectra were used to confirm these hypervalent carbon species **10** - **12**. In addition, Akiba and coworkers were able to obtain crystals of **10** and **12**. X-ray analysis



7[16,34] **8**[33,34] **9**[18]

Figure 1.9 Precursors to O-C-O pincer ligands for synthesis of hypervalent carbon species



10[16,33,34] **11**[34] **12**[18]

Figure 1.10 Some hypervalent carbon compounds with Akiba's O-C-O pincer ligands

showed a symmetrical structure (10-C-5) where the two C-O distances were almost identical, and longer than that of a covalent C-O bond, but shorter than the sum of the van der Waals radii.

The first hypervalent boron compounds were reported by Lee and Martin[35] in 1984 (Figure 1.11). They used pyridine diol **13** as starting material to synthesize isolable 10-B-5 and 12-B-6 hypervalent boron species **16** and **17**. ^{1}H-, ^{13}C-, and ^{19}F-NMR were all used to confirm the structures of **16** and **17**, but the very important evidence in support of these geometries was ^{11}B NMR chemical shifts. Compounds **16** (^{11}B NMR, -20.1 ppm) and **17**

(^{11}B NMR, -122.9 ppm) both displayed ^{11}B chemical shifts much farther upfield than any chemical shifts previously observed for 8-B-4 type compounds.

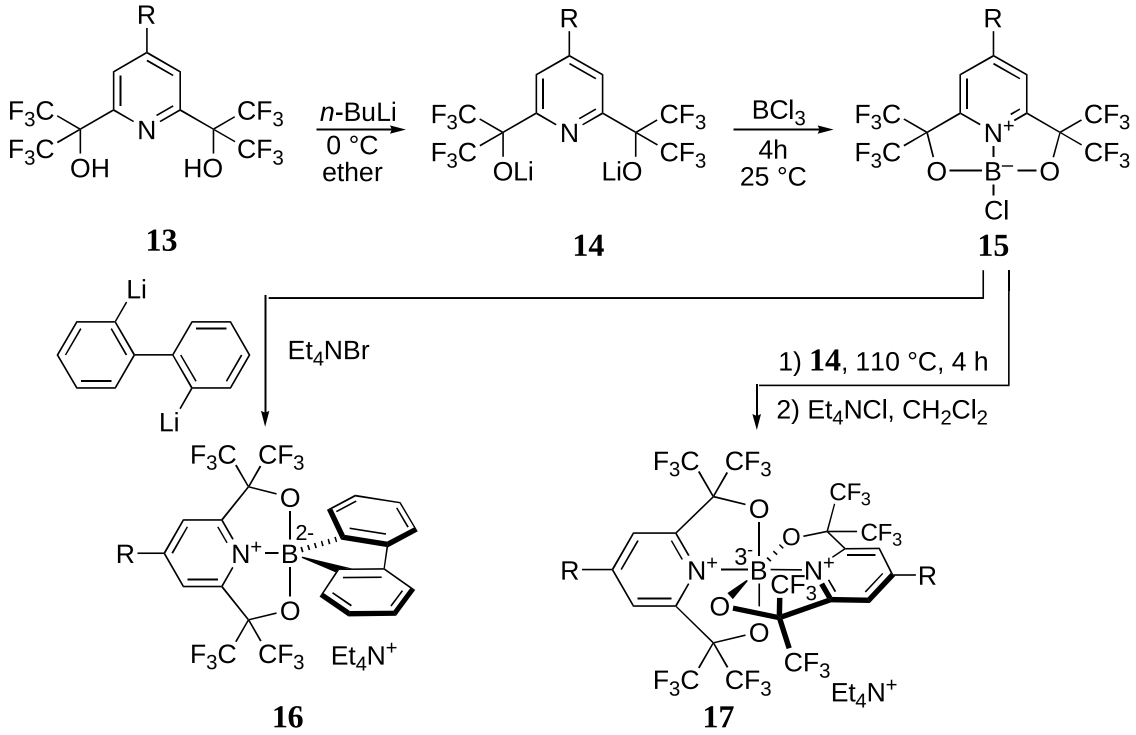
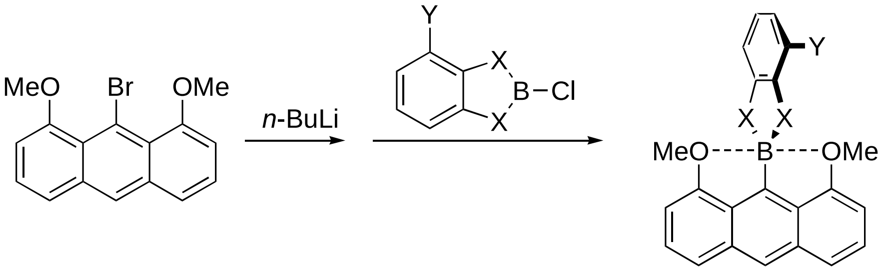


Figure 1.11 The synthesis of hypervalent boron species[35]

The first fully characterized hypervalent boron species was reported in 2000 by Akiba and coworkers.[36] As shown in Figure 1.12, they used the versatile tridentate anthracene ligand **18** to synthesize hypervalent (10-B-5) boron compounds **19.** Crystals of **19a-19c** for X-ray analysis were obtained. The X-ray analysis showed the sum of the bond angles around the central boron of **19** are all 360.0°, which means that in each case the central boron atom is planar with sp^2 hybridization. The two B-OMe bond lengths are identical (2.436 Å in **19c**) or almost identical (2.379 Å and 2.441 Å in **19a**, 2.398 Å and 2.412 Å in



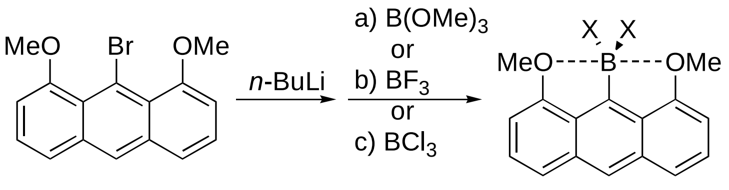
18

19a: X = O, Y = H
19b: X = O, Y = OMe
19c: X = S, Y = H

Figure 1.12 Synthesis of hypervalent boron compounds **19**

19b). These bond lengths are longer than those of covalent B-O bonds (1.394 - 1.400 Å),[36] but shorter than the sum of the van der Waals radii (3.48 Å).[37]

Recently, hypervalent boron compounds **20a-20c** were synthesized by Akiba and coworkers as shown in Figure 1.13.[34] The results of X-ray crystallographic analysis of **20a-20c** were very interesting. The structures of **20a** and **20b** were almost symmetrical, the two B-O distances almost identical.



20a: X = OMe
20b: X = F
20c: X = Cl

Figure 1.13 Synthesis of hypervalent boron compounds **20**[34]

1.3 Hypervalent nitrogen

1.3.1 Potential difficulties in forming hypervalent nitrogen

There have been three major reasons advanced for the reluctance of second row elements to expand their valence octet: (*i*) steric hindrance, (*ii*) high electronegativity and high first ionization potentials, and (*iii*) an inability to utilize d-orbitals.

The inability to utilize d-orbitals in the bonding scheme of second row elements has been cited in many papers as the reason second row elements are resistant to becoming hypervalent.[14, 38-42] But both quantum calculations and experimental results have proved that the role of d-orbitals in hypervalent bonding is not as crucial as many had thought.[9,10,38,40,42] For sulfur hexafluoride, Reed and Weinhold[43] found that the d-orbital contribution to the bonding system is small.[14,38-42] They commented, "The total 3d population in SF_6, however, is only around 0.25e, the $3d_\sigma$ population (0.16e) being only one-sixth of what would be required for sp^3d^2 hybridization on sulfur….We therefore concur with the suggestions of MacLagan and Kutzelnigg that models of sp^3d and sp^3d^2 hypervalent bonding in non-metals should no longer be taught in chemistry courses."

Steric hindrance is another reason for the failure of second row elements to bond to five or more ligands. The second row elements have very small atomic radii and the repulsion between the ligands is very strong.

Also harmful to the possible hypervalency of second row elements is their very high first ionization potentials, which means second row elements are reluctant to donate electrons to the axial ligands as shown in the hypervalent bonding scheme of Figure 1.1.

Compared to carbon and boron, nitrogen has a smaller atomic radius and higher first IP. These could be reasons that the syntheses of hypervalent species of nitrogen are particularly difficult. Fluorine has a smaller atomic radius and higher first IP than nitrogen. But a hypervalent fluorine is required to coordinate only two ligands linearly (*e.g.* F_3^-). The lack of steric repulsion between ligands in F_3^- may in fact overcome the destabilizing effects of having a highly electronegative central atom. As previously discussed, hypervalent carbon, boron, and fluorine species have been observed, but evidence for a hypervalent nitrogen species or even transient hypervalent nitrogen species[41,44] have been very difficult to obtain.

1.3.2 Some attempts to synthesize hypervalent nitrogen species

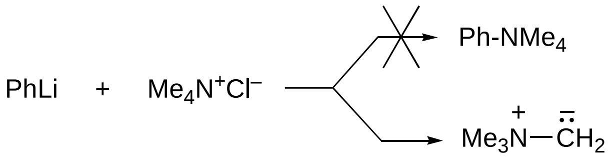
In 1916, Schlenk[45] believed he had synthesized pentacoordinate pentavalent nitrogen as in the following equations. But he failed.

$$\mathrm{Ph_3CNa} + \mathrm{Me_4NCl} \dashrightarrow \mathrm{Ph_3C\text{-}NMe_4} \qquad [1]$$

$$\mathrm{PhCH_2Na} + \mathrm{Me_4NCl} \dashrightarrow \mathrm{PhCH_2NMe_4} \qquad [2]$$

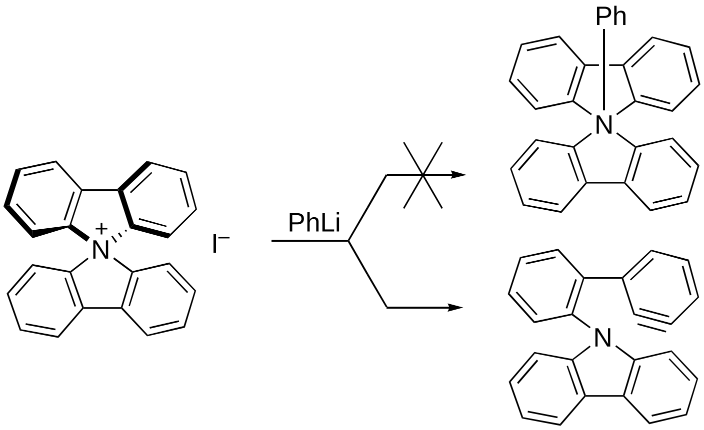
$$\mathrm{Ph_2NK} + \mathrm{Me_4NCl} \dashrightarrow \mathrm{Ph_2N\text{-}NMe_4} \qquad [3]$$

In 1947, Wittig[46] also tried to make a hypervalent nitrogen species as in equation 4. He got nitrogen ylides instead of hypervalent nitrogen species. Fortunately, this led to the eventual discovery of phosphorus ylides.



[4]

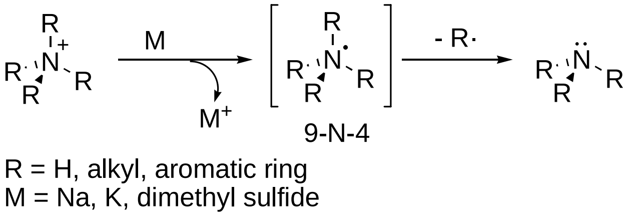
Hellwinkel and Seifert[47] thought it should be possible to add a fifth ligand to an ammonium salt lacking α-hydrogens as in equation 5. The experimental results showed that they were not successful.



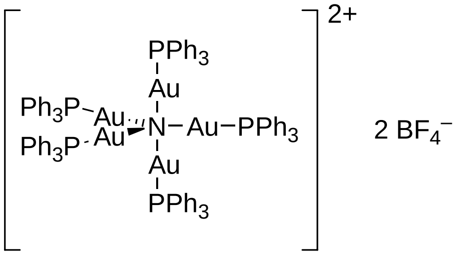
[5]

Nishikida and Williams[48] reported a 9-N-4 species, trifluoramine oxide radical anion $F_3N^{\bullet}$-O^-, in which the three fluorines were equivalent. It was detected and identified by a second-derivative ESR spectrum of a γ-irradiated solid solution of 5 mol % F_3NO in SF_6 recorded at –170 °C after irradiation at –190 °C. However, this radical anion is only stable at very low temperature. It loses F^- above 102 K to form F_2N-$O^{\bullet}$.

Hypervalent ammonium radicals (9-N-4), in which the nitrogen atoms have nine valence electrons, were reported by Scott *et al*.[49] Transient organic hypervalent ammonium radicals were produced in the gas phase by one-electron reduction of their ammonium ion counterparts, via collisional electron transfer (equation 6). Neutralization-reionization mass spectrometry was used to investigate hypervalent ammonium radicals and to study their dissociations.

 [6]

NF_5 (10-N-5) was speculated to be formed from NF_3-F_2 either by fission-fragment radiolysis at room temperature[50] or irradiation by 3-MeV bremsstrahlung at –196 °C[51] or from NF_4AsF_6 by pyrolysis at 175 °C.[52] However, in 1988 Christe, *et al.*[53] summarized all previous attempts, and finally concluded that five fluorines do not have enough space to bond to nitrogen. That means the repulsion between fluorines in NF_5 is very strong. However, Grohmann and coworkers recently discovered compound **21.**[54] The nitrogen atom in **21** is in the center of a trigonal bipyramidal cluster of five gold atoms. The gold-gold interactions are presumably attractive. The nitrogen is hypercoordinate, not hypervalent.



21

1. 3. 3 Ideas for the synthesis of precursors to hypervalent 10-N-5 species

From the previous review, one might wonder whether it is possible to synthesize a hypervalent nitrogen species. In our group, we have long been interested in seeing whether nitrogen can be made to form 10-N-5 systems. To design such a system is challenging.

a) Planarity at nitrogen. According to the hypervalent bonding scheme shown in Figure 1.1, oxidizing an 8-N-3 species to a 10-N-5 species involves changing the geometry at nitrogen as shown in Figure 1.14. Changing the pyramidal geometry of nitrogen to the planar geometry (step 1, Figure 1.14) will impose an energy cost. However, if one were to begin with an amine having a planar ground state geometry, step 1 and its energy cost would be eliminated.

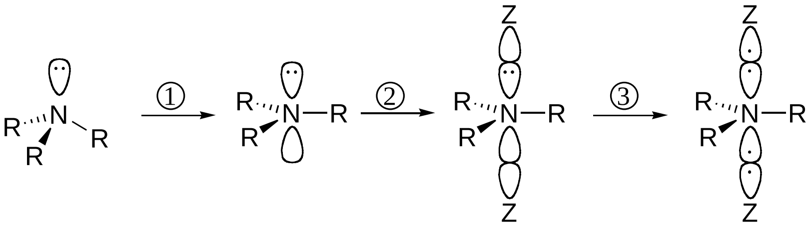
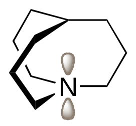
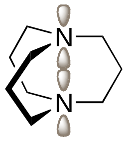


Figure 1.14 Conceptual steps in the conversion of an 8-N-3 species to a 10-N-5 species

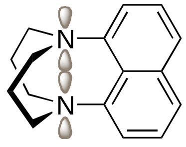
We know some amines have a planar geometry. For examples, the nitrogen atoms in following amines all have a planar geometry. The bicyclo[3.3.3]undecane system is an



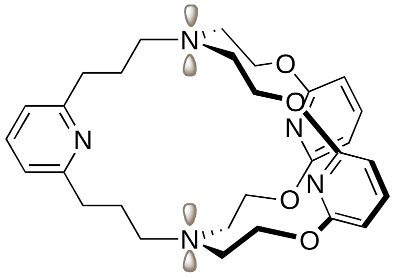
22[55]



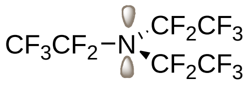
23[56]



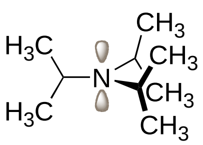
24[57]



25[58]



26[59]

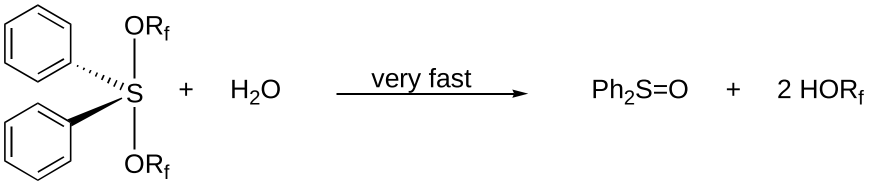


27[60]

obvious motif in **22, 23,** and **24.** So some confidence can be gained that synthesizing some precursors of 10-N-5 species including a planar nitrogen geometry is a possible goal, although it may turn out to be an elusive one requiring either extreme ingenuity or conditions.

b) Suitable axial ligands. As discussed, a 3c-4e bond has an accumulation of partial negative charge on the apical ligands and partial positive charge on the central atom. This charge distribution can be stabilized by using very electronegative apical ligands. Obviously, each apical ligand must have an orbital capable of good overlap with that of the central element. Not only should the central atom be more electropositive in order to stabilize the partial positive charge on the hypervalent atom, but the equatorial ligands should be electropositive for the same purpose.

c) Five-membered ring effect. Westheimer found that 10-P-5 species in which a five-membered ring that included an apical and an equatorial ligand in the trigonal bipyramidal geometry were several orders of magnitude more stable than model 10-P-5 species in which the five-membered ring was absent.[61] This has been called the "five-membered ring effect." Martin, *et al.* found the "five-membered ring effect" was also manifested in sulfurane (10-S-4) chemistry.[62] The evidence for "five-membered ring effect" was tested by a series of hydrolysis experiments. Sulfurane **28** is extremely reactive

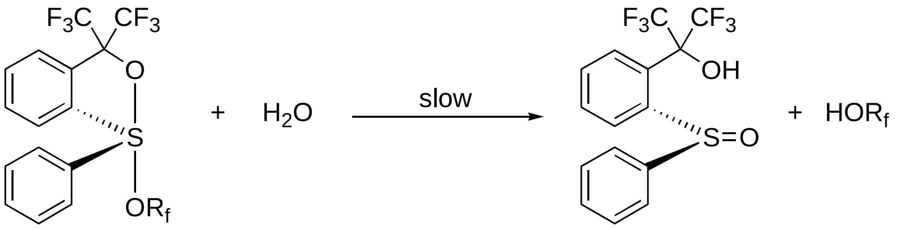


[7]

28

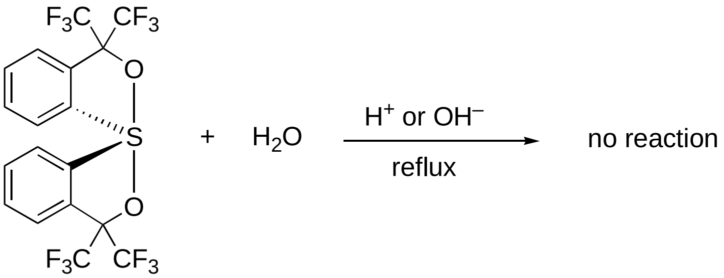
$OR_f = OC(CF_3)_2Ph$

toward water, producing the hydrolysis products alcohol and sulfoxide very fast at low temperature (eq. 7).[63] However, sulfurane **29** hydrolyzes very slowly (eq. 8), and **30** does not hydrolyze even after refluxing for two hours in HCl solution or aqueous sodium hydroxide (eq. 9). [62f,64] Kinetic and calorimetric[65] studies showed that the five-membered ring effect provided 10-12 kcal/mol stabilization for pseudo TBP sulfuranes such as **30** relative to acyclic analogue **28.**



29

[8]



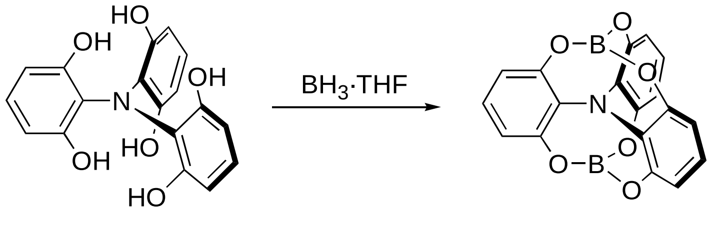
30

[9]

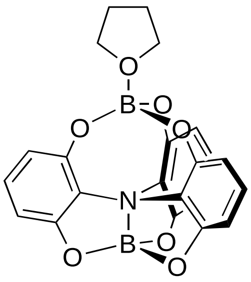
So the use of a bidentate ligand or ligands to form a five-membered ring spanning an apical and an equatorial position in a TBP geometry would be extremely useful. We think that it is wise to include the five-membered ring effect in one’s design of a 10-N-5 species, guessing that the species will have a TBP or pseudo-TBP geometry.

d) Framework to ensure collinear Z-N-Z array. We require to hold atoms above and below nitrogen at a distance suitable for bonding to nitrogen. Our idea is to trap nitrogen in a pre-formed pseudo TBP structure.

According to these considerations, Dr. John Northcott, a former student in our group, synthesized compound **31,** which reacted with excess THF·BH_3 complex to produce **32**.[66]

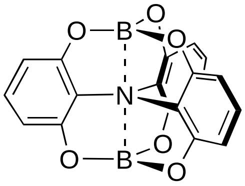


31 **32**

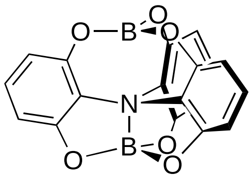


33

In fact, x-ray crystallography showed **32** contained a THF of crystallization as shown in **33**. Unfortunately, it was impossible to prepare **32** free of coordinating solvent, so it could not be determined experimentally whether this B-N-B array is intrinsically **34** or **35**. The *ab initio* calculations indicated that the system **34** (with the symmetrical 3c-2e [B···N···B] array) is only 2.66 kcal/mol higher in energy than the system **35** (with the un-symmetrical [B-N B] array).



34



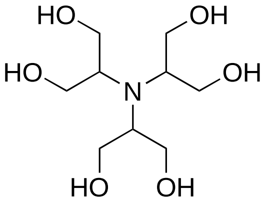
35

1.3.4 New target precursor for 10-N-5 species.

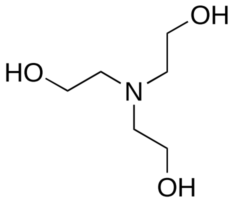
a) **Precursor 36 for 10-N-5 species**

Compared to **31**, the symmetry of **36** should be higher than **31** and should have less steric hindrance. So we think **36** may be a better precursor for 10-N-5 species. Compound

36 is an extension of the well-known triethanolamine, **37**. Reaction of suitable reagents with the three hydroxy groups of triethanolamine produces so-called"atranes" **38** or **39**

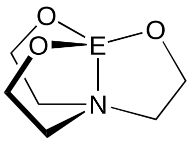


36



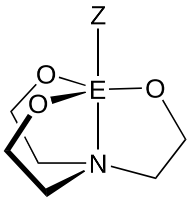
37

(E = B, Al, Si, P, Sn, Ge, *etc.*). Compounds **38** and **39** have been made and there has been much discussion about the length of the dative bond made between nitrogen and the other



(E = B, Al, P)

38

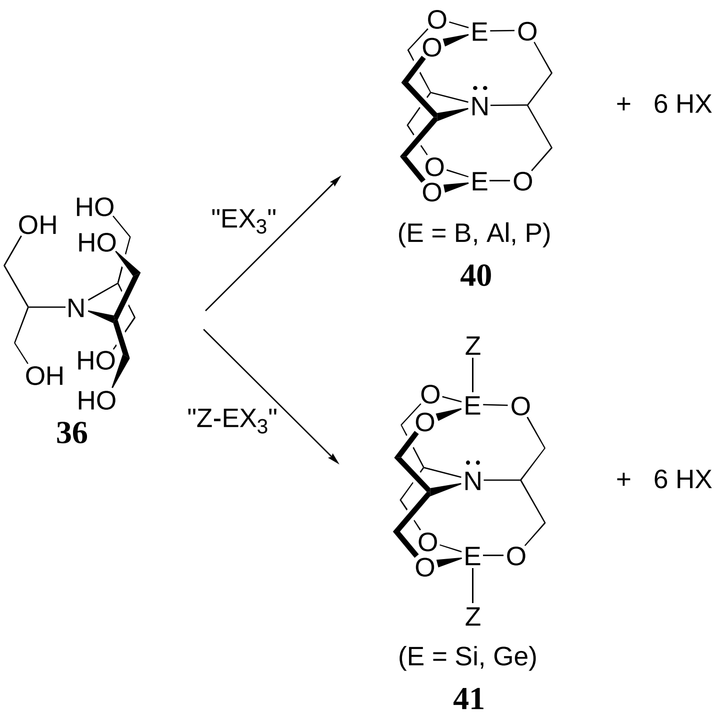


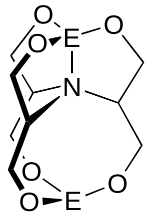
(E = Si, Ge)

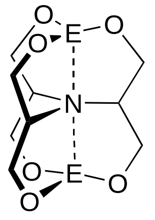
39

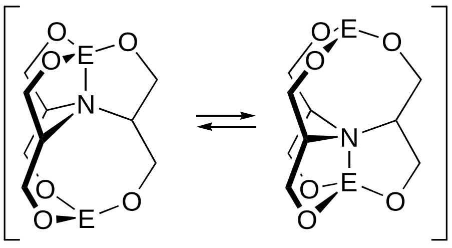
heteroatom, the geometry enforced by this fourth bond, and the properties.[67] We hope **36** could incorporate some main group elements just like triethanolamine to provide **40** and **41.** As mentioned before, molecules like **40** or **41** may have a static unsymmetrical structure **42**, a static symmetrical structure with a 3-center bond **43** or a dynamic structure.

Compounds **40** and **41** are σ-allyl cation analogues. To create the possibility of nitrogen hypervalency, two electrons must be added to **40** (or **41**) to become σ-allyl anion analogues in which N is engaged, in a formal sense, in five single bonds.





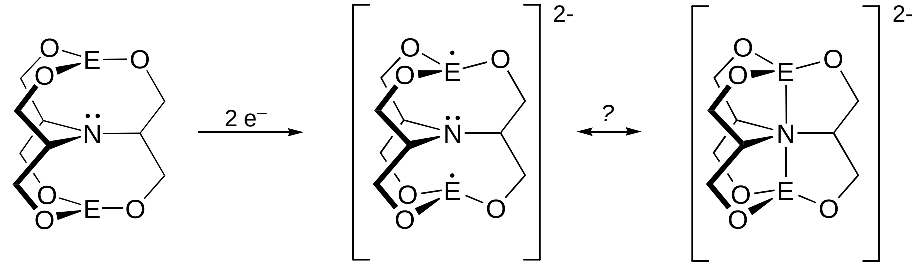




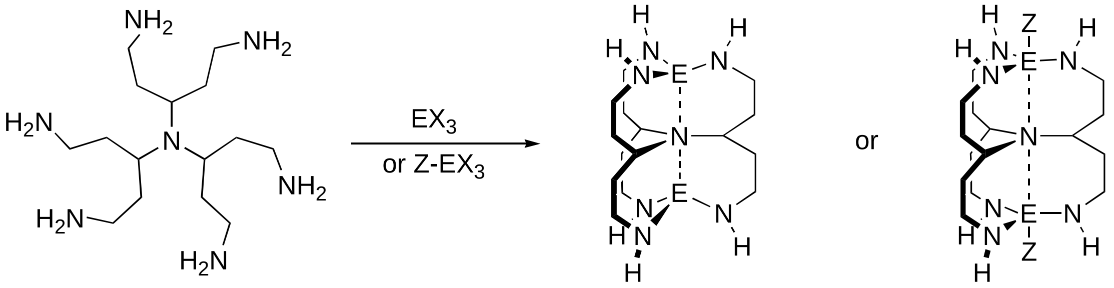
42 **43**

b) Precursor 45 for 10-N-5 species

As discussed, the five-membered ring as a design element seems like a good idea. How about a six-membered ring? In view of Alder's studies of ring size effects on bridgehead-bridgehead interactions in bicyclic compounds,[68] it may be well to explore variants of the proposed systems in which other ring sizes are present. One example, **46** (or **47**), and its precursor **45** are shown.



40 **44** **10-N-5**



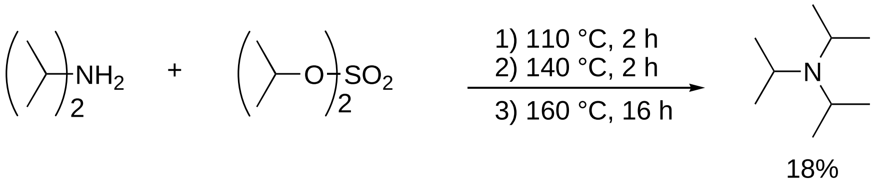
45 **46** **47**

RESULTS AND DISCUSSION

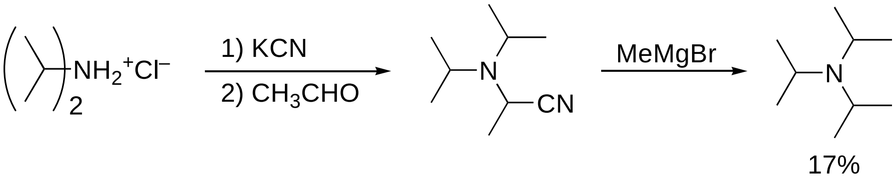
2.1 The synthesis of tertiary amine 36.

2.1.1 Previous work in our lab.

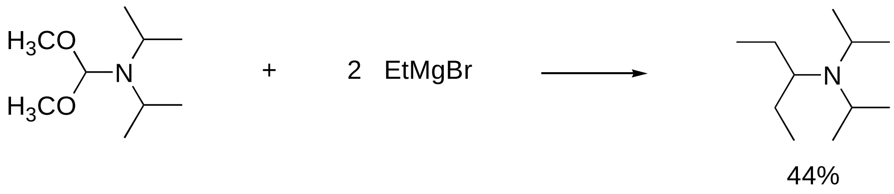
Tertiary amine **36** can be regarded as an analogue of triisopropylamine, which is among the most sterically hindered tertiary amines prepared to date.[70] There are only a few reported syntheses of triisopropylamine, and most of them required rather harsh conditions.[60,70,71] There are many methods for the synthesis of hindered secondary amines, but there are few general methods available for the preparation of extremely hindered tertiary amines, and these give the hindered amine product in low or modest yields. In 2001, Minmin Yang *et al.*[72] collected all reported routes to such compounds. These are shown in equations 10 - 15. There seems to be no simple, general method for the synthesis of extremely hindered tertiary amines. In fact, many approaches for synthesizing tertiary amine **36** in our laboratory were fruitless.[77]



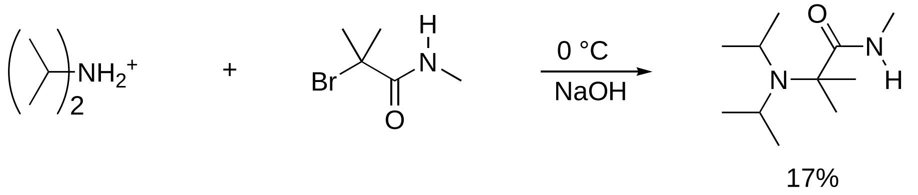
[10][70,71]



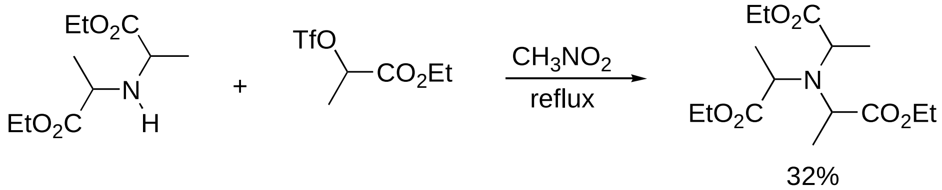
[11][60]



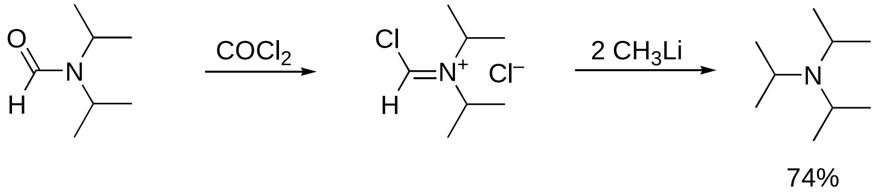
[12][73]



[13][74]



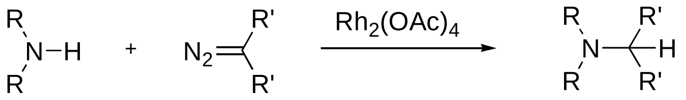
[14][75]



[15][76]

In 1999, Scott, Krülle, Finn, Nash, Winters, Asano, Butters and Fleet ("SKFNWABF")[78] also failed to synthesize **36** (Scheme 2). As shown in Scheme 2, dihydroxyacetone dimer **48** underwent reductive amination to produce intermediate primary amine **49**, secondary amine **50**, but not hindered tertiary amine **36**. So tertiary amine **36** would be expected to be a challenging synthetic target.

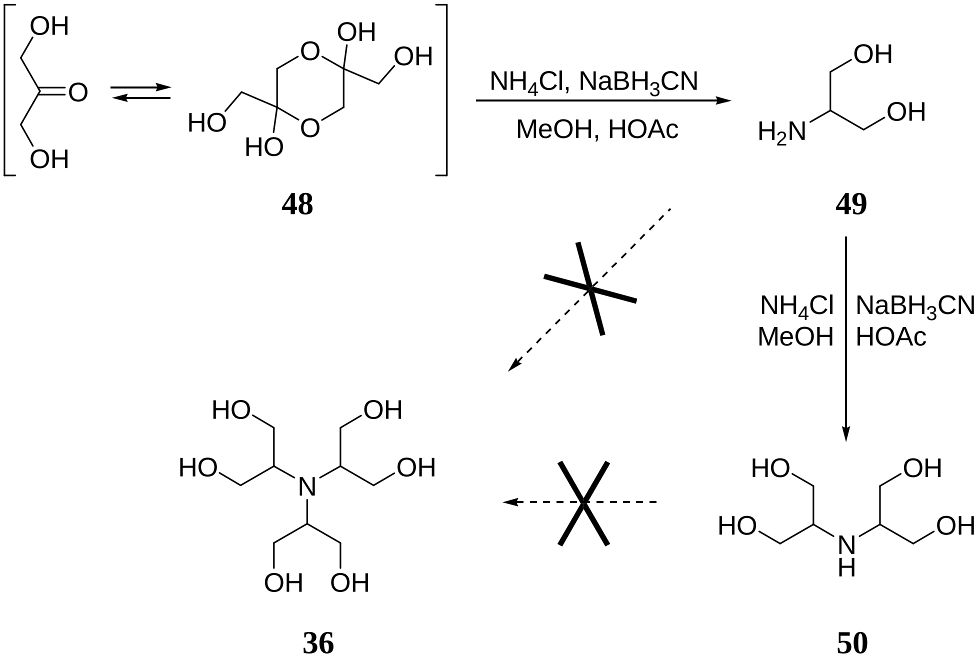
Fortunately, recent work in our laboratory[79] pointed to a possible synthesis of tertiary amine **36**. That work involved the Rh-stabilized carbene N-H insertion reaction (eq. 16).[80] Using this reaction, it was possible to produce sterically hindered tertiary amines, a



[16]

facet of this reaction which had been previously unexplored. In our laboratory, we have been exploring carbenoid N-H insertion into various congested secondary amines. Some results are shown in Table 1.[72,81] These results gave us confidence that the N-H insertion methodology might be used successfully to prepare **36**.

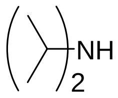
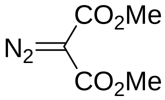
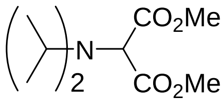
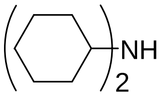
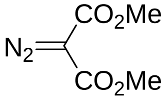
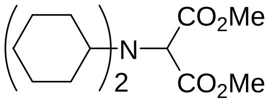
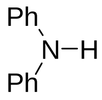
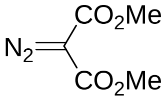
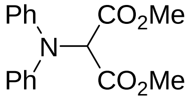
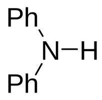
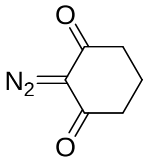
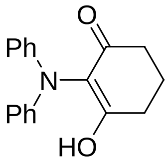
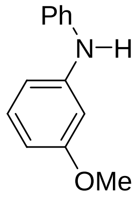
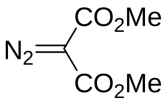
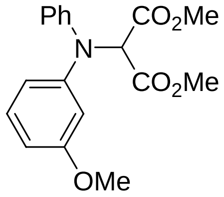
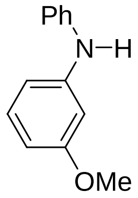
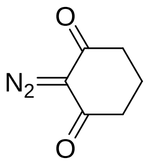
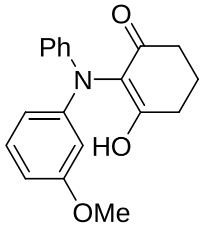
Scheme 2 Failure to prepare **36** by reductive amination



2.1.2 The synthesis of compound 36 starting with dihydroxyacetone

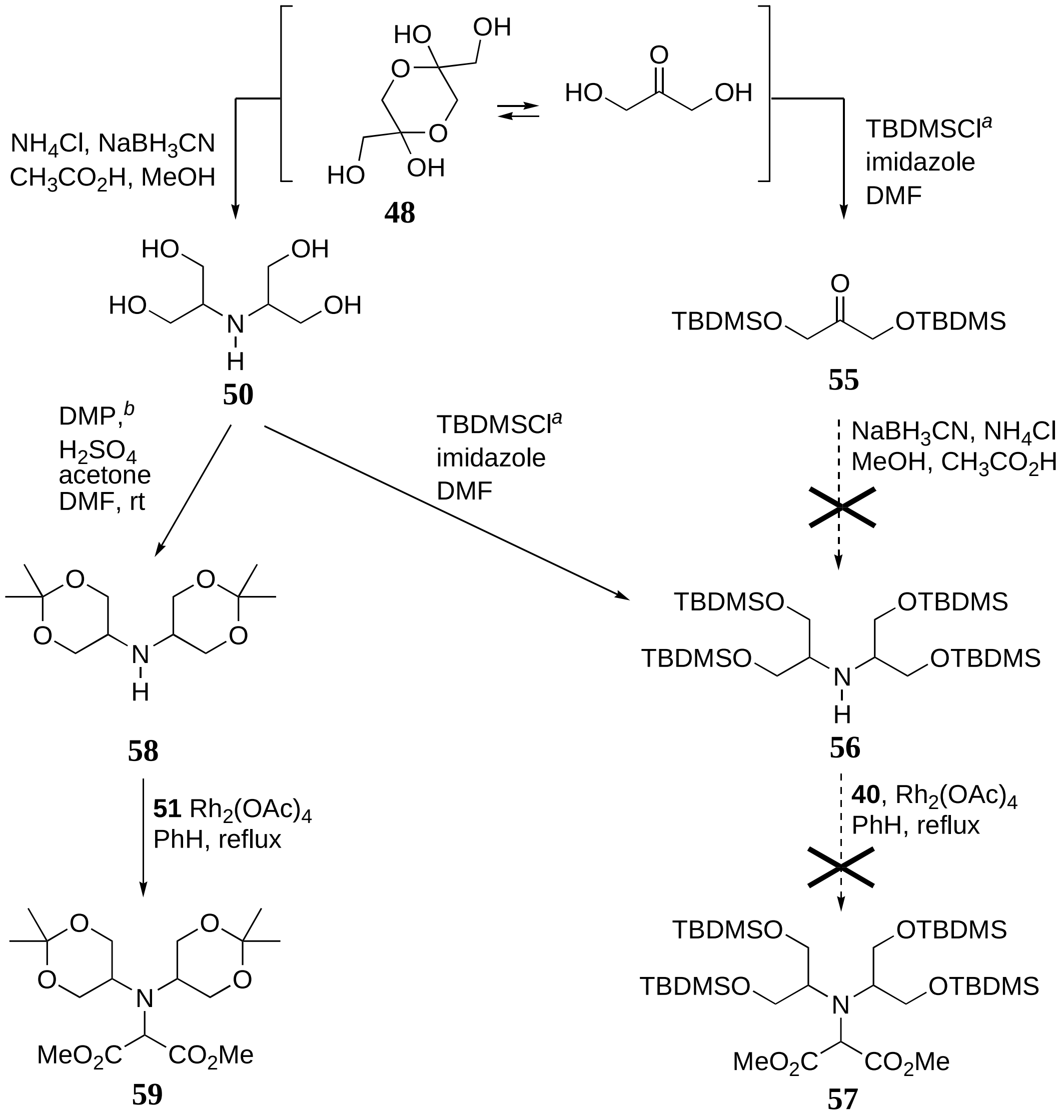
Based on SKFNWABF's work[78] and previous work in our laboratory, we decided to use cheap, commercially available dihydroxyacetone as the starting material. Our work in realizing this plan is shown in Scheme 3. We envisioned making secondary amine **50** by reductive amination (see Scheme 2) and using a carbenoid N-H insertion to complete the carbon skeleton of **36**.

Table 1. Some reactions of hindered secondary amines with diazo compounds catalyzed by $Rh_2(OAc)_4$

Amine	Diazo compound	Product	Isolated yield	Ref.
	 **51**		73%	72
	 **51**		85%	72
	 **51**		84%	72
	 **52**		75%	81
	 **51**		78%	72
	 **52**		70%	81

In order for the N-H insertion to succeed, the OH groups must be protected. We initially decided to protect the OH groups prior to the reductive amination. SKFNWABF's method for preparing **50** using unprotected dihydroxyacetone involved ion exchange chromatography to isolate the water-soluble product. We felt that OH-protected

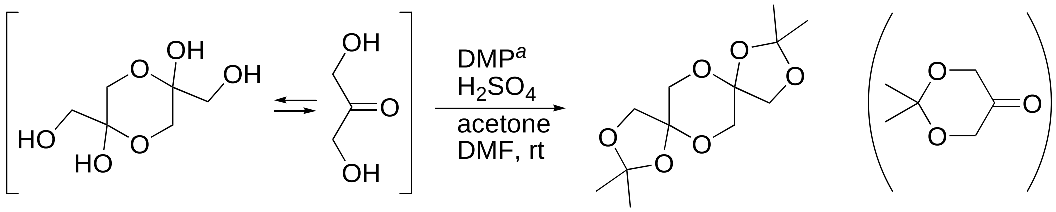
Scheme 3. Initial investigations into the synthesis of **36**



[a] TBDMS = *tert*-butyldimethylsilyl [b] DMP = 2,2-dimethoxypropane

dihydroxyacetone would give a protected, organic-soluble analogue of **50** which would simplify isolation. Considering that TBDMS ethers[82] are more stable than TMS ethers and are easy to deprotect, first we chose TBDMSCl as protecting reagent. With DMF as solvent, imidazole as catalyst, dihydroxyacetone dimer reacted with TBDMSCl to produce **55** in very high yield (92.0 %). We tried to prepare **56** from **55** by a reductive amination reaction. Sodium cyanoborohydride or sodium triacetoxyborohydride was used as reducing reagent, ammonium chloride or ammonium acetate was used as amination reagent, and a variety of reaction times and temperatures were chosen. Unfortunately, we always got an intractable mixture. We failed to produce **56** from **55**, perhaps because the TBDMS group is too large.

Then 2,2-dimethoxypropane was chosen as protecting reagent. According to previous work in our laboratory, dihydroxyacetone dimer **48** reacted with 2,2-dimethoxypropane (DMP) to give **53**, not the desired **54** (eq. 17).[79]



[17]

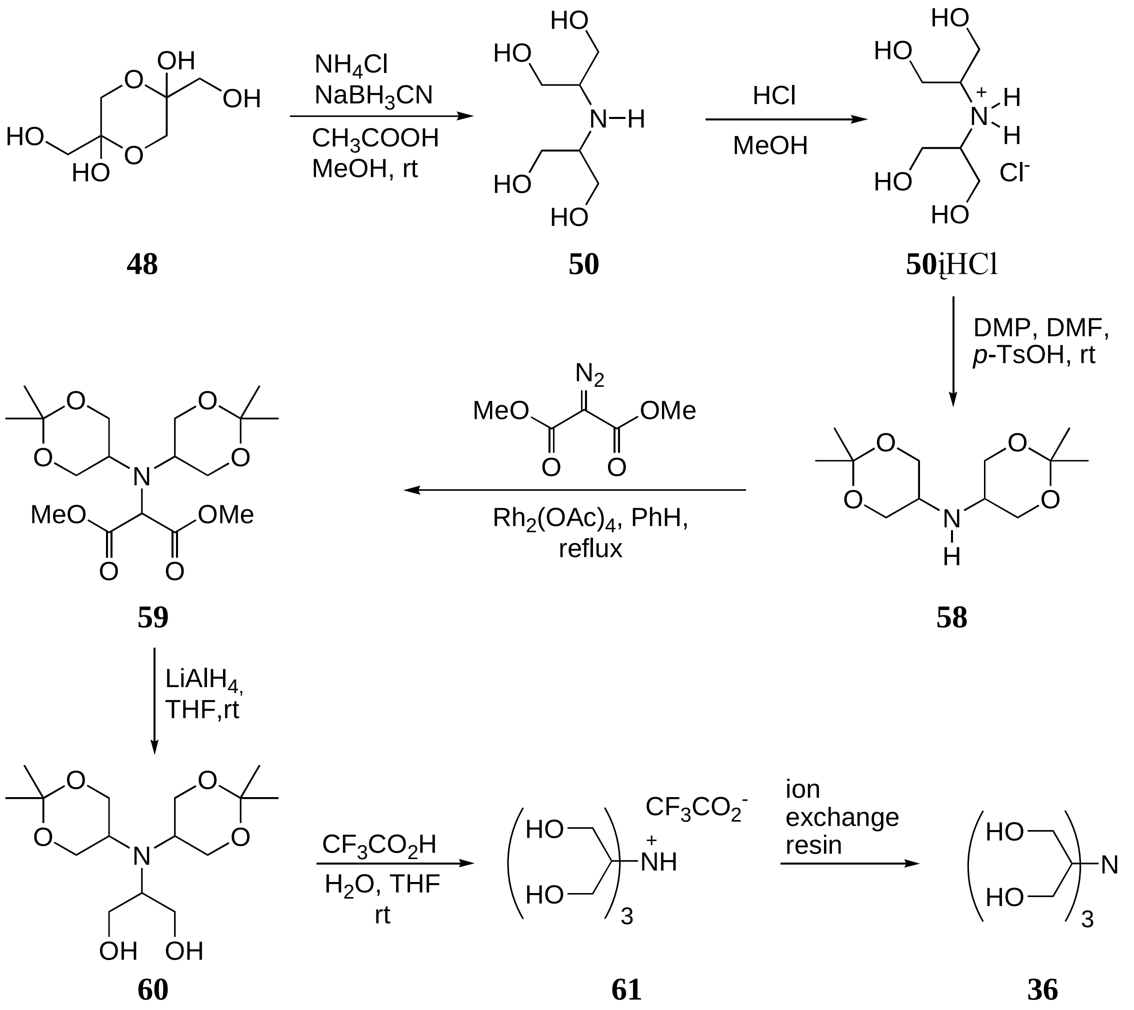
48 **53** **54**

[a] DMP = 2,2-dimethoxypropane

not formed

Rather than protect dihydroxyacetone, we prepared **50** by the method of SKFNWABF.[78] With compound **50** in hand, we wanted to use TBDMS as a protecting group for the hydroxyls. Secondary amine **50,** catalyzed by imidazole, reacted with TBDMSCl in DMF solvent to afford compound **56** in good yield (78.5 %). However, the carbenoid insertion into the N-H bond of **56** went poorly. In refluxing benzene, dimethyl diazomalonate (DDM) catalyzed by $Rh_2(OAc)_4$, reacted with protected secondary amine **56** to afford **57** in very low yield (5%). Again, the steric bulk of the TBDMS group may be a factor here. When we used DMP as protecting reagent with secondary amine **50** to afford protected secondary amine **58**, the subsequent N-H insertion to form **59** went smoothly. The target **36** was obtained after **59** was reduced and the acetonide protecting groups were removed. The overall synthesis of tertiary amine **36** in five steps from dihydroxyacetone dimer is shown in Scheme 4, and discussed in more detail in the following sections.

Scheme 4. Route from dihydroxyacetone to tertiary amine **36**



a) Synthesis of Acetonide 58

The first two steps of our synthesis are based on the work of SKFNWABF.[78] The first step was carried out by the method of SKFNWABF, but we modified the second step. In the second step, according to the literature method, secondary amine **50** reacted with

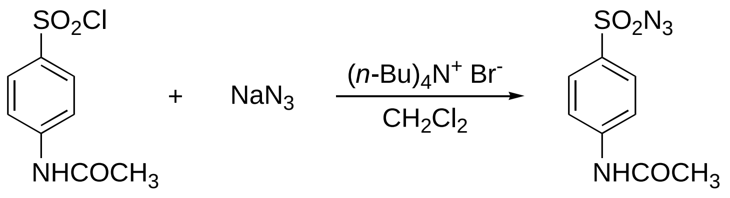
DMP in DMF and acetone catalyzed by concentrated sulfuric acid, then solid sodium bicarbonate was used to neutralize the reaction solution. The solvent was removed on the rotary evaporator and the residue was partitioned between ethyl acetate and water. The aqueous layer was extracted with ethyl acetate, and the organic layer was washed with brine, dried with $MgSO_4$, filtered, and concentrated to give 78% crude product **58**. In our hands, the yield ranged from 30% to 70%. Also, this crude product **58** didn't work for the next step (N-H insertion reaction). According to the paper,[78] pure **58** was obtained through the recrystallization from ether and hexane (however the yield was not reported). When we used this method to purify **58**, we got a very low yield. Perhaps the following two reasons caused the yield to vary so widely: (*i*) solid sodium bicarbonate does not dissolve in DMF/acetone solvent, so it is hard to completely neutralize the reaction solution. If the reaction solution cannot be totally neutralized, some protonated **58** still exists, and this protonated **58** will dissolve in the aqueous layer. Because it will not be extracted into ethyl acetate, it will lead to low yield. (*ii*) After removal of most of the solvent, a sticky solid was formed. The removal of the remainder of the DMF was difficult because of the high boiling point of DMF. Furthermore, the product **58** dissolves in DMF. The residual DMF will also entrain the secondary amine **58** to dissolve in the aqueous layer.

In our improved method, secondary amine **50** was dissolved in methanolic HCl to form **50**·HCl. Then **50**·HCl was reacted with DMP in DMF, catalyzed by *p*-toluenesulfonic acid monohydrate[83] (*p*-TsOH). The solution was neutralized with triethylamine. The mixture was concentrated *in vacuo,* the residue diluted with triethylamine and ethyl acetate. The ammonium salts were simply filtered off, and the solvent evaporated to afford crude product **58**. This crude product could be purified by column chromatography (73%)

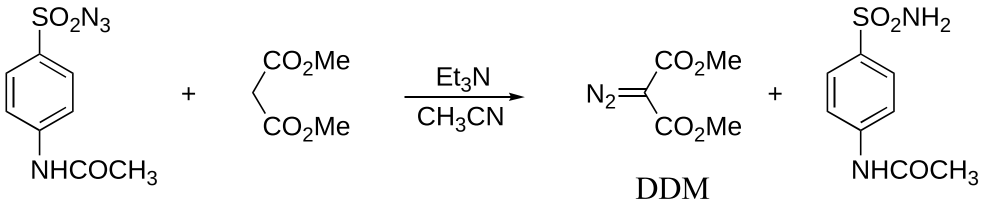
or crystallized from hexane (82%). Compared to the SKFNWABF method, we simplified the workup and improved the yield from 78% (*crude* yield of SKFNWABF[78] method) to 82% (*purified* yield of our improved method). Furthermore, we got very pure **58**. This is very important for the next step: the N-H insertion reaction.

b) Synthesis of tertiary amine 59 through N-H insertion reaction of rhodium(II) carbenoids

The insertion of a carbene or carbenoid generated from a diazocarbonyl compound into an N-H bond is a very useful process which leads to C-N bond formation. Also, since the desired compound **36** has hydroxymethyl groups which can be generated by the reduction of ester groups, dimethyl diazomalonate ("DDM") was chosen as the source of carbenoid. DDM was synthesized by a diazo transfer reaction (eq. 19).[84]



[18]



[19]

Dirhodium tetraacetate-catalyzed insertion of DDM into the NH bond of secondary amine **58** is the key step for synthesizing hindered tertiary amine **36**. However, dirhodium tetraacetate is well-known to form strong complexes with Lewis bases (including some amines),[85] which may inhibit the catalytic decomposition of DDM (Figure 2.1). In fact, Porter and his coworkers[86] found that the catalytic activity of $Rh_2(OAc)_4$ was totally inhibited by primary amines. This result is relevant to the N-H insertion reaction used to prepare tertiary amine **59**. If the secondary amine **58** we used was impure, and included a

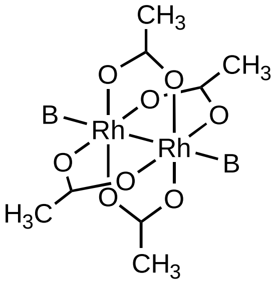


Figure 2.1 Complex of dirhodium tetraacetate with Lewis base B

little of the corresponding primary amine (*i.e.*, the acetonide of **49**), when the $Rh_2(OAc)_4$ catalyst was added, the reaction solution immediately become red-brown instead of the normal green color of $Rh_2(OAc)_4$. The red-brown color of the reaction solution indicated that $Rh_2(OAc)_4$ was poisoned.[87] After 10 h of refluxing in benzene, the reaction mixture showed by TLC unreacted DDM and **58** remaining. In such cases the yield of tertiary amine **59** was very low. The purity of acetonide **58** is therefore of crucial importance for this reaction. Fortunately, very pure crystalline **58** can be simply obtained by crystallization from hexane. In this key N-H insertion step, the yield was improved from 71% (using 4 mole% $Rh_2(OAc)_4$)[79] to 81% (using 2 mole% $Rh_2(OAc)_4$).

Compared to acetonide **58**, DDM is easy to prepare.[84a] In order to attempt to drive all acetonide **58** to the desired tertiary amine **59**, excess DDM was employed. However, it is very hard to convert all acetonide **58** to tertiary amine **59**, even though 50% excess DDM was used. By TLC analysis, amine **58** still was present after DDM had disappeared. But the yield was improved from 81% to 84% by using a 20% excess of DDM (the yield was the same even when 50% excess DDM was used).

c) Reduction of diester 59

In order to reduce the ester groups of **59** to alcohols, the most commonly used reagents are lithium aluminum hydride (LAH)[88] and lithium borohydride.[89] According to previous work in our lab,[79] reduction of tertiary amine **59** with lithium borohydride afforded a mixture of the fully reduced diol, the partially reduced monoalcohol, and starting material **59**, which never disappeared completely even when excess lithium borohydride was used.

So, we chose LAH as reducing reagent.[79,87,88a] The reduction of **59** with $LiAlH_4$ afforded the corresponding diol **60** at room temperature in THF under nitrogen. The yield of diol **60** was related to the ratio of diester **59** to $LiAlH_4$. The 1:6 molar ratio of diester **59** to LAH was the best ratio, affording 93% isolated yield of diol **60**. The yield of diol **60** could not be improved by using a larger excess of LAH; the diester **59** spot was still visible by TLC at the end of the reaction. But unreacted diester **59** is easy to recycle. The crude product was applied to a silica gel column. About 5% low-polarity starting material **59** was eluted first with hexane/EtOAc 1:3. Polar product **60** could be eluted next with ethyl acetate. The yield of diol **60** based on recovered starting material is 98%.

d) Deprotection of acetonide 60

The acetonide functionality is commonly used as a protecting group for hydroxyl groups in polyhydroxylated compounds due to its stability to mildly acidic as well as basic conditions.[82] As a consequence, many methods have been developed for deprotection.[82,90] Basically, deprotection of acetals requires the use of protic or Lewis acids. However, many of these methods suffer from disadvantages such as high acidity, long reaction times, inconvenient work up, unsatisfactory yields. Recently, some alternative methods have been developed, including acid ion-exchange resins,[91] silica-supported sodium hydrogen sulfate as a heterogeneous catalyst,[92] and lanthanum(III)nitrate hexahydrate.[93]

Acetonide **60** is a tertiary amine. At first, we thought if protic acids were employed as catalysts to deprotect the acetal groups of **60**, the nitrogen would be protonated to form a salt (*e.g.* **61)**. We know that a salt like **61** would be soluble in water, and insoluble or sparingly soluble in organic solvents. So it would be challenging to purify **61** and get free tertiary amine **36.**

First, we tried to use insoluble acidic matrices such as silica supported sodium hydrogen sulfate in THF,[92] or acidic ion-exchange resin (Amberlyst) in ethanol as catalysts to deprotect acetonide **60**.[91] However, neither method worked for our compound **60**. Previous work in our lab showed HCl solution needed long reaction times.[79] Finally, trifluoroacetic acid in aqueous THF was employed to cleave the acetal groups of **60**, affording tertiary amine **36** and its trifluoroacetate salt. This mixture was applied to an ion-exchange resin column, Amberlite, IR-120, H^+. The column was eluted with water first, and then a solution of 1 M aqueous ammonia. A white sticky liquid was obtained. The sticky liquid was kept on the vacuum line overnight, and it became a white solid. NMR spectra showed it was our target compound **36**. ^1H and ^{13}C NMR spectra (in D_2O) of compound **36** are shown in Figure 2.2.

The ^{13}C NMR spectrum of **36** is easily assigned: According to the DEPT spectrum of **36,** we knew the resonance at 61.0 ppm should be from carbon D, and 56.8 ppm peak is due to carbon E (methanol, 49.2 ppm by definition) in D_2O. The ^1H NMR spectrum for **36** is analyzed as follows: the multiplet at 3.16 ppm is from H_c. The two AB quartets at

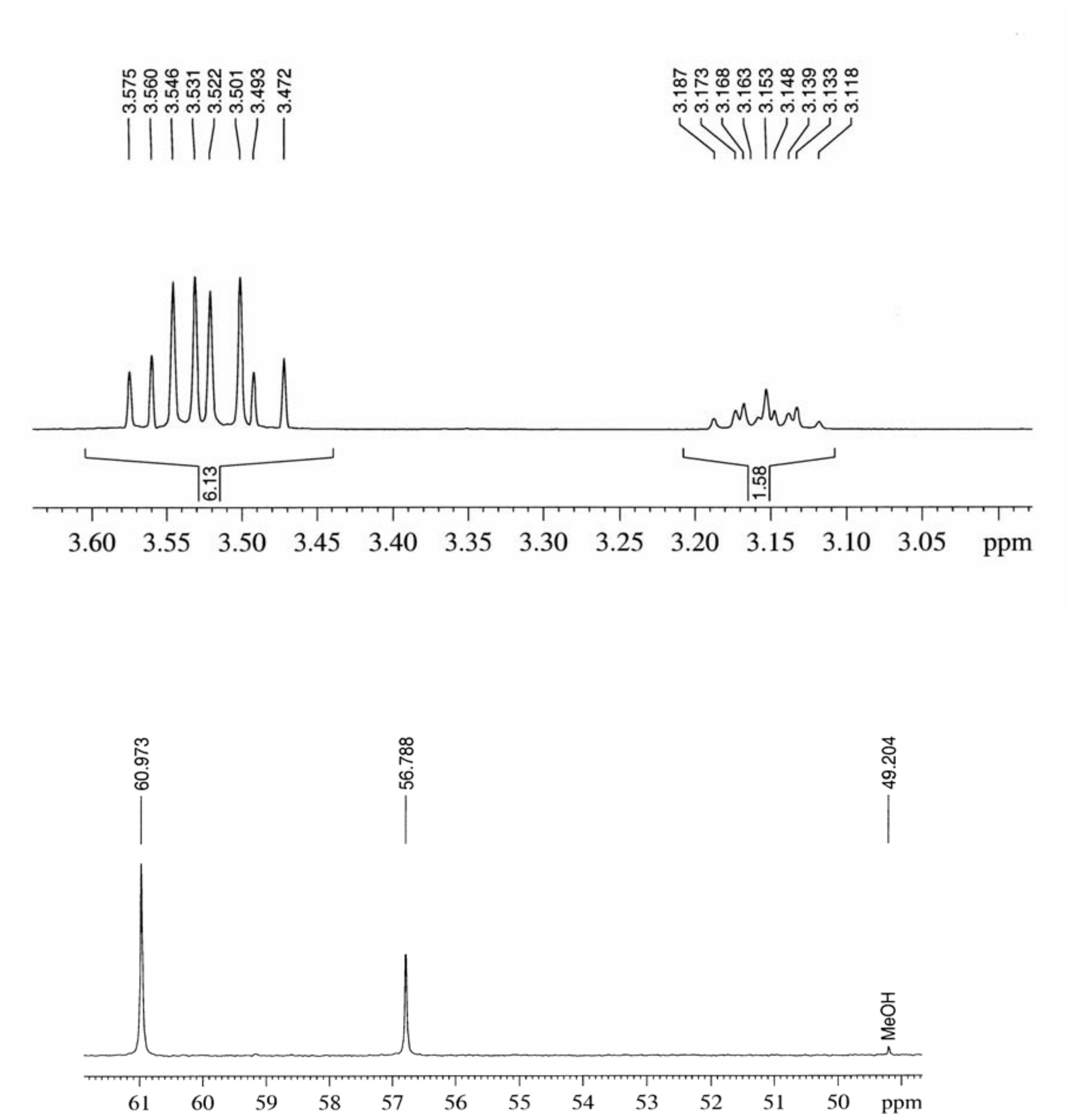
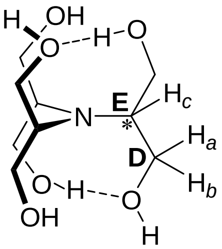


Figure 2.2 NMR spectra of compound **36** in D_2O. Top: 400 MHz ^1H spectrum of **36** (HDO was set to 4.80 ppm). Bottom: 100 MHz ^{13}C spectrum (A trace of CH_3OH is present as a chemical shift standard)

3.50 - 3.58 ppm are from H_a and H_b, which means H_a and H_b are magnetically non-equivalent. So H_a and H_b couple with each other and are also split by H_c. A factor here is the chiral carbon (**E)** and hydrogen bonding shown below. Because of the hydrogen bonds, C_E—C_D and C_D—O bonds cannot rotate freely, which results in H_a and H_b protons being more magnetically non-equivalent than in a freely rotating system. The ^{1}H NMR spectrum of **36** in DMSO-d_6 showed a triplet for the OH proton at 4.91 ppm. This means exchange of the OH protons was slow in this solvent, which very tentatively lends weight to the suggestion that H-bonding might be strong enough to hinder bond rotation.



36

2.1.3 Some properties of tertiary amine 36

In order to further prove the structure of **36**, we worked very hard to get a single crystal of **36**. Finally, we grew a very beautiful single crystal of **36** from THF solution. The structure of **36** as determined by X-ray crystallography is shown in Figure 2.3. For clarity, hydrogens bound to carbon have been omitted. Hydrogens bound to oxygen were located and refined during solution of the structure.

From this X-ray crystal structure of **36,** the distance between O_4---H_3 , O_2---H_1 is 1.80778 Å, 1.91697 Å respectively. These distances are shorter than the sum of van der Waals contact distance (2.6 Å)[113] of H···O for O-H···O hydrogen bond system. It is clear there are intramolecular hydrogen bonds ($O_4\cdots H_3$, $O_2\cdots H_1$) in **36**, just as the ^{1}H NMR spectrum suggested.

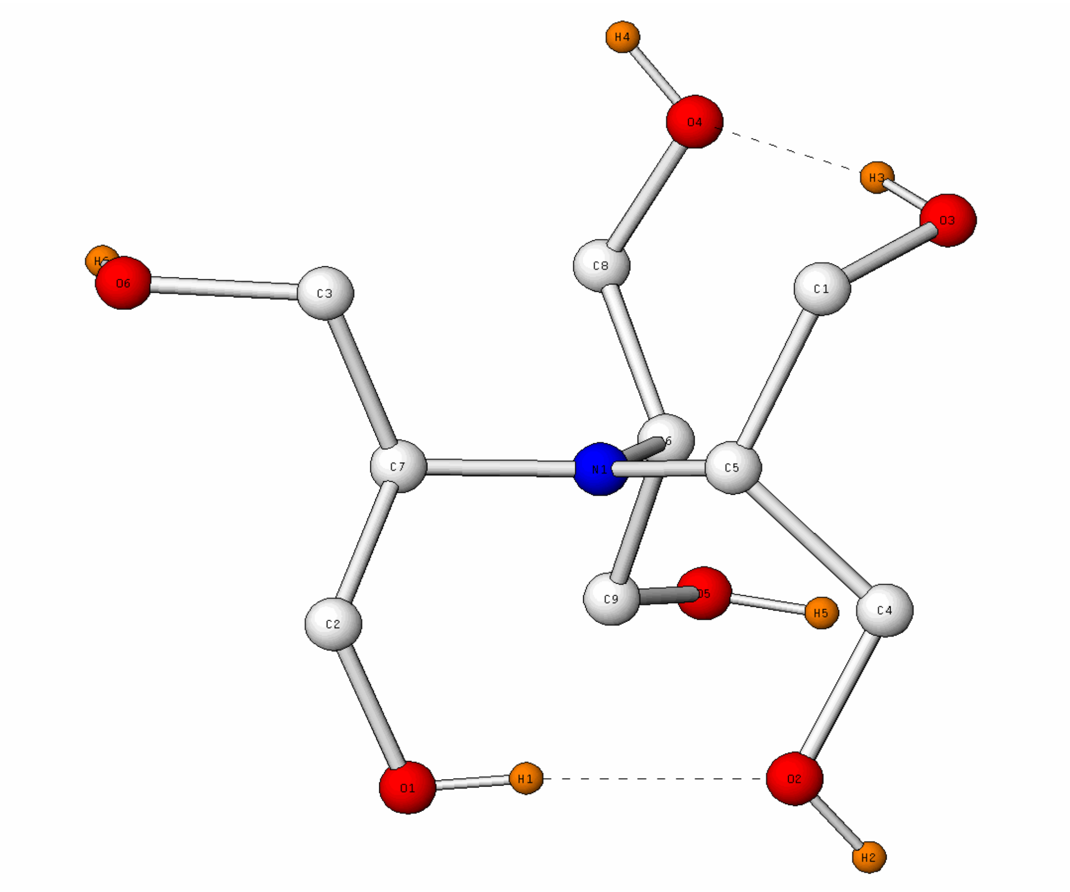
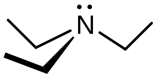
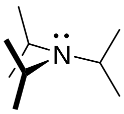
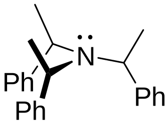
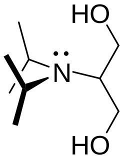
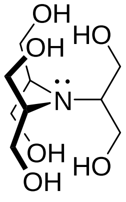
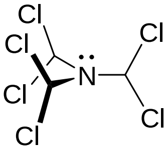


Figure 2.3 The X-ray crystal structure of compound **36**. Atoms are represented as spheres of arbitrary diameter. Hydrogens bound to carbon have been omitted.

More importantly, this crystal structure proves the nitrogen of **36** is essentially planar. There are two ways to quantify the planarity of nitrogen in tertiary amines. One is the sum of C-N-C angles, which will be 360° for a perfectly planar nitrogen. Another is the distance from nitrogen to the plane defined by the three carbons bound to nitrogen, which we will denote as "*h*". In tertiary amine **36**, the sum of C-N-C angles is 359.05(7)°, and *h* is 0.082 Å. In Table 2, the *h* of **36** is compared to *h* for an ordinary trialkylamine (Et_3N)

and several sterically congested trialkylamines. It is clear that **36** is one of the most planar trialkylamines known (taking the term "trialkylamine" to refer to nitrogen bound to three saturated (*i.e.* sp^3) carbons). Compound **36** is the key precursor of hypervalent nitrogen (10-N-5) for our project. As was previously discussed, oxidizing an 8-N-3 species to a 10-N-5 species includes changing the geometry of nitrogen from a pyramidal to a planar geometry, which will impose an energy cost. Now the tertiary amine **36** already has an almost planar geometry and the energy cost of changing geometry would be eliminated. So it should be a better precursor of hypervalent nitrogen species than **31**.

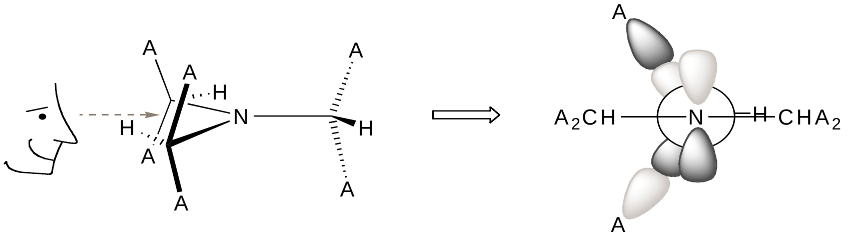
Table 2. *h* for various trialkylamines

Trialkyl amine					 **36**	
h	0.467 Å[94]	0.282 Å[94]	0.140 Å[95]	0.136 Å[87]	0.082 Å	0.000 Å[96]

The average $C(sp^3)$–$N(sp^3)$ bond length among 1042 trialkylamines is 1.469 ± 0.014 Å, with the middle 50% in the range 1.460 – 1.476 Å.[97] Remarkably, the average of the three C–N bond lengths in **36** is 1.4545(11) Å; that is, the C–N bonds of **36** are extremely short. Considering the steric crowing around nitrogen (every α-carbon is branched), one might have predicted long C–N bonds rather than short ones.

To explain this anomaly, we offer a qualitative argument based on orbital interactions. Consider *planar* **36**, shown below (with CH_2OH groups replaced by the letter A).

The Newman projection down an N-C bond suggests that the nitrogen p-orbital will interact with adjacent orbitals involved in A-C-A σ-bonding. In particular, the specific sidechain orbital shown, an antibonding 2a" orbital, is of proper symmetry for an interaction with the p-orbital of nitrogen, also a". A more complete orbital diagram is given in Figure 2.4. The strength of the favorable N 2p – 2a" interaction is inversely proportional to ΔE. When A = CH_3, the antibonding 2a" orbital is relatively high-lying, and the stabilization of the planar form by this orbital interaction is modest. However, as A becomes more electronegative, all the sidechain orbitals move to lower energy while the N 2p orbital remains unchanged. This decreases ΔE and in turn strengthens the filled-unfilled orbital interaction favoring the planar form of the amine. Having A = CH_2OH provides significant stabilization of the planar amine. When A = Cl, the amine is absolutely planar, as noted in Table 2. The strengthening of the N 2p – sidechain interaction along this series results in progressively shorter C-N bonds. In triisopropylamine (A = CH_3), the C-N bond length is 1.469(1) Å (at T = 84 K);[94] in **36** (A = CH_2OH), it is 1.4545(11) Å; in $N(CHCl_2)_3$ (A = Cl), it is 1.418(2) Å.[96]



36

Some interesting structural parameters of **36** from x-ray crystallography compared to various trialkylamines are shown in Table 3.

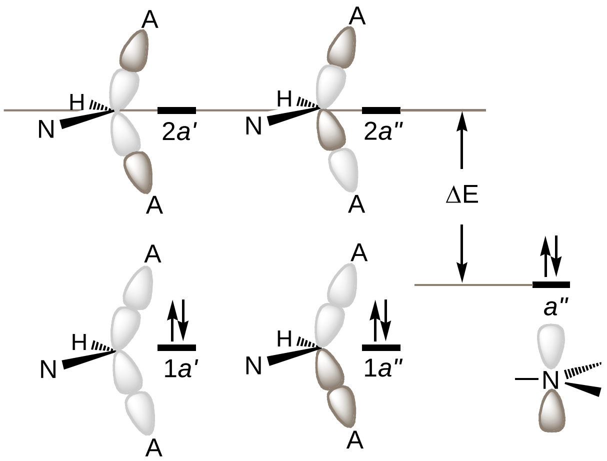
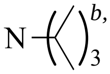
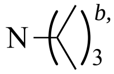


Figure 2.4. Orbital interaction diagram for an N-CHA_2 fragment

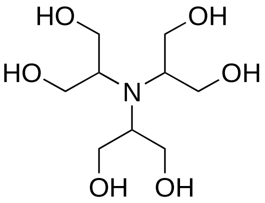
Table 3. Structural parameters of **36** and various trialkylamines from X-ray crystallography

Compound	*h* (Å)	Sum of C-N-C Angles (°)	C-N Bond Lengths (Å)[a]
36	0.082	359.05(7)	1.4509(11), 1.4561(11), 1.4566(10)
NMe_3[b]	0.454	331.9	1.448, 1.448, 1.448
NEt_3[b]	0.467	□[c]	□[c]
NEt_3[d]	0.444	335.1	1.490, 1.517, 1.514
NEt_3[e]	0.425	336.0	1.471, 1.475, 1.471
 [b, f]	0.292	348.6	*1.469(1)*
 [b, g]	0.282	349.2	*1.469(1)*

[a]Italics indicate an average value [b]reference 94 [c]disorder [d]Brady, S. F.; Singh, M. P.; Janso, J. E.; Clardy, J. *Org. Lett.* **2000**, *2*, 4047. [e]Born, M.; Mootz, D.; Schaefgen, S. *Z. Naturforsch, Teil B* **1995**, *50*, 101. [f] $T = 84$ K [g]$T = 118$K

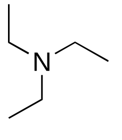
The pK_a of **36** was measured by titration of a 0.01 M aqueous solution of **36** with standard 0.01 M HCl at 25 °C, and was found to be 3.08 ± 0.03. (We thank Dr. Yu Qin of this Department for performing this measurement). When compared with simple trialkylamines like triethylamine (Figure 2.5), it is clear that **36** is an unusually weak base.

The diminished basicity of **36** might be due to difficulty in deforming the essentially-planar nitrogen of **36** to accommodate the additional ligand (H^+) in the conjugate acid. Examination of X–ray crystal structure of **36**·HCl (Figure 2.6) lends support to this idea. (As a product of another experiment (*vide infra*), **36**·HCl was available).



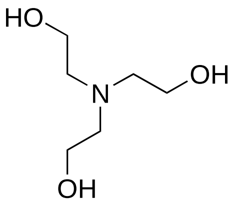
36

pK_a = 3.08



62

pK_a = 10.71[98a]



37

pK_a = 7.78[98b]

Figure 2.5. Comparison of basicities of **36** and other trialkylamines

As shown in Table 4, the ammonium cation derived from **36** is severely flattened at nitrogen. Indeed it is even more deformed than the ammonium cation derived from triisopropylamine.[94]

According to Hamilton's[113] tabulation, the H···O distance is 2.6 Å in an N-H···O hydrogen bonding system. From the X-ray crystal structure of **36**·HCl, we can see the “triple” intramolecular hydrogen bond ($H_1\cdots O_4$, $H_1\cdots O_5$, $H_1\cdots O_6$) in **36**·HCl. It is very similar to what Holmes[114] reported in compounds **63A**, **63B**, and **64**. The “triple” hydrogen bonding interactions of some tertiary amine cations are summarized in Table 5.

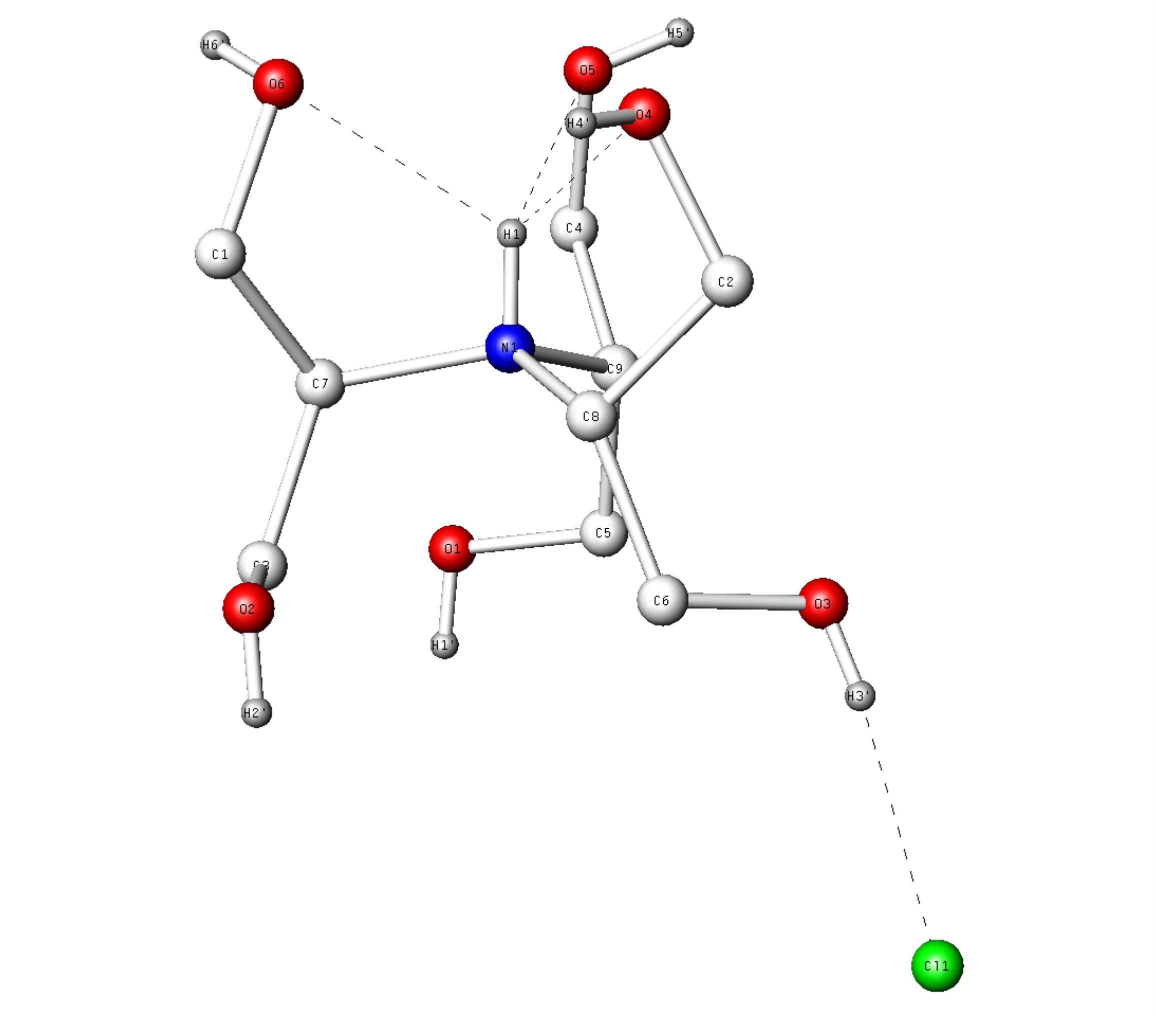
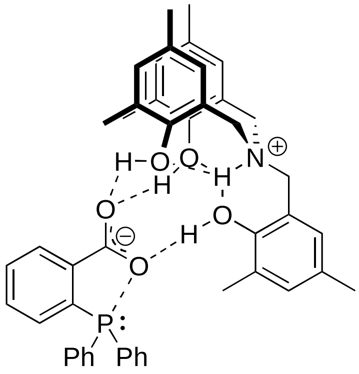


Figure 2.6. The X-ray crystal structure of compound **36**·HCl. Atoms are represented as spheres of arbitrary diameter. Hydrogens bound to carbon are not shown.

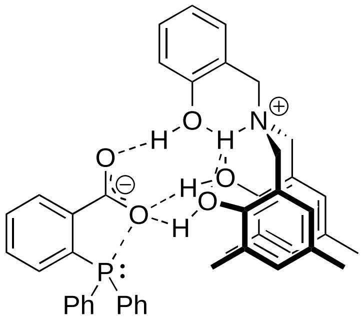
Table 4. Geometries of protonated trialkylamines

Ammonium ion	Average N-C length (Å)	Average H-N-C angle (°)	Average C-N-C angle (°)	Number of examples[a]
Uncongested				
$(CH_3)_3NH^+$	1.48	107.5	111.4	49
$(HOCH_2CH_2)_3NH^+$	1.50	107.0	111.8	21
Congested (acyclic)				
$((CH_3)_2CH)_3NH^+$[b]	1.533	105.1	113.5	1
$((HOCH_2)_2CH)_3NH^+$[c] **36**·HCl	1.528	102.3	115.6	1

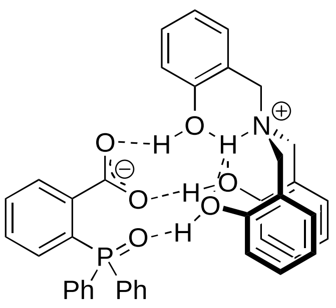
[a] Examples found in the Cambridge Crystallographic Database. [b] Bock, H.; Göbel, I.; Bensch, W.; Solouki, B. *Chem. Ber.* **1994**, *127*, 347-351 [c] This work



63A



63B



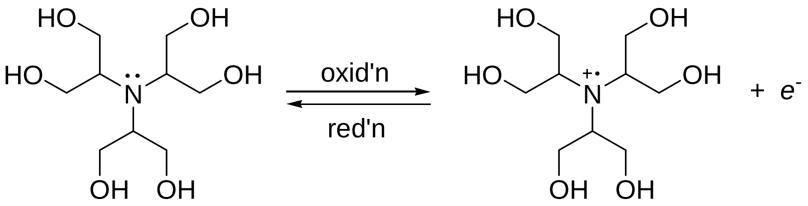
64

$E_{1/2}^{ox}$ of **36** (eq. 20) was found to be 0.88 V from cyclic voltammetry on **36** (Au electrode, in aqueous Na_2SO_4, 100 mV/sec scan rate, 0 to 1.5 V, Ag/AgCl reference electrode). (We thank Dr. Wei Zhu of this Department for performing this measurement). This is in the same range as other hindered tertiary aliphatic amines (Figure 2.7).[87]

Table 5. "Triple" hydrogen bonding interactions of some tertiary ammonium cations

tertiary anime cations	$d_{N\text{-}H}$(Å)	$d_{O\text{--}H}$(Å)	Avg of $d_{O\text{--}H}$(Å)
36□HCl[a]	0.90	2.22 2.26 2.18	2.22
63A[b]	0.91	2.40 2.26 2.24	2.3
63B[b]	0.91	2.21 2.18 2.50	2.30
64[b]	0.91	2.37 3.29 2.17	2.27

[a] This work. [b] see ref. 114



$E_{1/2}$ = 0.88 V
(reversible)

[20]

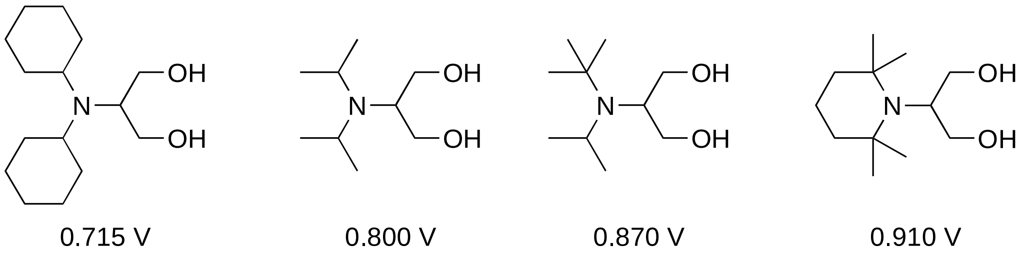
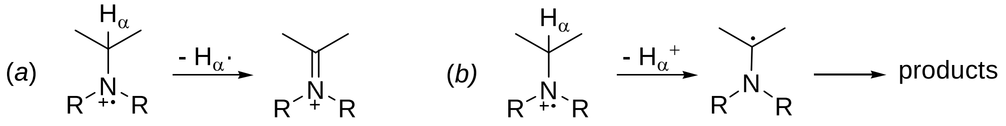
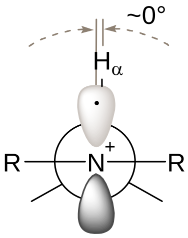


Figure 2.7. Oxidation potentials ($E_{1/2}^{ox}$) of several sterically congested trialkylamines

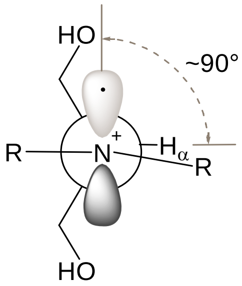
However, in contrast to other sterically unhindered tertiary amines, the redox process for **36** was reversible. This suggests that the radical cation derived by oxidation of **36** is kinetically stable. Usually, for unhindered tertiary amines, the radical cation will lose α-H· to form the iminium cation (eq. 21 (*a*)), or lose α-H$^+$ to form different products (eq. 21 (*b*)) according to electrochemical oxidation conditions (for example, secondary amine R$_2$NH and aldehyde[115a] under water) as shown below[115] (eq. 21). The C-H$_\alpha$ bond can achieve periplanarity with the N p-orbital (*i.e.* dihedral angle = 0° or 180° as shown in (*c*)). Thus the loss of α-H· or α-H$^+$ is rapid and the redox process for unhindered tertiary amines is not usually reversible. However, in **36**$^{+•}$, the α-H is *in the nodal plane* of the p-orbital of nitrogen (dihedral angle = 90º as shown in (*d*)). This strongly disfavors loss of α-H· or α-H$^+$ and since rotating the sidechain so that the C-H$_\alpha$ bond is periplanar with the nitrogen p-orbital is sterically very difficult, the radical cation of **36** is relatively long-lived.



[21]



(*c*) unhindered amine radical cation

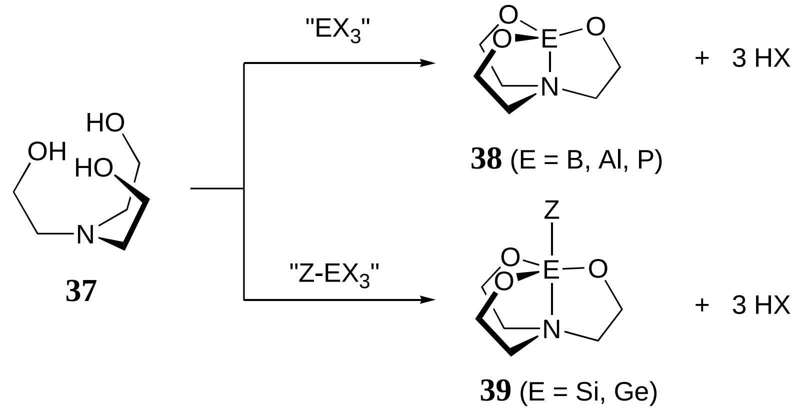


(*d*) **36**$^{+•}$

Amine hexaol **36** is a highly atypical and fascinating tertiary amine. We hope it will prove to be useful in the synthesis of **41**, **44**, or similar systems.

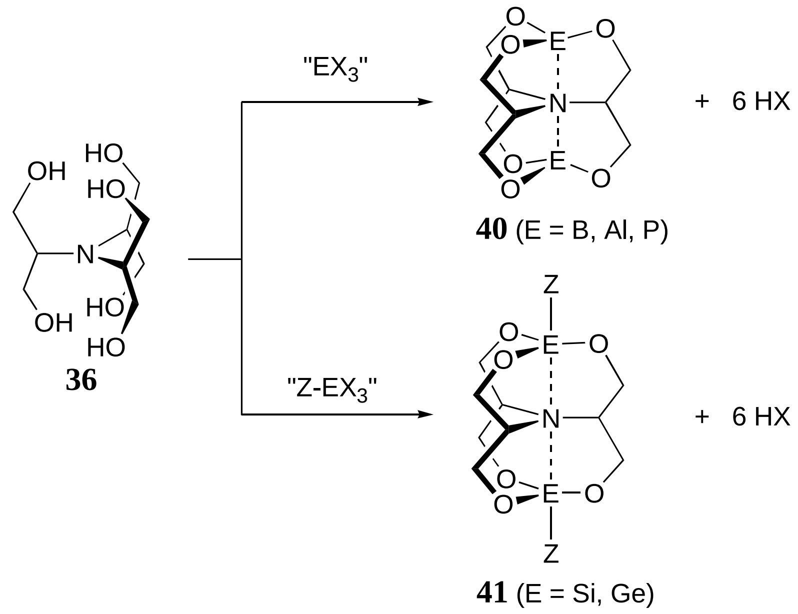
2.2 Tris(1,3-dihydroxy-2-propyl)amine 36 incorporating some main group elements

Triethanolamine reacts with a variety of main group element reagents to form the large and extensively studied class of compounds called atranes,[67] *e.g.* **38**, **39** (eqs 22 and 23). Amine hexaol **36** may be thought of as a “doubled” analogue of triethanolamine. So with **36** in hand, we explored a variety of reagents which might be used analogously to form compounds **40**, or **41** (eqs 24 and 25).



[22]

[23]



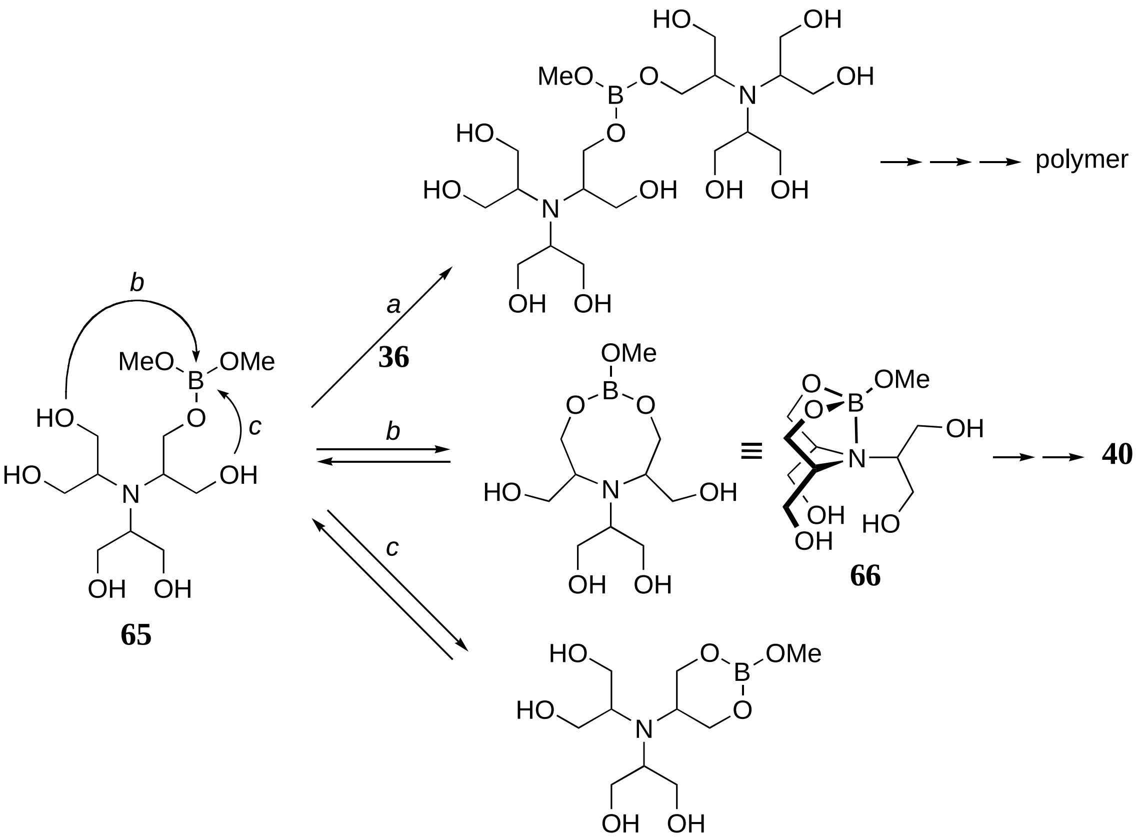
[24]

[25]

2.2.1 Reactions of 36 with various sources of boron

"Double closure" of **36** to **40** or **41** is not without potential problems. Consider the reaction of **36** with "EX_3" reagent $B(OMe)_3$, for example (see Scheme 5). To reach **40** (E = B), six transesterification steps are required. Intermediate **65** is formed after the first transesterification. The next transesterification may proceed either intramolecularly or intermolecularly. The latter is illustrated in Scheme 5 as path *a*. Further steps of this type type would eventually lead to polymeric products. Intramolecular transesterification may occur in one of two ways, shown in Scheme 5 as paths *b* and *c*. Path *b* could be called the "inter-sidearm" mode of cyclization, and path *c* the "intra-sidearm" mode of cyclization.

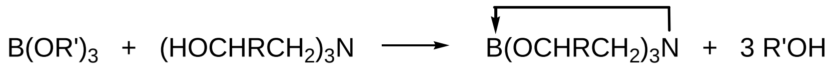
Scheme 5 Possible pathways in the reaction of **36** with $(MeO)_3B$



Path *b* is the only path which would lead to the desired product **40**. Path *b* involves formation of an eight-membered ring and path *c* a six-membered ring, which would tend to favor path *c* over path *b* on entropic grounds. However, the B-N dative bond possible in path *b* (**66)** may provide an enthalpic driving force sufficient to favor path *b* over path *c*. If paths *b* and *c*, as well as subsequent transesterification steps, are reversible, and if the reaction is carried out under conditions of thermodynamic control, it is possible that **40** could represent the deepest thermodynamic sink and so be formed in high yield regardless of whether path *b* or *c* is preferred. Against the background of such considerations, investigations of the "double closure" of **36** were undertaken.

a) The reaction of 36 with trimethyl borate, $(MeO)_3B$

A well-investigated method to prepare boratranes is transesterification of trialkylborates with tris(2-hydroxyalkyl)amines[98] (eq. 26). Normally, the reaction occurs upon



$$B(OR')_3 + (HOCHRCH_2)_3N \longrightarrow B(OCHRCH_2)_3N + 3\ R'OH \qquad [26]$$

short heating of the reagent mixture without any solvent.[99] So, the first source of boron tried with **36** was trimethyl borate. Under N_2, the reaction proceeded on heating excess trimethyl borate and **36**. Unfortunately the product didn't dissolve in most organic solvents, but very easily dissolved in D_2O. The NMR spectra are shown in Figure 2.8. The ^1H NMR spectrum was complex, but the ^{13}C NMR spectrum appeared much simpler. Peak A is methanol (as chemical shift standard), peak B and peak C are due to starting material **36**. The other three peaks are from the product in this reaction. We tried to purify it, but it was insoluble in most common organic solvents. Our attempts to purify the product failed, so finally we gave up.

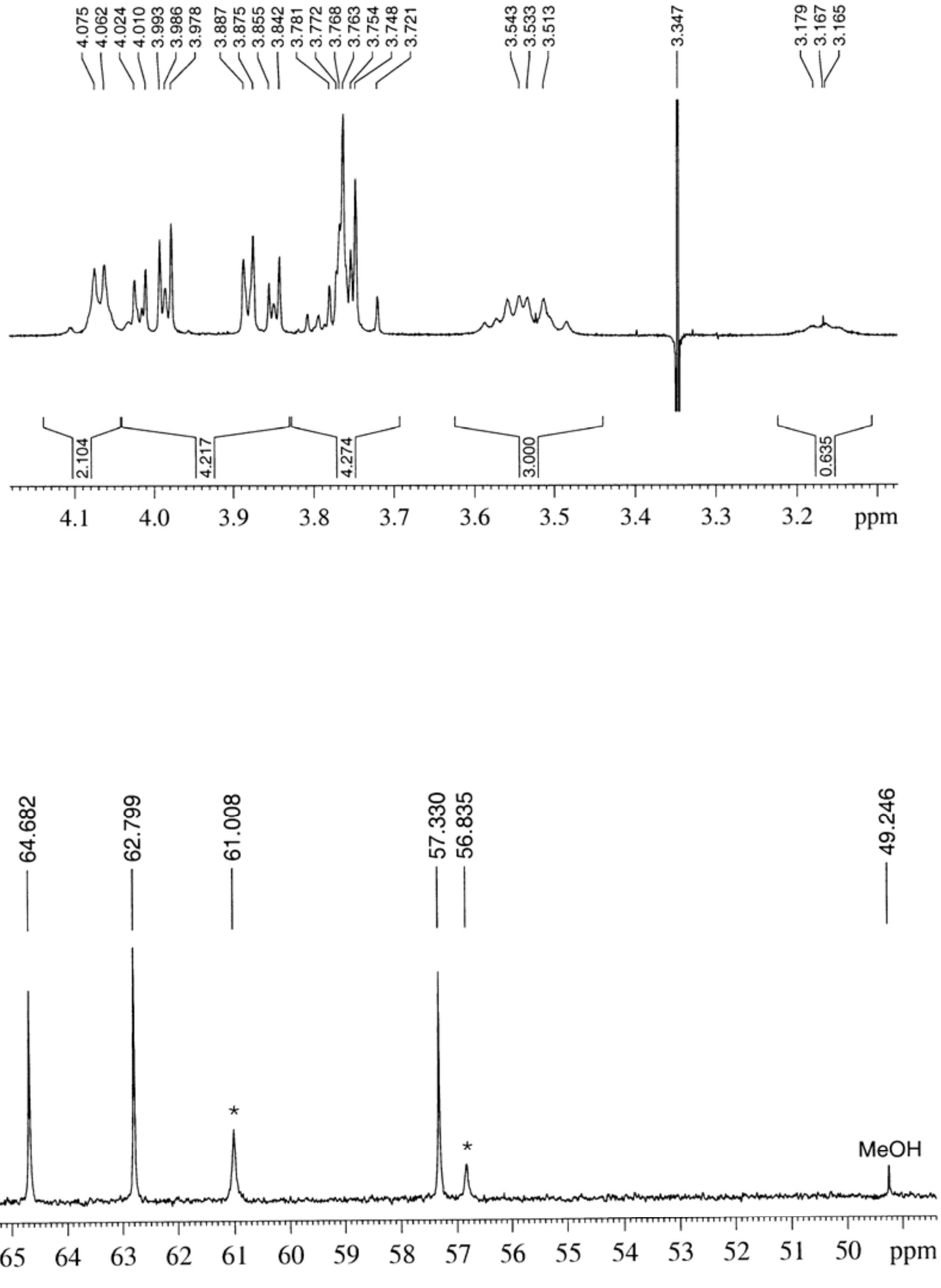
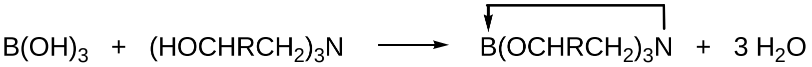


Figure 2.8 NMR spectra of the product of reaction of **36** with $(MeO)_3B$. (a) 400 MHz ^1H NMR spectrum (b) 100 MHz ^{13}C NMR spectrum

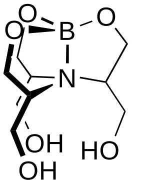
b) The reaction of 36 and boric acid, H_3BO_3

The simplest route to prepare boratranes is esterfication of boric acid by tris(2-hydroxyalkyl)amines[98] (eq. 27). The second source of boron tried with **36** was boric acid.

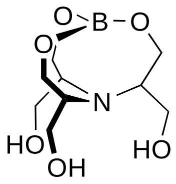


$$B(OH)_3 + (HOCHRCH_2)_3N \longrightarrow B(OCHRCH_2)_3N + 3\,H_2O \qquad [27]$$

A mixture of boric acid and **36** in DMF was heated under nitrogen (oil bath 130-150 °C). A white precipitate formed after several hours. This white precipitate also didn't dissolve in most organic solvents ($CHCl_3$, acetone, THF, ethyl acetate, ether, DMF, DMSO), and very easily dissolved in D_2O (the NMR spectra were the same as in Figure 2.8). So it's hard to determine its structure. But in an NMR tube, this white solid dissolved in DMSO-d_6 after heating for 2 - 3 h. The ^1H and ^{13}C spectra are shown in Figure 2.9. The mass spectrum showed molecular ions at m/e 247, and m/e 246, in the intensity ratio 5:1, as well as peaks at m/e 208, 148, and 44. The elemental analysis was (C, 43.88; H, 7.28; N, 5.55). Based on these data, this white solid may be assigned the structure **67** or **68** (cal'd for $C_9H_{18}NO_6B$: C 43.76; H 7.34; N 5.67; molecular weight $C_9H_{18}NO_6{}^{11}B$ = 247 g/mol, $C_9H_{18}NO_6{}^{10}B$ = 246 g/mol). For convenience we will refer to this compound as



67



68

the "one-boron" compound. Structure **67**, a "triptych," implies a transannular dative bond between boron and nitrogen, and structure **68** implies none. Does the one-boron compound resemble triethanolamine borate (TEAB, **38** E = B), which was proved to have the

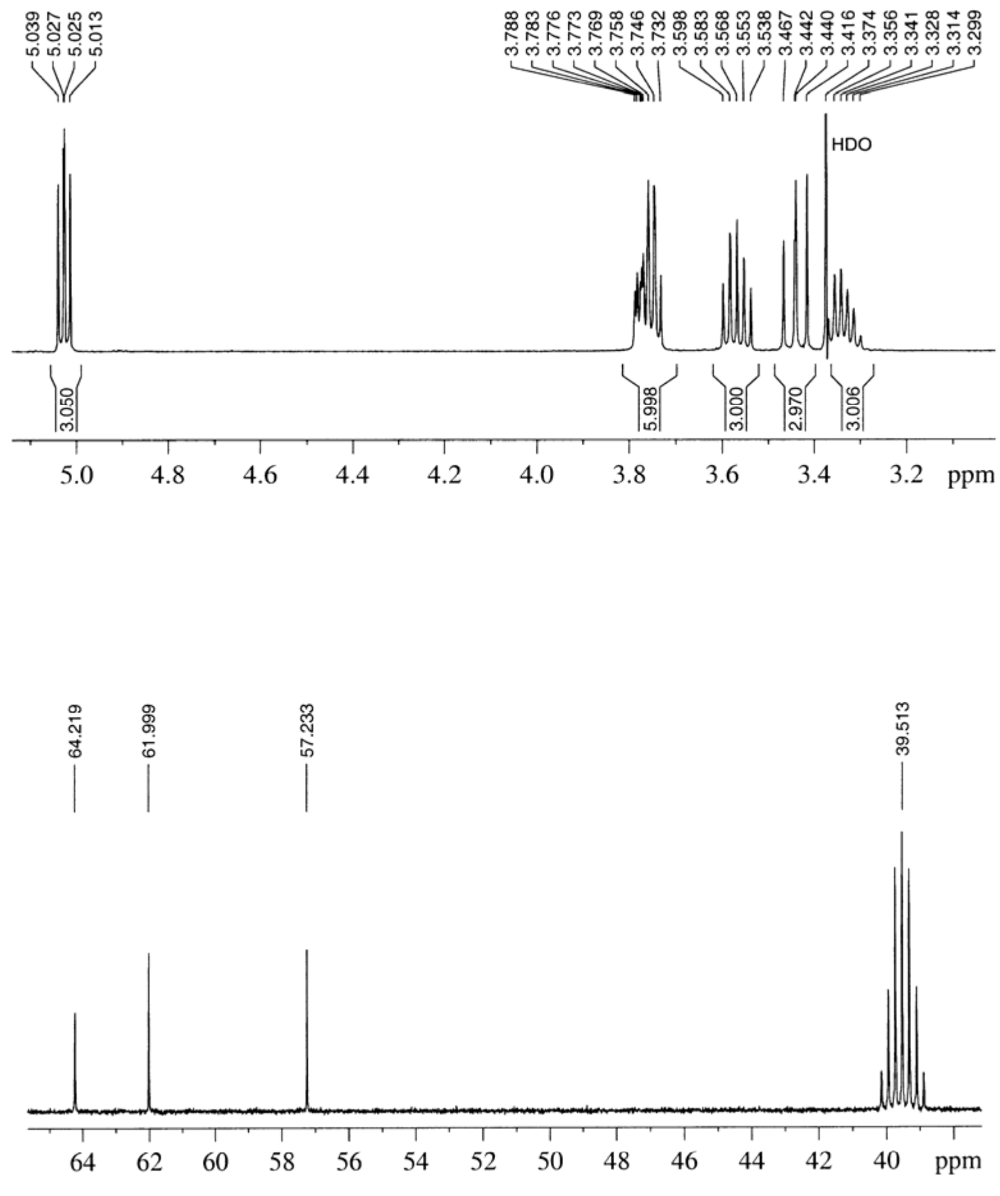
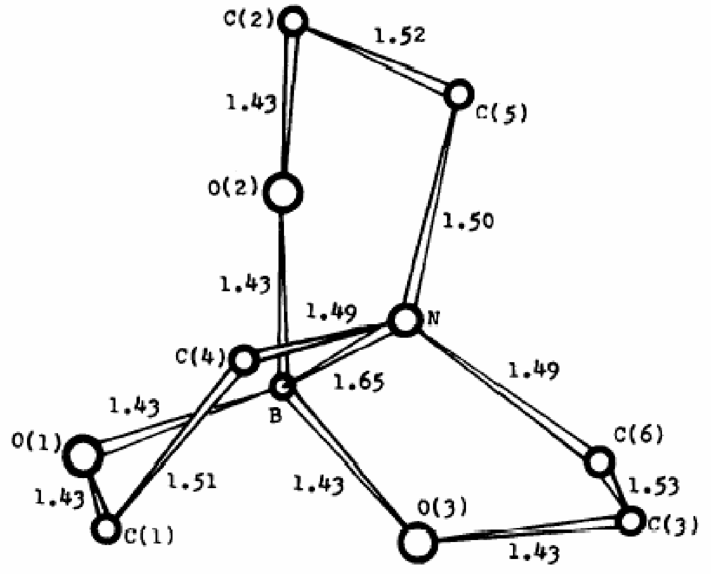


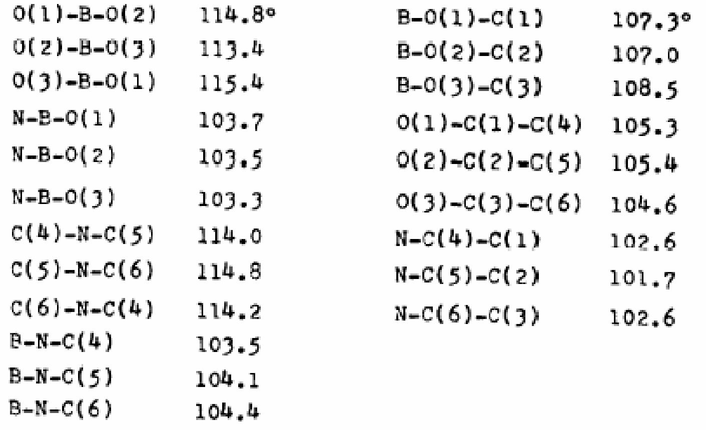
Figure 2.9 NMR spectra of the reaction of **36** with boric acid. (DMSO-d_6 solvent) Top: 400 MHz ^{1}H NMR spectrum. Bottom: 100 MHz ^{13}C NMR spectrum.

triptych structure?[100] The X-ray crystal structure, intramolecular bond distances and angles of TEAB are shown in Figure 2.10.[100c]

(a) The molecular structure of TEAB with some bond distances (Å).



(b) Bond angles



O(1)-B-O(2)	114.8°	B-O(1)-C(1)	107.3°
O(2)-B-O(3)	113.4	B-O(2)-C(2)	107.0
O(3)-B-O(1)	115.4	B-O(3)-C(3)	108.5
N-B-O(1)	103.7	O(1)-C(1)-C(4)	105.3
N-B-O(2)	103.5	O(2)-C(2)-C(5)	105.4
N-B-O(3)	103.3	O(3)-C(3)-C(6)	104.6
C(4)-N-C(5)	114.0	N-C(4)-C(1)	102.6
C(5)-N-C(6)	114.8	N-C(5)-C(2)	101.7
C(6)-N-C(4)	114.2	N-C(6)-C(3)	102.6
B-N-C(4)	103.5		
B-N-C(5)	104.1		
B-N-C(6)	104.4		

Figure 2.10. X-Ray crystal structure and some structural data for TEAB[100c]

In order to distinguish **67** from **68**, we tried to grow a crystal of the one-boron compound. Crystallization from DMSO/ethyl acetate (open to air for several days) gave a crystal suitable for X-ray analysis. The X-ray analysis (Figure 2.11) revealed that the one-boron compound has the triptych structure **67**, and the existence of the transannular B-N bond is confirmed by the experimental distance of 1.6875(13) Å. This is comparable with the sum of the van der Waals radii of boron and nitrogen, 3.11 Å,[101a] and the sum of

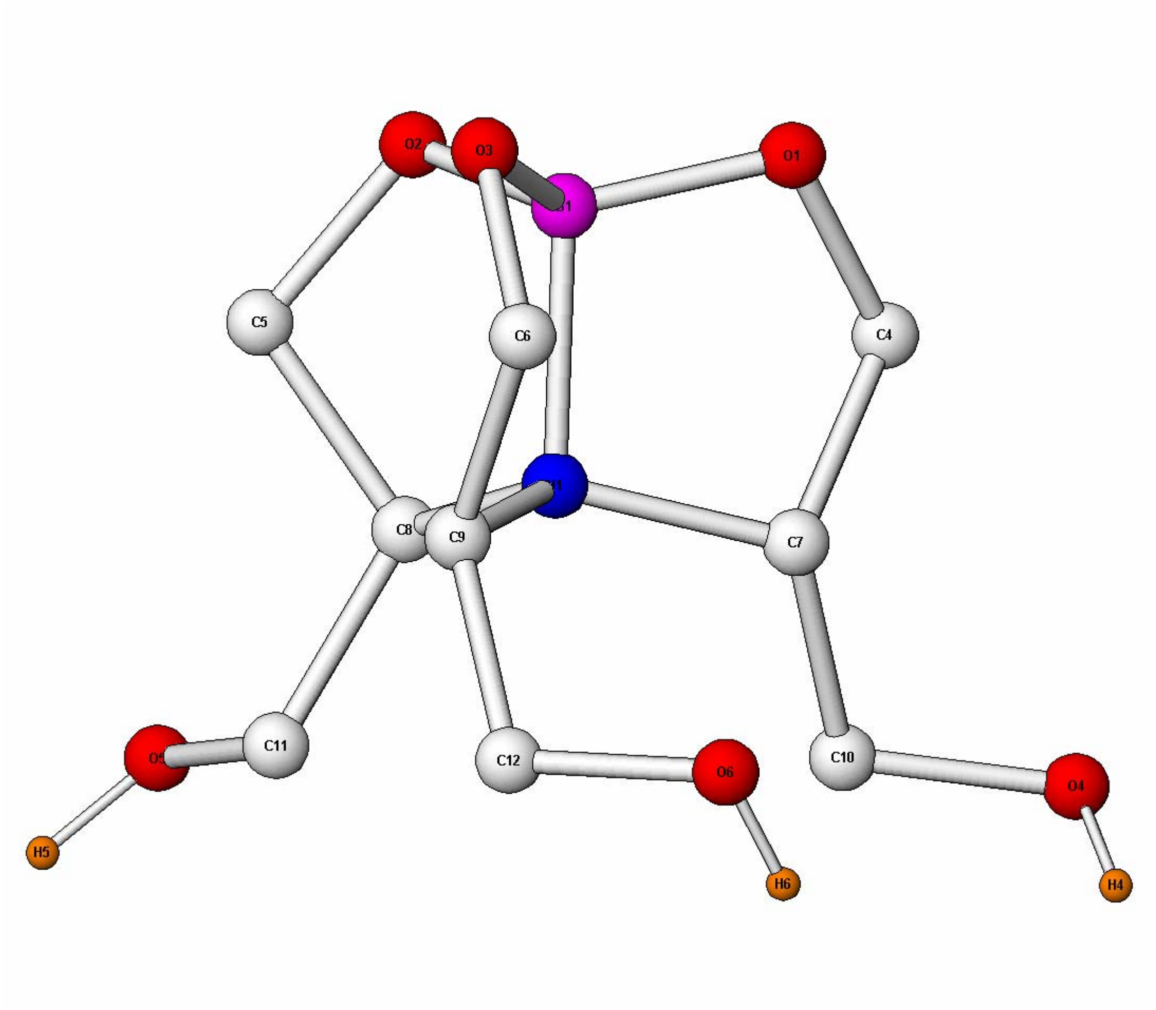


Figure 2.11 X-ray crystal structure of one-boron compound **67**. Hydrogens bonded to carbon have been omitted.

the covalent B-N bond, 1.58 Å.[101b] The average C-N-C and B-N-C bond angles are 115.88(7)° and 101.87(7)°, respectively. All five-membered rings, *e.g.* N-B-O(3)-C(5)- C(8), are non-planar. Some geometric parameters of **67** and TEAB are summarized in Table 6. From the X-ray crystal structure (Figure 2.11) of one-boron **67**, one may note there is no intramolecular hydrogen bonding in **67**.

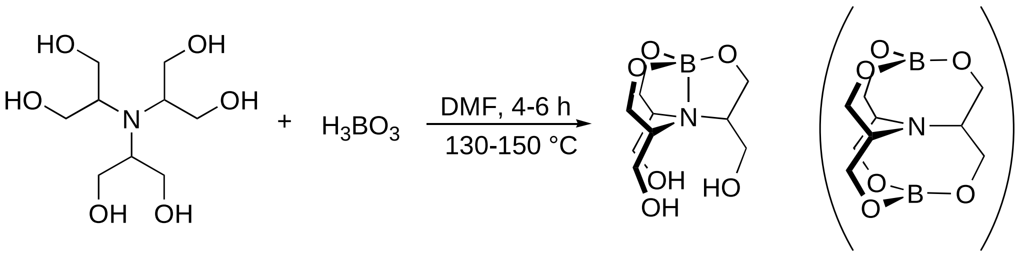
The ^{1}H NMR spectrum of **67** in DMSO-d_6 showed a triplet for the OH proton at 5.025 ppm. This means exchange of the OH protons was slow in this solvent, which provides evidence to the suggestion that H-bonding might be strong enough to somewhat hinder bond rotation.

Table 6. Geometric parameters of **67** and **TEAB**

Compound	Average N-C length (Å)	Average B-O length (Å)	B-N length (Å)	Average C-N-C angle(°)	Average B-N-C angle(°)	Average O-B-O angle(°)
67[a]	1.5093 (12)	1.4380 (13)	1.6875 (13)	115.88 (7)	101.88 (7)	114.62 (9)
TEAB[b]	1.49	1.43	1.647 (9)	114.3	104.0	114.7 (6)

[a]This work [b]ref. 100c

Initially, we thought the reaction of **36** with boric acid produced solely the one-boron compound **67**; the two-boron compound **69** was not detected in this reaction (eq. 28).

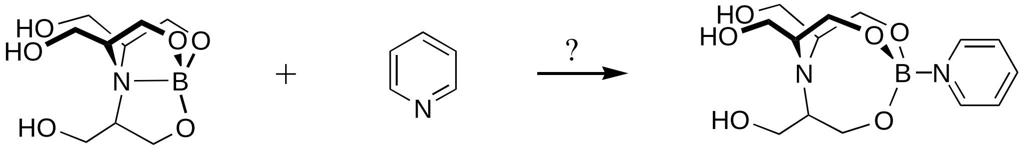


[28]

36 **67** **69**

not formed ?

We were interested in testing the strength of the internal B-N dative bond of **67** by reacting **67** with various nucleophiles, *e.g.* pyridine or triethylamine (eq. 29).



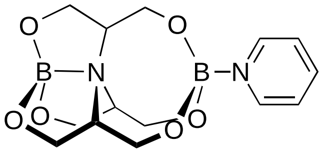
67 **70** [29]

We repeated the reaction of equation 28 to obtain some white solid. When we had done so several times, we were faced with results that were confusing. Sometimes the white solid product very easily dissolved in pyridine. Sometimes it was very hard to dissolve in pyridine, even after heating for several hours. We also found this white solid was very moisture sensitive (open to air just a few minutes). Eventually, we noted this white solid was very easily dissolved in pyridine *before* it hydrolyzed in moist air. *After* it was hydrolyzed, it was very hard to dissolve in pyridine. But the hydrolyzed product easily dissolved in DMSO-d_6 and the ^{1}H and ^{13}C NMR spectra were those of the one-boron compound **67** (Figure 2.9).

At this point, we realized the white precipitate in equation 28 was not compound **67**, but rather it was possibly the two-boron compound **69**, which dissolves in pyridine. Compound **69** then hydrolyzes rapidly to one-boron compound **67**, which does not dissolve in pyridine.

To confirm this proposal, we very carefully did the reaction of equation 28 at different temperatures under nitrogen, with attention paid to the exclusion of moisture. At rt, no precipitate was formed after **36** and boric acid in DMF were stirred for one day. No reaction occurred according to the NMR spectra. The same reaction was done at 85 – 90 °C for one day and also no white precipitate was formed. But some white solid was obtained after DMF was very carefully removed under nitrogen. This white solid did not dissolve in pyridine, but it dissolved in DMSO-d_6. The NMR spectra were the same as **67** (Figure 2.9). However, at a reaction temperature over 130 °C, some white precipitate was formed after approximately 4 - 6 h. This white precipitate easily dissolved in pyridine.

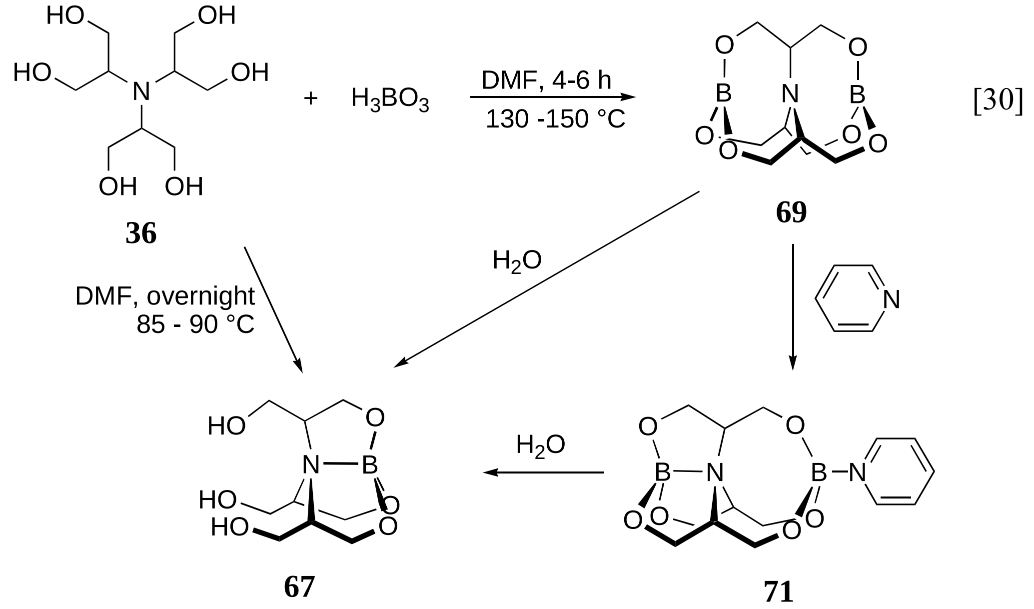
In order to determine the molecular structure of the precipitate formed at 130 °C, it was carefully dissolved in pyridine under nitrogen and the excess pyridine was slowly removed in a stream of nitrogen. A very nice crystal was formed. X-ray analysis revealed that this white crystal was **71**, a complex of two-boron compound **69** with one pyridine (Figure 2.12).



71

Consequently, when tertiary amine **36** reacted with boric acid in DMF, at various reaction temperatures, the product could be one-boron **67** (reaction temperature below 100 °C) or "two-boron" **69** (reaction temperature over 100 °C). So, equation 28 must be revised; the real product (white precipitate) is the two-boron compound **69** (eq. 30). The one-boron compound **67** dissolved in DMF, DMSO, but did not dissolve in pyridine and triethylamine. Perhaps the dative bond between nitrogen and boron in **67** is sufficiently strong that **67** doesn't react with nucleophiles such as pyridine or triethylamine. Two-boron compound **69** didn't dissolve in most organic solvents including DMF and DMSO, however it very easily dissolved in pyridine because of reacting with pyridine to form compound **71**. That means in the two-boron compound there was weaker or no dative bond between nitrogen and boron compared to one-boron compound. Thus the boron of **69** has stronger electrophilicity and reacts with pyridine (a nucleophile). Both **69** and **71** are extremely moisture sensitive, hydrolyzing to give one-boron compound **67** as shown in Scheme 6.

Scheme 6. Reaction of **36** with H_3BO_3



For **71**, the crystal structure is shown in Figure 2.12. The unit cell contains two independent molecules, labeled A and B. The X-ray analysis revealed that **71** has a "trip-tych-and-cage" structure. Some structural parameters of **71** are shown in Table 7. The existence of the transannular (*i.e.* triptych) B-N bond is confirmed by the B-N distance of 1.701(4) Å (average of molecules A and B). The "cage" B····N distance is 3.093(4) Å (average of molecules A and B). The average C-N(3)-C and B-N(3)-C bond angles are 115.8(2)° and 101.99(13)°, respectively. Compared to TEAB and one-boron **67**, the triptych B-N(sp^3) dative bond in **71** (1.701(4) Å) is longer and weaker than that of TEAB (1.647(9) Å) and **67** (1.6875(13) Å).

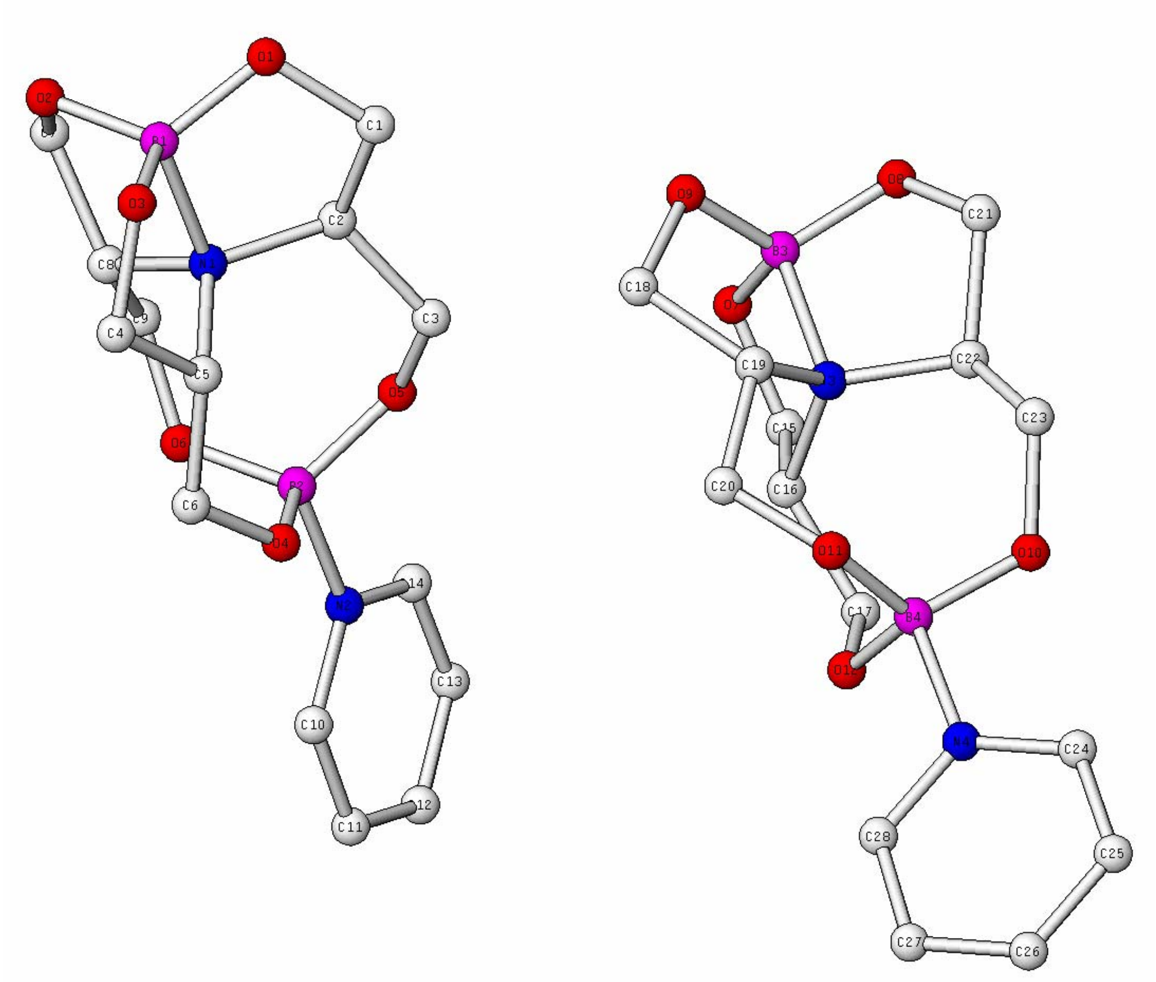


Figure 2.12. X-ray crystal structure of compound **71**. There are two independent molecules in the unit cell. Atoms are represented by spheres of arbitrary diameter. All hydrogens have been omitted.

Formation of two-boron compound **69** (and its hydrolysis to **67**) is amazingly easy. We found the one-boron compound **67** could be prepared by mixing **36** and excess boric acid together in a mortar and grinding it for 5-10 minutes with a pestle. Excess boric acid was removed by washing with hot THF and very pure **67** was obtained in more than 98% yield.

Table 7. Geometric data of **71** from X-ray crystallography

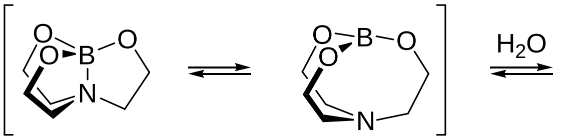
Entry	Average N-C length (Å)	B-N^a length (Å)	B-N^b length (Å)	Average C-N^a-C angle (°)	Average B-N^a-C angle (°)
71(A)^c	1.505(3)	1.7029 3.0911	1.642(4)	115.8(2)	101.99(13)
71(B)^c	1.495(4)	1.6992 3.0958	1.645(4)	115.8(2)	101.93(2)

^{a} Tertiary amine nitrogen ^{b} Pyridine nitrogen ^{c} The labels A and B refer to two independent molecules in the unit cell

c) Some properties of 67

1. Stability with water and nucleophilic reagents

In 1960, Steinberg and Hunter[102] reported the hydrolysis rate of boratrane is 130 times as slow as that of triethylborate under neutral conditions. Such a result suggested an equilibrium between two boratrane forms with planar and tetrahedral boron configuration, the tetrahedral configuration having a B←N bond. From the kinetic data, a hydrolysis mechanism includes initial B←N bond cleavage (equation 31).[103]



$N(CH_2CH_2OH)_3$ + H_3BO_3 [31]

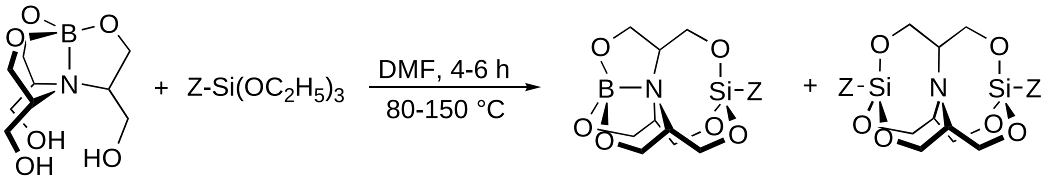
A B←N dative bond also exists in **67**, according to the X-ray crystal structure of one-boron compound **67**. This dative bond should stabilize **67**. The following facts will prove it.

NMR spectra in D_2O demonstrated that **67** only partially hydrolyzed to tertiary amine **36** at rt and the hydrolysis ratio did not change several days later. That means **67** could not be hydrolyzed completely in water at rt. And **67** was stored in a small white vial for almost 17 months under air at rt. The NMR spectra of **67** (in DMSO-d_6) illustrated that no **67** was hydrolyzed to tertiary amine **36**. So, **67** is very stable at rt.

Attack of a nucleophilic reagent at the boron atom of **67** should be slowed by the existence of the B←N transannular bond. This decreases the electrophilicity of the boron of **67**. Perhaps, it is the reason that boratrane **67** is very hard to dissolve in pyridine and triethylamine, even after heating it.

2) Reaction of 67 with Z-Si(OC_2H_5)$_3$ (Z = Me, Ph)

In DMF, mixtures were obtained when **67** reacted with Z-Si(OC_2H_5)$_3$ (Z = Me, Ph) at a molar ratio of 1:1. The mixtures were starting material **67**, one-boron one-silicon compound **72** and two-silicon compound **73**. But only **73** was obtained when the reaction ratio was 1:2. That means the siloxane is more stable than the borate for tertiary amine **36**.



67 **72** **73** [32]

d) Properties of two-boron compound 69

As discussed, two-boron compound **69** is extremely moisture sensitive and insoluble in virtually all organic solvents. It did not melt or sublime at 350-400 °C in vacuum (2 - 5 Torr). So, it is difficult to determine its molecular structure.

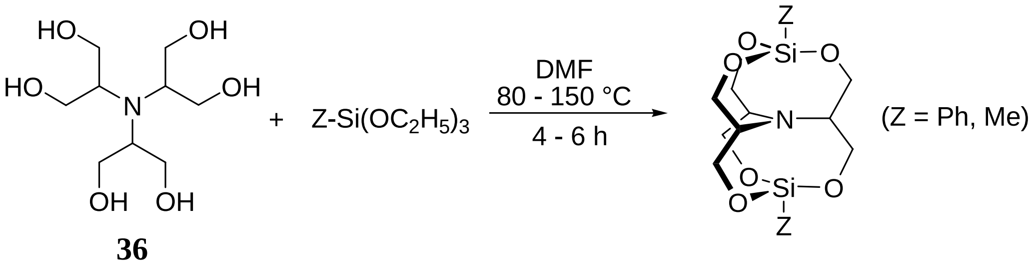
2.2.2 Reactions of 36 with various sources of silicon

a) Reactions with Z-Si(OC_2H_5)$_3$ (Z = Ph, Me)

Phenylsilatrane was first prepared by Finestone[104] through azeotropic distillation of triethanolamine and phenyl triethoxysilane with benzene (eq. 33). The same method was employed for the synthesis of silatranes by Frye and coworkers.[105]

$$\mathrm{PhSi(OC_2H_5)_3} + \mathrm{(HOCH_2CH_2)_3N} \longrightarrow \mathrm{PhSi(OCH_2CH_2)_3N} + 3\ \mathrm{C_2H_5OH} \qquad [33]$$

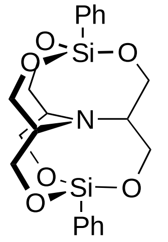
This method of transesterification of Si-substituted trialkoxysilanes was also used in the case of tertiary amine **36** to try to synthesize two-silicon silatranes (eq. 34). This method in DMF solution was successful in our hands in preparing two-Me two-Si compound **76** and two-Ph two-Si compound **75** in high yield (> 90 %). TLC was employed to follow the reactions. During these reactions, there were two new spots on TLC plates.



36

[34]

The more polar spot of the two gradually disappeared. Finally, there was only one new spot, which was identified as the two-Si compound, (either **74** or **76**). The more polar spots which disappeared during the course of the reaction were regarded as intermediate one-Si compounds **75** and **77**. These materials were obtained by stopping the reaction at the point at which the concentration of the polar intermediate was greatest, and



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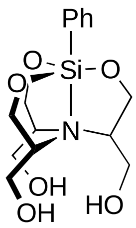

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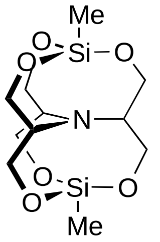

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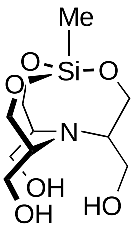
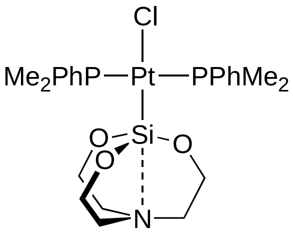


77

performing silica gel chromatography of that reaction mixture. The ^{1}H and ^{13}C NMR spectra were consistent with the proposed structures of **75** and **77**. (Figure 2.13 and 2.14)

Silatranes were the first examples of atrane to be reported[105] and have been reviewed exhaustively by Voronkov.[106] The molecular structure of silatranes has been elucidated by X-ray crystal structural and conformational methods. Bond angles and lengths, including distances in silatranes ($ZSi(OCH_2CH_2)_3N$) could presumably range between 1.87 Å (the sum of the covalent radii of silicon and nitrogen) and 3.65 Å (the sum of the van der Waals radii of silicon and nitrogen).[107]

The reported longest Si←N distance in a silatrane is in **78** (2.89(1) Å), which is 21% shorter than the sum of the van der Waals radii.[116] The shortest one is in **79** (1.965(5) Å).[117]



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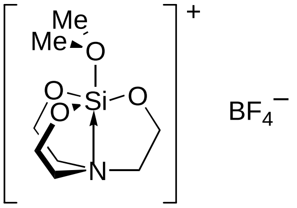


79

However, in almost all of the silatranes which have been studied, the distance between the silicon and nitrogen is in the range 2.0 - 2.4 Å. This distance is considerably

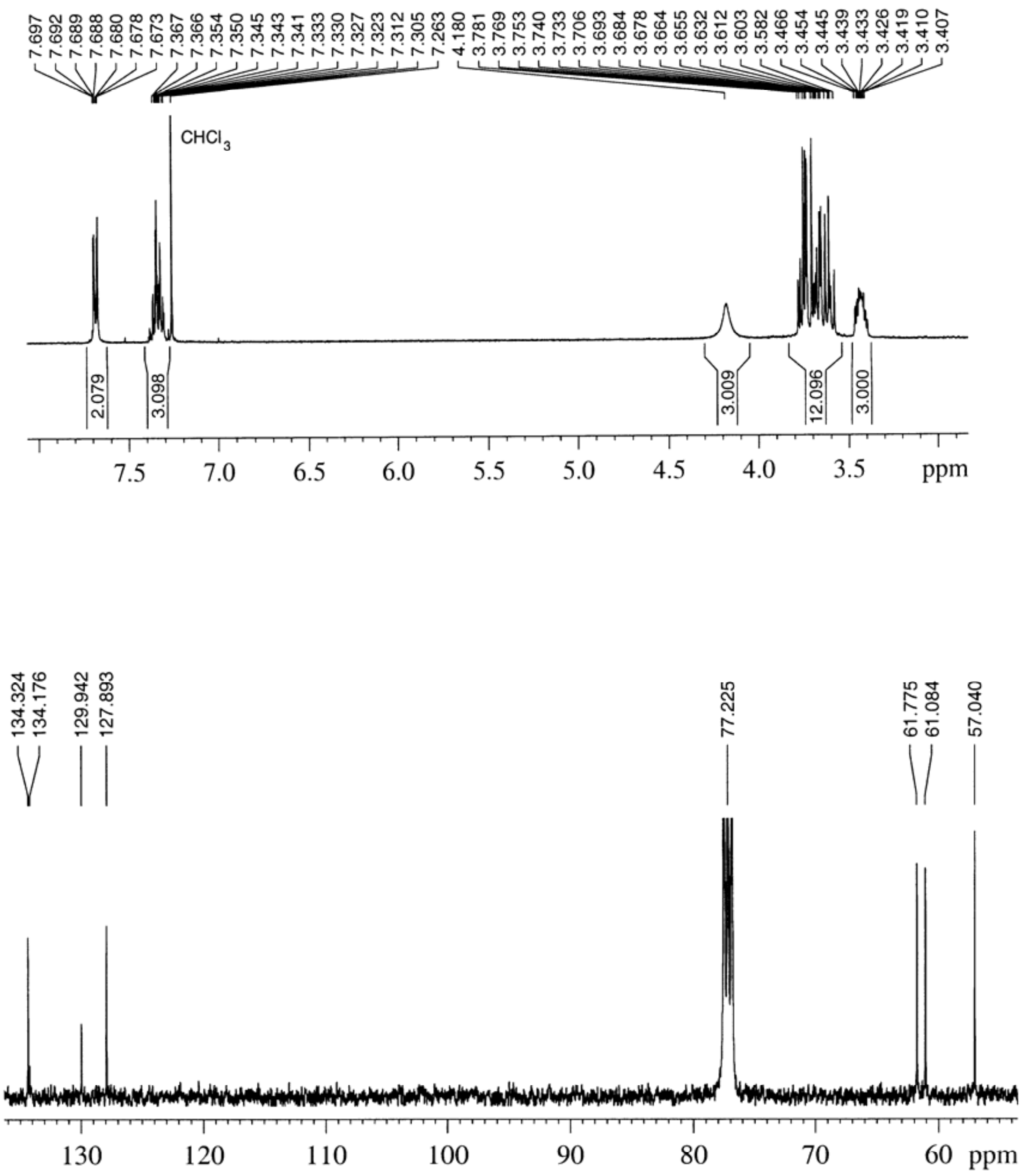


Figure 2.13 NMR spectra of compound **75**. ($CDCl_3$ solvent) Top: 400 MHz ^1H NMR spectrum. Bottom: 100 MHz ^{13}C NMR spectrum.

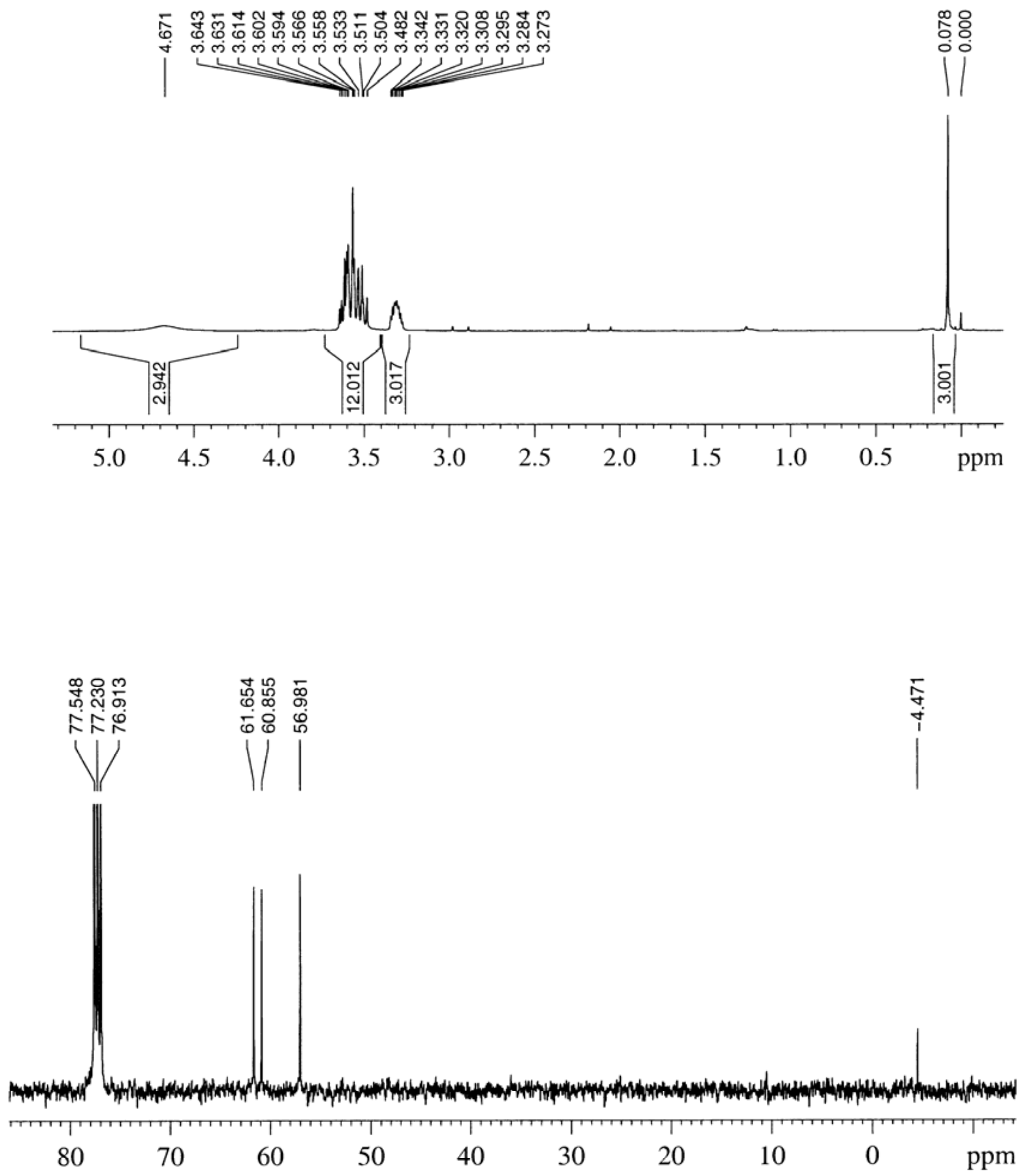


Figure 2.14 NMR spectra of compound **77**. ($CDCl_3$ solvent) Top: 400 MHz ^1H NMR spectrum. Bottom: 100 MHz ^{13}C NMR spectrum.

shorter than the sum of van der Waals radii of the silicon and nitrogen atoms. This is persuasive evidence for the existence of a transannular interaction between the silicon and nitrogen in silatranes.

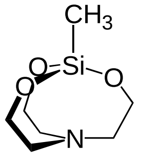
In silatranes $ZSi(OCH_2CH_2)_3N$, the Si←N dative bond length is essentially dependent on the substituent (Z) at the silicon atom (see Table 8). Thus, for example, the presence of an electron-withdrawing substituent at the silicon atom (Cl, CH_3CH_2O, 3-$O_2NC_6H_4$) should shorten the Si←N bond length.

Table 8. Some structural features of silatranes $ZSi(OCH_2CH_2)_3N$

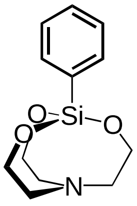
Entry	Z	Si—N length (Å)	Si—Z length (Å)	Si—O length (Å)	Average O-Si-O Angle( )	Average Z-Si-O Angle( )
1[a]	Me_2O^+	1.965	1.830	1.642	120.0	96.4
2[b]	Cl	2.02	2.15	1.65	120.0	
3[b]	$ClCH_2$	2.12	1.91	1.67	119.0	96.0
4[b]	3-$O_2NC_6H_4$	2.12	1.91	1.66	119.0	96.0
5[b]	Ph(γ)	2.13	1.89	1.65	118.0	96.0
6[a]	EtO	2.152	1.658	1.648	118.9	93.6
7[b]	CH_3	2.17	1.87	1.67	118.0	93.0
8[b]	$Cl(CH_2)_3$	2.18	1.88	1.66	119.0	
9[b]	Et	2.21	1.88	1.66	118.0	
10[b]	[c]	2.89	2.29	1.65	110.0	108

[a] ref. 117 [b] ref. 106 [c] $(C_6H_5(CH_3)_2P)_2PtCl$

Does a dative bond between the silicon and nitrogen exist in compounds **74** - **77**? Our greatest interest is in compounds **74** and **76**. The nitrogen in **74** and **76** should be considered hypervalent (10-N-5) if there is a maximal transannular interaction between the silicon and nitrogen in **74** or **76**. The solid-state structures of **74** and **76** will certainly offer unambiguous structural information. Therefore, we tried to grow crystals of **74** and **76**. Recrystallization of **74** from benzene and **76** from hexane gave nice crystals suitable for X-ray analysis. The X-ray crystal structures are shown in Figure 2.15 and Figure 2.16. The results of X-ray crystallographic studies on **74** and **76** are summarized and compared to those for 1-methylsilatrane **80** and 1-phenylsilatrane **81** in Table 9.



80



81

From Table 9, it is clear the distances between silicon and nitrogen in **74** and **76** are significantly shorter than the sum of van der Waals radii for the silicon and nitrogen atoms, 3.65 Å.[106] This provides evidence for the existence of an attractive transannular interaction between silicon and nitrogen in **74** and **76**. That means there exists to some extent a 5c-6e bond (C···Si···N···Si···C) in **74** and **76**.To the extent the 5c-6e description applies, the nitrogens in **74** and **76** would be hypervalent (10-N-5). But the O-Si-O and C-Si-O angles in **74** and **76** are closer to pure tetrahedral values than the corresponding

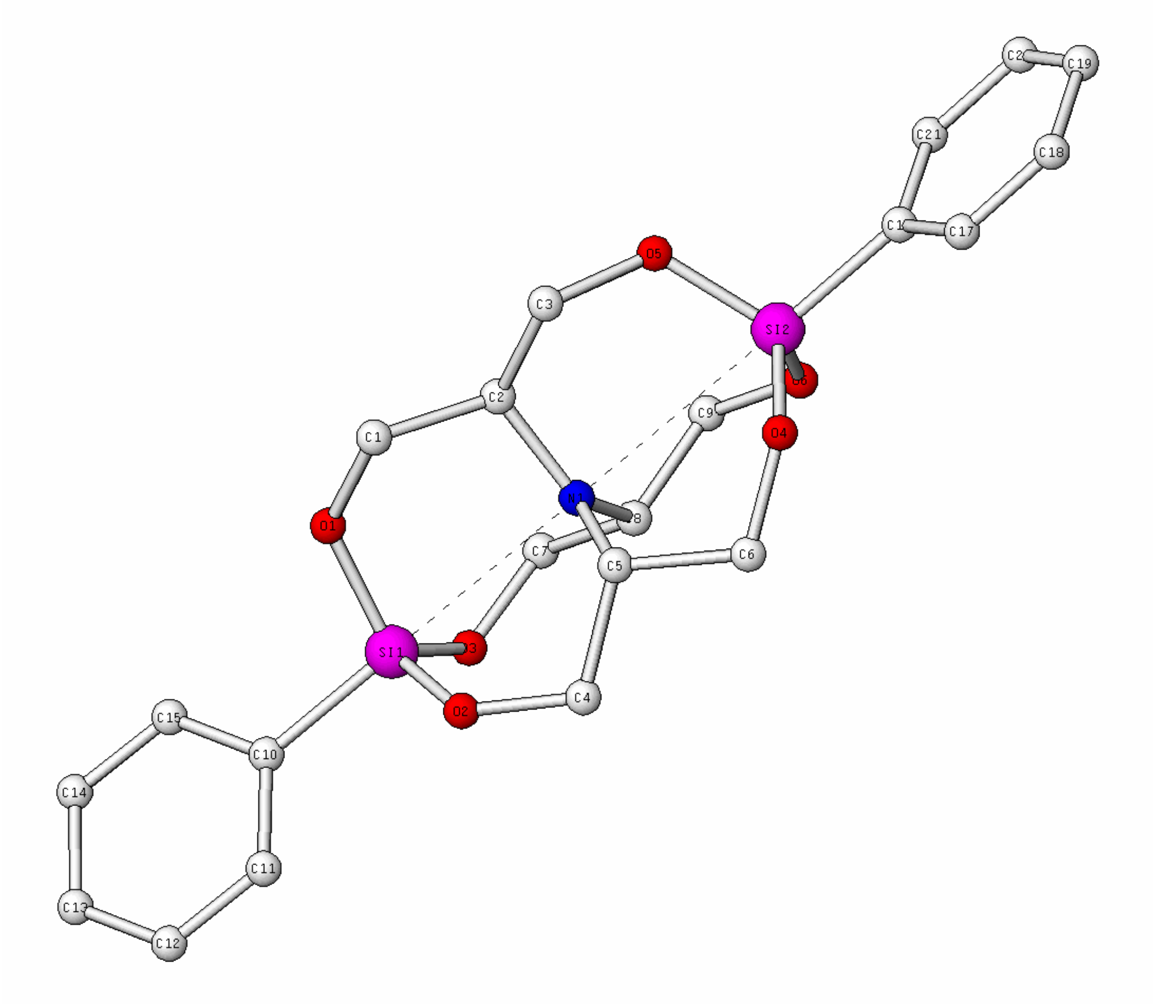


Figure 2.15 X-ray crystal structure of compound **74**. Atoms are represented by spheres of arbitrary diameter. All hydrogens have been omitted.

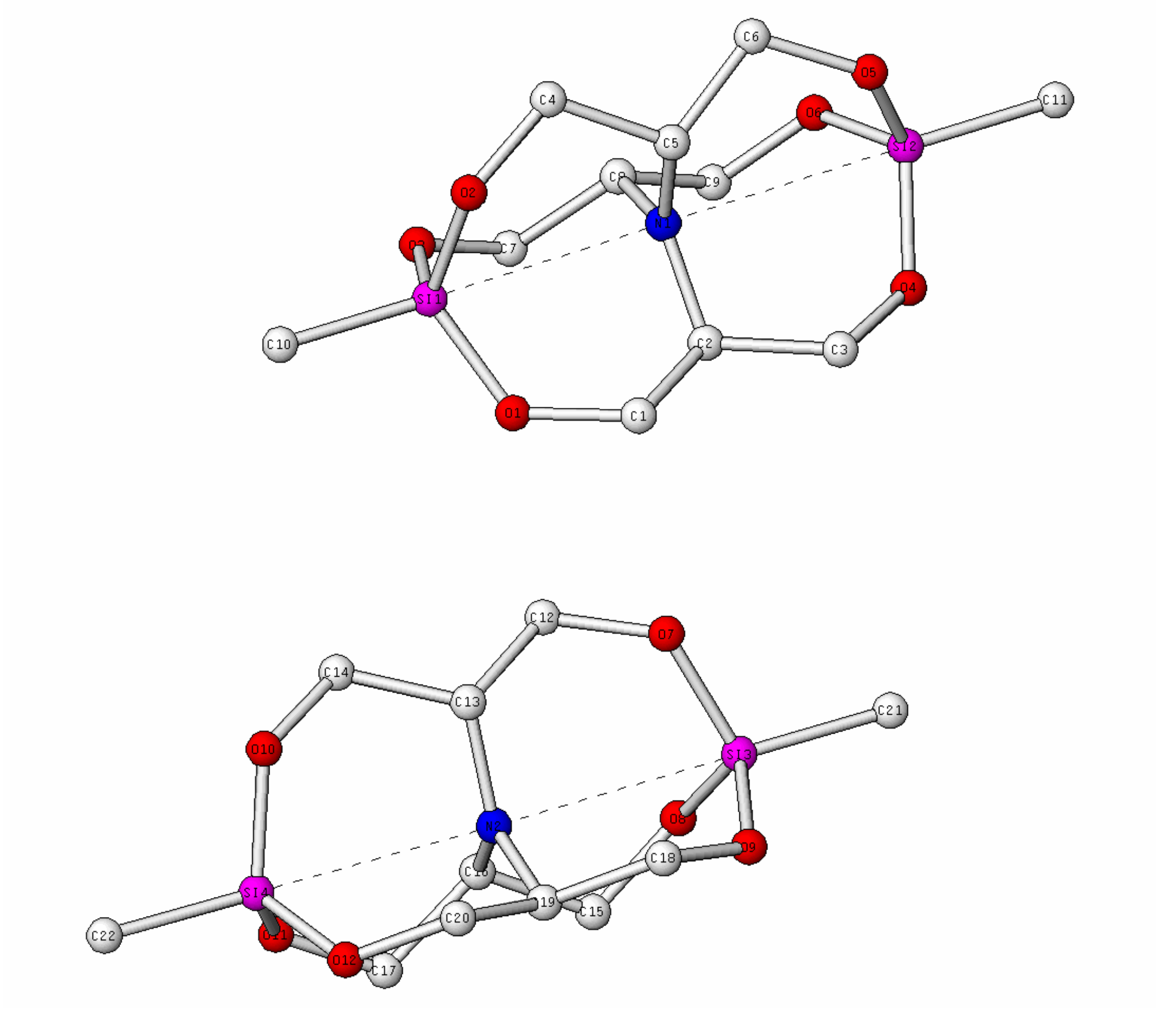


Figure 2.16. X-ray crystal structure of compound **76**. The unit cell contains two independent molecules. Atoms are represented by spheres of arbitrary diameter. All hydrogens have been omitted.

Table 9. Some interesting X-ray structural parameters of **74**, **76** compared to **80**, **81**

Compound	Average N-C Length (Å)	Si-N Length (Å)	Si-C Length (Å)	Average C-Si-O Angle (°)	Sum of C-N-C Angle (°)	Average O-Si-O Angle (°)
74[a]	1.4652	2.7662 3.0182	1.8592 1.8531	104.99(16) 107.47(17)	359.0(3)	113.56(18) 111.39(18)
76(A)[a]	1.452(6)	2.8717 2.9736	1.829(5) 1.826(5)	106.8(2) 107.9(2)	359.9(4)	112.0(2) 111.0(2)
76(B)[a]	1.455(5)	2.8808 2.9607	1.829(5) 1.833(5)	107.8(3) 106.8(2)	359.9(4)	111.1(2) 112.0(2)
80[b]	1.47	2.17	1.87	93	342	118
81(α)[c]	1.46	2.19	1.88	97	345	119
81(β)[d]	1.46	2.15	1.91	97	342	118
81(γ)[e]	1.47	2.13	1.89	96	339	118

[a] This work. The labels A and B refer to independent molecules in the unit cell
[b] ref. 110 [c] ref. 111a [d] ref. 111b [e] ref. 111c

angles in **80** and **81**. Distances between silicon and nitrogen are longer in **74** and **76** than in **80** and **81**. Perhaps this is due to the absence of a strong transannular interaction between silicon and nitrogen in **74** and **76**. So, it is hard to say to what extent a transannular interaction exists between silicon and nitrogen in **74** and **76**.

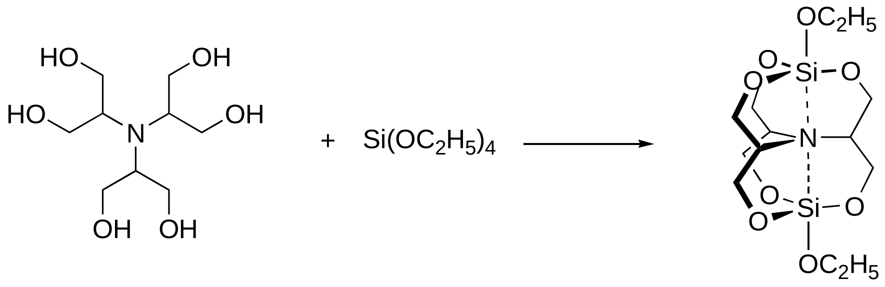
b) Reaction with $Si(OC_2H_5)_4$

In 1960, Finestone[104] tried to use transesterification to synthesize 1-ethoxysilatrane (equation 35). He failed to obtain pure 1-ethoxysilatrane due to the low melting point

$$Si(OC_2H_5)_4 + (HOCH_2CH_2)_3N \longrightarrow C_2H_5OSi(OCH_2CH_2)_3N + 3C_2H_5OH \qquad [35]$$

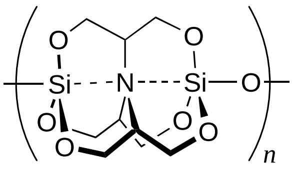
reported (35-37 °C). However, Fry, Vogel and Hall using the same method synthesized 1-ethoxysilatrane.[105] Maybe we can also use this method to produce **82** (eq. 36).

Under N_2, **36** and tetraethoxysilane were heated (oil bath below 100 °C) in DMF solution. Some white solid was obtained after removal of solvent. This white solid partly dissolved in $CDCl_3$. NMR spectra showed it was **82**. But it was not pure and not stable.



36 **82** [36]

It gradually deposited a white precipitate from $CDCl_3$ solution. This white precipitate didn't dissolve in any organic solvent (C_6H_6, $CHCl_3$, THF, CH_3OH, DMF, DMSO, acetone, ether) or H_2O. We got the white precipitate directly from the reaction solution if the reaction temperature was over 130 °C. We thought this precipitate might be the polymer **83**. But the elemental analysis results demonstrate it is not the simple polymer **83**.



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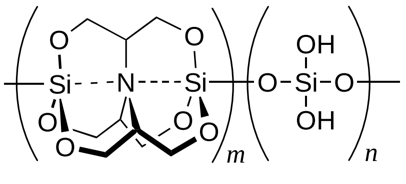


84

The elemental analysis results were as follows: Calculated for $C_9H_{15}NSi_2O_7$: C, 35.40; H, 4.95; N, 4.59. Found: C, 21.65; H, 4.69; N, 2.47. A copolymer like **84** ($n/m = 2.5$) fits the elemental analysis more closely; Calculated for **84**: C, 21.59; H, 4.03; N, 2.80. Found: C, 21.65; H, 4.69; N, 2.47.)

c) Reaction with $HSi(OC_2H_5)$ to form 85

First we tried to use transesterification method (eq. 38) to synthesize **85**. We failed to obtain **85**. Instead, a white precipitate was always formed which didn't dissolve in any organic solvent. We repeated this reaction and used CaH_2 to dry DMF. This time, no precipitate was formed. After removal of solvent, some solid was obtained. This solid easily dissolved in chloroform. NMR spectra (Figure 2.17) were consistent with **82**, not **85**, as the product of this reaction.

36 **85** [38]

Voronkov and coworkers[106] thought the reactivity of the Si-H bond in trichloro-, triacetoxy- and trialkoxysilanes didn't permit the preparation of 1-hydrosilatrane and its derivatives. Maybe this is the reason we failed to produce **85** by the method shown in equation 37. But Voronkov and coworkers[119] performed the reaction of 1-hydrosilatranes with alcohols and phenols in the presence of sodium alkoxide or phenoxide to form the corresponding 1-organoxysilatranes (eq. 38). We dried DMF by adding CaH_2 and letting it stand for two days. This DMF was used in the reaction of **36** with $HSi(OEt)_3$ without filtration or distillation. So, the solvent may have contained basic species (*e.g.* CaH_2 or $Ca(OH)_2$). A by-product of the formation of **85** is ethanol. Under basic conditions, as Voronkov found, ethanol may react with **85** to form **82**. (eq. 39).

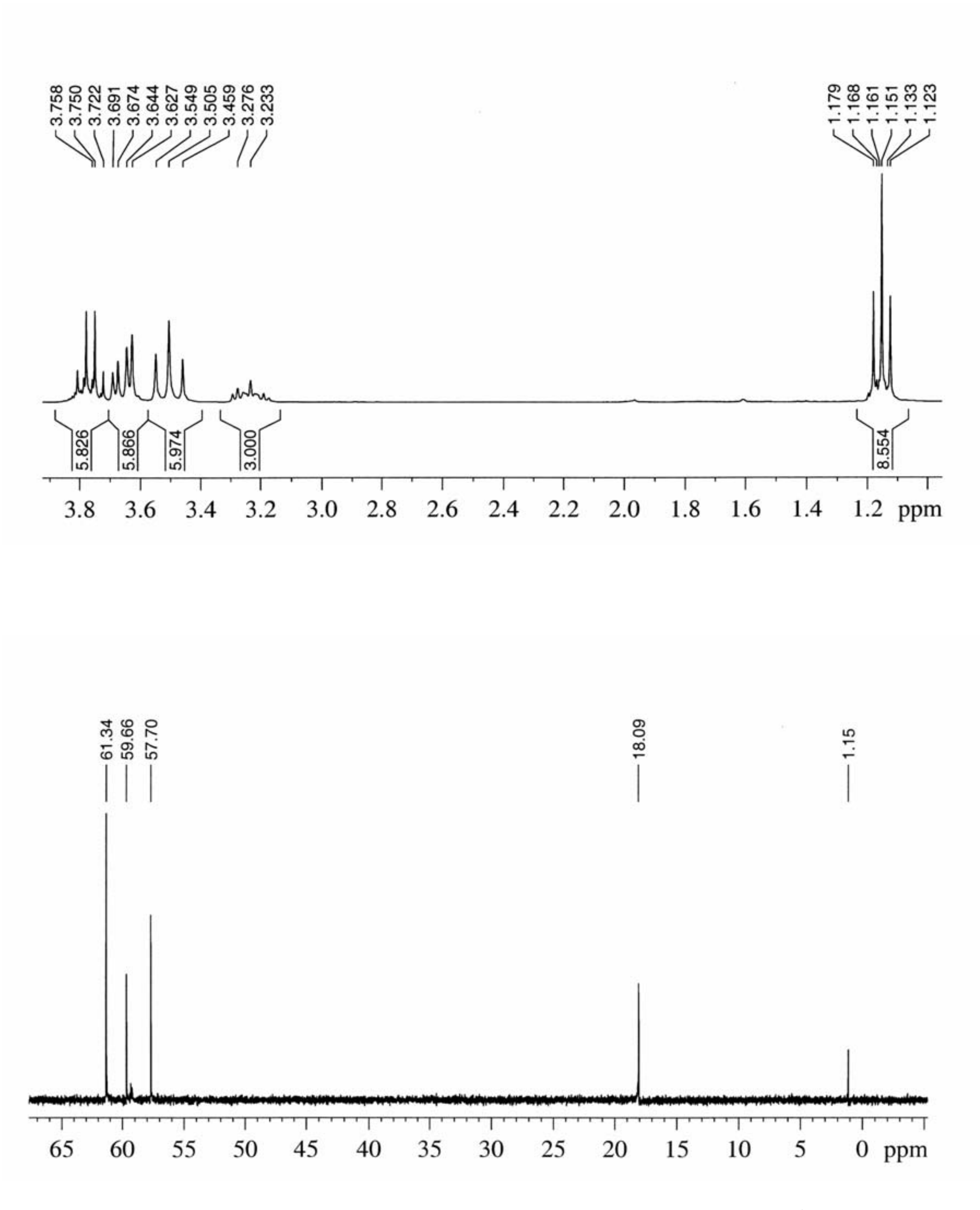
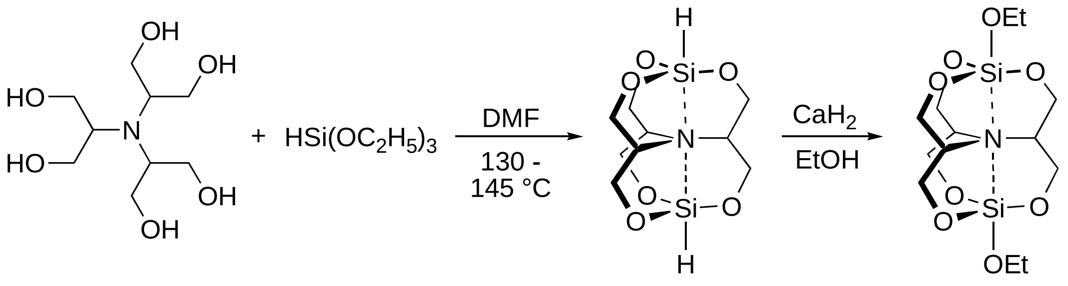


Figure 2.17 NMR spectra of compound **82** ($CDCl_3$ solvent). Top: 400 MHz ^1H NMR spectrum. Bottom: 100 MHz ^{13}C NMR spectrum.

$$\mathrm{HSi(OCHRCH_2)_3N} \;+\; \mathrm{ROH} \xrightarrow{\mathrm{RO^-}} \mathrm{ROSi(OCHRCH_2)_3N} \;+\; \mathrm{H_2} \qquad [38]$$



[39]

36 **85** **82**

In 1967, Zelchan and Voronkov found an interesting method for preparing difficultly accessible 1-hydrosilatranes. That was the transesterification of trialkoxysilanes with the corresponding boratranes (eq. 40).[108,109]

$$\mathrm{HSi(OR')_3 + B(OCHRCH_2)_3N} \xrightarrow{\mathrm{Al(OR'')_3}} \mathrm{HSi(OCHRCH_2)_3N} \qquad [40]$$

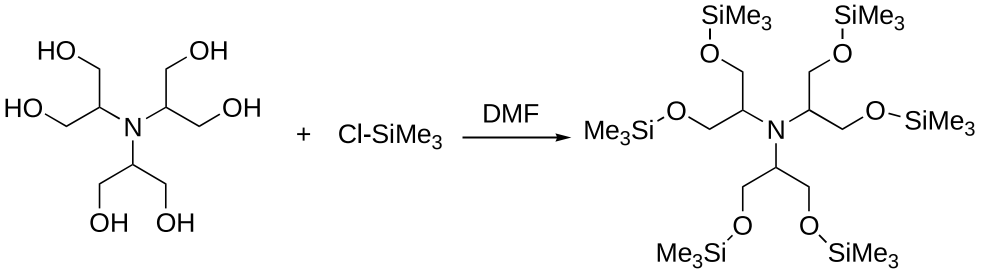
$\mathrm{R = H, CH_3;\ R' = CH_3, C_2H_5;\ R'' = alkyl}$

The synthesis was carried out by heating a mixture of one-boron **67** and triethoxysilane in DMF under nitrogen. A white solid was obtained after removal of the solvent. NMR spectra showed it was **85**. However, does a dative bond between the silicon and nitrogen exist in compound **85**? The nitrogen in **85** should be hypervalent (10-N-5) if there is a transannular interaction between the silicon and nitrogen in **85**. Therefore, we tried to grow up a crystal of **85**. Unfortunately, it was not successful.

2.3 Synthesis of tertiary amine 86

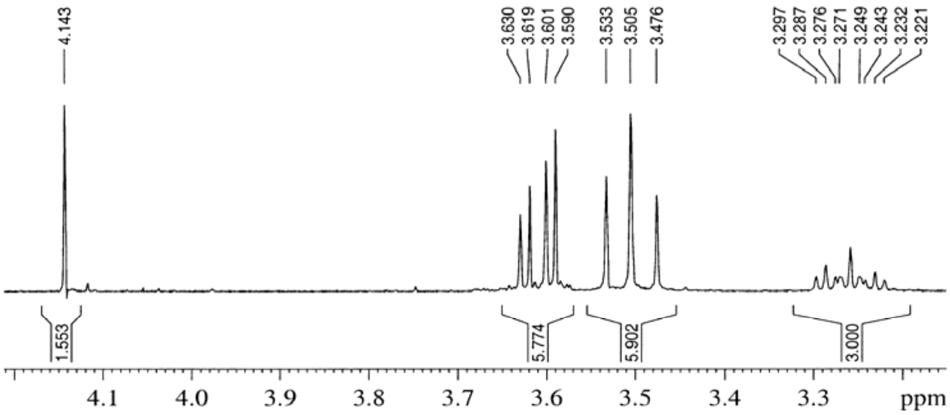
Tertiary amine **36** has six hydroxyl groups. It dissolves only in very polar organic solvents (DMF, DMSO) or water. Most reactions of **36** require the use of DMF as solvent. Reaction work-up is inconvenient because DMF has a high boiling point.

Therefore, we protected the hydroxyl groups of **36** using $ClSi(CH_3)_3$ (eq. 41). Compound **86** dissolves in many low polarity organic solvents. Compound **86** was prepared as shown in equation 41 in 82% yield.



[41]

36 **86**



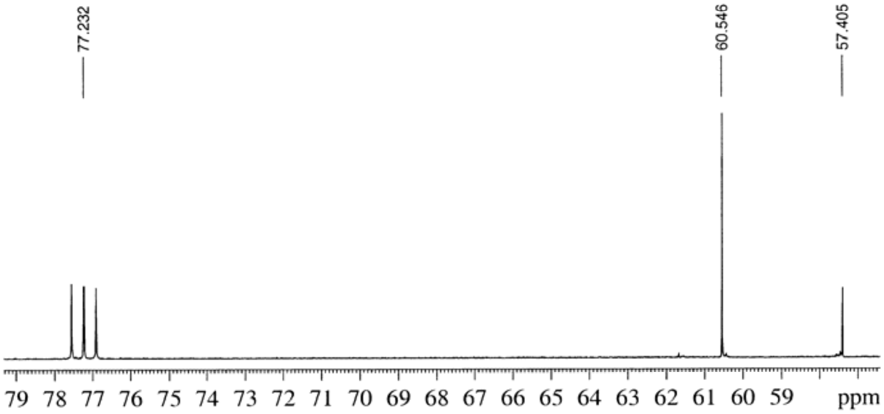


Figure 2.18 NMR spectra of compound **85** ($CDCl_3$ solvent). Top: 400 MHz ^1H NMR spectrum. Bottom: 100 MHz ^{13}C NMR spectrum.

CONCLUSIONS

1. A very interesting precursor to a proposed hypervalent 10-N-5 species, very hindered hexaolamine **36**, was imagined many years ago in our group. But many approaches for synthesizing tertiary amine **36** in our laboratory were fruitless. Fortunately, we have finally achieved the preparation of **36** with an overall yield of 49%, which was obtained in five steps by using cheap, commercially available dihydroxyacetone dimer as the starting material.

2. Some properties and structure of **36** have been studied. The pK_a of **36** was found to be 3.08 ± 0.03, a low value for a tertiary amine. The X-ray crystal structure of **36** showed the nitrogen is essentially planar (sum of C-N-C angles 359.05(7) °), and the average C-N bond length (1.454 Å) was shorter than normal. An explanation of this bond contraction is offered. The oxidation potential $E_{1/2}^{ox}$ of **36** measured by cyclic voltammetry was found to be 0.88 V. The oxidation was reversible; oxidations of ordinary tertiary amines are usually irreversible.

3. The X-ray crystal structure of **36**·HCl revealed a severely flattened tetrahedral geometry about nitrogen (average H-N-C angle 102.3 °). That is the reason why tertiary amine **36** is an unusually weak base.

4. The reaction of **36** with boric acid is very easily led to a “one- boron” compound, **67** which is very stable. The X-ray crystal structure of **67** showed a dative bond between

nitrogen and boron (1.6875(13) Å).

5. Under nitrogen, “two-boron” compound **69** was formed in the reaction of **36** with boric acid in DMF solution. The compound **69** is very hydrolytically unstable, but the X-ray crystal structure of a complex (**71**) of **69** with pyridine confirmed the presence in **69** of two borons.

6. The reaction of **36** with Z-Si(OEt)$_3$ (Z = Me, Ph) led to analogous "one-silicon" and "two-silicon" compounds. The X-ray crystal structures of both two-silicon compounds revealed a nearly symmetrical SiNSi array (Z = Me) and an unsymmetrical one (Z = Ph).

7. The “2H, 2Si” compound **85** was prepared by the reaction of “one-boron” compound **67** with HSi(OEt)$_3$.

8. The reaction of **36** with HSi(OEt)$_3$ in the basic DMF solution led to form “2EtO, 2Si” compound **82.**

Experimental

General: DMF was dried by stirring with calcium hydride, followed by distillation under vacuum after removing calcium hydride, and then storage over calcium hydride. Benzene, THF, and toluene were distilled over sodium benzophenone ketyl under nitrogen. Acetone was dried with anhydrous calcium sulfate followed by distillation after removing calcium sulfate and storage over 4A molecular sieves. $Rh_2(OAc)_4$ and other reagents used in the syntheses were purchased from the Aldrich Chemical Company and were used without further purification.

Melting points were determined on a Mel-Temp® apparatus in open capillaries and are uncorrected.

The ^1H and ^{13}C NMR spectra were obtained on a Bruker AC-250 (operated at 250 and 62.5 MHz respectively) and Bruker Avance-400 (operated at 400 and 100 MHz respectively) spectrometers. TMS (0.00 ppm) was used as internal standard for ^1H NMR chemical shifts in all solvents except deuterium oxide, in which case, HDO was used as an internal reference (4.80 ppm). ^{11}B NMR was referenced to boron trifluoride etherate as 0.00 ppm. The results are reported as parts per million and coupling constant are reported in Hz. The spin multiplicities are indicated by the symbols s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), m (multiplet) and br (broad). DEPT experiments were conducted at θ = 135°. A z-gradient magnitude-mode COSY microprogram was used to record COSY spectra.

In ^{13}C NMR, chemical shifts were reported in ppm relative to the centerline of the multiplet for deuterium solvent peaks ($CDCl_3$, 77.23 ppm; DMSO-d_6, 39.51 ppm; acetone-d_6, 29.92 ppm). For deuterium oxide, methanol was used as an internal reference (49.2 ppm).

Mass spectral data were obtained using either a Finnegan 3300 or a VG 7070E mass spectrometer using a solid probe. The results are presented in terms of intensity percentage relative to the base peak.

Elemental analysis was performed by Atlantic Microanalytical Lab, GA.

X-ray crystallography was performed on a Bruker SMART APEX CCD X-ray diffractometer by Dr. Thomas Albrecht-Schmitt and his graduate students.

Some reactions were followed by thin-layer chromatography (TLC) using pre-coated silica gel plates and visualized using a Mineralight UVGL-25 lamp, or by exposure to iodine vapor, or dipping in $KMnO_4$ solution. Column chromatography was performed on Sorbent Technologies silica gel (60 Å) and eluted with the indicated solvent system.

Bis(1,3-dihydroxy-2-propyl)amine, 50. Sodium cyanoborohydride (10.0 g, 159 mmol) dissolved in 50 mL methanol was added dropwise to a solution of dihydroxyacetone dimer (28.7 g, 159 mmol) and ammonium chloride (2.84 g, 53.0 mmol) in a mixture of methanol (400 mL) and acetic acid (40.0 mL). After stirring for 20 to 24 h, aqueous hydrochloric acid (2.00 M, 100 mL) was added and stirring was continued for 4 h. The reaction was concentrated on a vacuum rotary evaporator. The sticky liquid residue was dissolved in methanol (100 mL), filtered and concentrated once more. The viscous residue was dissolved in water and applied to an ion-exchange column (Amberlite, IR-120, H^+) prepared as described in the following paragraph. The column was eluted with water first, and then a solution of aqueous ammonia (1.00 M). The solvent was removed to give secondary amine **50**, a hygroscopic sticky liquid (yield 80 - 87%). ^{1}H NMR (400 MHz, D_2O) δ_H: 2.98 (2 H, quin, *J* = 5.6, NCH), 3.58 (4 H, dd, *J* = 6.6, 11.8, OCH_2), 3.65 (4 H, dd, *J* = 5.6, 11.8, OCH_2); ^{13}C NMR (62 MHz, D_2O) δ_C: 57.6 (NCH), 61.3 (OCH_2).

Preparing ion exchange column. The resin (Amberlite, IR-120, H^+) was soaked in 7% HCl solution 24 h twice (fresh HCl solution for second time). The ion exchange column was set up as an ordinary chromatography column. The column was flushed with deionized water until the eluate was neutral, at which time the column was ready for use.

Bis(4,4-dimethyl-3,5-dioxanyl)amine, 58. Method A: Under nitrogen, acetone (30 mL), 2,2-dimethoxypropane (10.0 mL, 81.6 mmol) and concentrated sulfuric acid (1.00 mL) were added to a solution of **50** (1.71 g, 10.4 mmol) in DMF (10.0 mL) at room temperature. An initially formed precipitate gradually dissolved. The reaction mixture was stirred for 4 h, after which solid sodium bicarbonate (5.00 g) was added until the pH had risen to 7 (overnight). The solvent was removed on the rotary evaporator and the sticky residue was partitioned between ethyl acetate (100 mL), and water (50.0 mL). The aqueous layer was extracted with ethyl acetate (2 × 50 mL), and organic layer was washed with brine (50 mL), dried with $MgSO_4$, filtered, and concentrated. The residue was purified with column chromatography (elution solvent; hexane:ethyl acetate = 1:1 to 1:10) (yield 30-70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 1.41 (6 H, s, CCH_3), 1.42 (6 H, s, CCH_3), 2.75 (2 H, tt, *J* = 4.1, 6.8, NCH), 3.62 (4 H, dd, *J* = 6.8, 11.7, OCH_2), 3.93 (4 H, dd, $J = 4.1, 11.7$, OCH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 23.2, 24.7 ($C(\underline{C}H_3)_2$), 50.0 (NCH), 64.7 (CH_2), 98.4 ($\underline{C}(CH_3)_2$).

Method B: Secondary amine **50** (4.00 g, 24.2 mmol) was dissolved in methanol (60 mL), 37.5% HCl solution (10 mL) was added and stirred for 2 h at rt. The solvent was removed on the rotary evaporator. The residue was dissolved in DMF (40 mL). Under nitrogen, PTSA (0.700 g, 3.60 mmol) and 2,2-dimethoxypropane (10.0 mL, 81.6 mmol) were added to the solution. The resulting clear solution was allowed to stir overnight (at least 12 h) at which time Et_3N (0.600 mL, 4.00 mmol) was added and allowed to stir for an additional 10 min. The mixture was concentrated *in vacuo* and treated with Et_3N (3.40 mL, 24.2 mmol) and EtOAc (150 mL). The precipitate was removed via filtration and the filtrate was concentrated. The residue was purified as method **A** to obtain **58** (4.30 g, 73.0%) or crystallized from hexane to give 82% yield.

***p*-Acetamidobenzensulfonyl azide, 87.**[112] At 0 °C, a solution of sodium azide (16.2 g, 0.250 mol) in 50 mL water was added dropwise to a suspension of *p*-acetamido-benzenesulfonyl chloride (50.0 g, 0.220 mol) and tetrabutylammonium iodide (0.500 g) in 500 mL CH_2Cl_2. The reaction was allowed to reach rt and was stirred overnight. The organic layer was separated and washed with water (2 × 80 mL) and brine (100 mL), dried with Na_2SO_4 and evaporated to give pure product **87** (49.7 g, 95.7%), mp 107-109 °C. (Lit.[112] 106-108 ^{0}C)

Dimethyl diazomalonate (DDM), 51. To a stirred solution of dimethyl malonate (14.3 g, 0.110 mol) and *p*-acetamidobenzenesulfonyl azide (29.4 g, 0.120 mol) in acetonitrile (600 mL) at 0 °C was added dropwise triethylamine (22.2 g, 0.220 mol). The mixture was allowed to reach rt and was stirred for 18 h. The mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was washed with ether/hexanes (1:1), filtered, and the solvent was evaporated. Further purification by column chromatography (hexanes/ethyl acetate = 4:1) gave light yellow liquid (15.2 g, 86.7%). ^{1}H NMR (250 MHz, $CDCl_3$) δ_H: 3.85 (s).

Dimethyl 2-(N,N-bis(4,4-dimethyl-3,5-dioxanyl)amino)malonate, 59. Under N_2, to a solution of acetonide amine **58** (0.980 g, 4.00 mmol) in benzene (20 mL), was added 0.760 g DDM (4.80 mmol) and rhodium(II)acetate dimer (32.0 mg, 0.0700 mmol) at rt. The mixture was heated to reflux and continued for 2.0 to 2.5 h, at which time TLC showed the absence of diazo compound and acetonide amine. The solvent was removed in vacuo. The residue was purified by silica gel chromatography (EtOAc/hexane 1:3 v/v), which yielded white tertiary amine **59** (1.25 g, 83.3%). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 1.36, 1.40 (12H, 2s, $C(CH_3)_2$), 3.34 (2 H, m, 2NCH), 3.72 (4H, dd, *J* = 6.9, 12.0, 4 OCH), 3.77 (6H, s, OCH_3), 3.96 (4H, dd, OCH); 4.99 (1H, s, NCHCO). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 23.0, 24.3 ($C\underline{C}H_3$), 51.4 (NCH), 52.6 (OCH_3), 63.5 (NCH_2O), 64.3 (NCHCO), 98.2 ($O\underline{C}CH_3$), 170.3 (CO).

2-(N,N-bis(4,4-dimethyl-3,5-dioxanyl)amino)-1,3-propanediol, 60. Tertiary amine **59** (0.380 g, 1.00mmol) was dissolved in THF (4 mL) and added dropwise to a suspension of LAH (0.230 g, 6.00 mmol) in THF (10 mL). The reaction was stirred overnight at room temperature and then were added sequentially water (0.230 mL), 15% sodium hydroxide (0.230 mL) and water (3 × 0.230 mL). The mixture was filtered and the filtrate was evaporated. The residue was purified by silica gel chromatography (ethyl acetate) to give a colorless sticky liquid **60** (0.300 g, 93.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 1.38, 1.45 (12 H, s, $C(CH_3)_2$), 3.15 (2 H, m, NCH), 3.27 (1 H, quint, NCH), 3.47 (2 H, dd, *J* = 7.4, 10.7, CH_2OH), 3.59 (2 H, dd, *J*= 10.9, 6.05, CH_2OH), 3.71 (4 H, dd, *J* = 12.0, 5.5, CH_2O), 3.82 (4 H, dd, *J* = 12.0, 9.54 CH_2O). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 20.4, 27.0, 49.1, 58.8, 62.3, 63.7, 97.7.

Tris(1,3-dihydroxy-2-propyl)amine, 36. At 0 °C, trifluoroacetic acid (1.00 mL) was added to a solution of **60** (1.49 g, 4.67mmol) in THF and H_2O (25 mL, THF/H_2O = 4:1 (v/v)). The resulting solution was allowed to warm to rt and was left overnight. Then solvent was removed *in vacuo*. The residue was purified on an ion exchange column (Amberlite, IR–120, H^+). The column was eluted with water first, and then a solution of aqueous ammonia (1 M). The solvent was removed to give white solid tertiary amine **7** (1.10 g, 92.0 %). mp > 190 °C (dec.); pK_a = 3.08 (T = 25 °C, 0.01 M, titrant: 0.1 N HCl standard solution). $E_{1/2}$ = 0.88 V (rt, 0.5 M Na_2SO_4, in water, Au electrode); ^1H NMR (400 MHz, D_2O) δ_H: 3.16 (3 H, m, NCH), 3.54 (12 H, m, CH_2O); ^{13}C NMR (100 MHz, D_2O, methanol, 49.2) δ_C: 56.8, 61.0; ^1H NMR (400 MHz, DMSO-d_6) δ_H: 2.91 (3H, m, NCH), 3.31(12H, CH_2O); 4.91 (6H, q, OH); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 57.1, 61.8; Anal. Calcd for $C_9H_{12}NO_6$: C, 45.18; H, 8,85; N, 5.85. Found: C, 45.02; H, 8.82; N, 5.74. A crystal 0.32 mm × 0.20 mm × 0.39 mm was selected for X-ray crystallography with 0.71073 Å (Mo Kα) radiation. Unit cell dimensions a = 10.915(2) Å, b = 8.9100(18) Å, c = 23.635(5) Å, $\alpha = \beta = \gamma = 90°$; Z = 8. Ambient temperature, absorption coefficient = 0.114 mm^{-1}; 2858 reflections were collected, 2682independent (R_{int} = 0.0239), $-14 \leq h \leq 14$, $-11 \leq k \leq 11$, $-31 \leq l \leq 30$; Full-matrix least-squares on F^2, data-to-parameter ratio = 16.8, Goodness-of-fit 1.026, R1 = 0.0361, wR2 = 0.1009 (I>2σ (I)), R1 = 0.0378, wR2 =

0.1032 (all data); extinction coefficient = 0.0235(19). Complete details are given in Appendix 1.

1,3-Bis(*tert*-butyldimethylsilyloxy)-2-propanone, 55. At 0 °C, *tert*-butyldimethylsilyl chloride (2.11 g, 14.0 mmol) was added to a stirred solution of 1,3-dihydroxyacetone dimer (504 mg, 2.80 mmol) and imidazole (958 mg, 14.1 mmol) in DMF (4 mL) and the mixture was stirred at rt for 7 h. It was cooled to 0 °C, water (15 mL) was added and the reaction mixture was extracted with ether (2 × 15 mL). The organic layer was washed with brine (25 mL), dried (Na_2SO_4) and evaporated. The residue was purified by column chromatography (hexane/ethyl acetate 15:1 (v/v)) to give **55** (0.820 g, 92.0%) as a colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$) δ_H: 4.46 (4 H, s, OCH_2), 0.96 (18 H, s, $SiC(CH_3)_3$), 0.13 (12 H, s, $Si(CH_3)_2$); ^{13}C NMR (62.0 MHz, $CDCl_3$) δ_C: -5.4, 18.5, 25.9, 68.0, 208.8.

Bis(1,3-di-*tert*-butyldimethylsilyloxy-2-propyl)amine, 56. Under N_2, at 0 °C, TBDMSCl (1.36 g, 9.00 mmol) was added to a solution of bis(1,3-dihydroxy-2-propyl)amine **50** (0.300 g, 1.80 mmol) and imidazole (0.610 g, 9.00 mmol) in DMF (3 mL). The mixture was gradually warmed to rt and stirred for 3 – 4 h. Workup was the same as compound **55** to give white solid compound **56** (0.880 g, 78.5%). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 3.57 (8 H, d, J = 5.6 Hz, OCH_2), 2.74 (2 H, J = 5.6 Hz, NCH), 0.89 (36 H, s, $SiC(CH_3)_3$), 0.03 (24 H, s, $Si(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 63.0, 58.8, 25.9, 18.3, -5.39, -5.41. Anal. Calcd for $C_{30}H_{71}NO_4Si_4$: C, 57.91; H, 11.50; N, 2.25. Found: C, 58.11; H, 11.62; N, 2.23; EI–MS, m/e: 622 (M^+), 606, 564, 490, 477, 412, 330, 274, 186, 147, 71, 53.

56 + DDM, 57. Under N_2, a mixture of dimethyl diazomalonate (DDM) (0.240 g, 1.50 mmol), protected secondary amine **56** (0.620 g, 1.00 mmol) and rhodium(II)acetate (15.0 mg, 0.0300 mmol) in dry benzene (10 mL) was heated (oil bath 55−60 °C) overnight. The solvent was removed under reduced pressure. The residue was purified by column chromatography with CH_2Cl_2 as eluent to give the title compound (0.300 g, 40.0%). ^{1}H NMR (250 MHz, $CDCl_3$) δ_H: 4.95 (1 H, s, CHCOO), 3.68–3.86 (14 H, m, CH_2OSi and OCH_3), 3.23 (2 H, m, NCH), 0.88 (36 H, s, $SiC(CH_3)_3$), 0.34 (24 H, s, $Si(CH_3)_2$); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ_C: 170.7, 64.6, 62.8, 58.9, 52.0, 25.9, 18.2, 14.1, -5.6; Anal. Calcd for $C_{35}H_{77}NO_8Si_4$: C, 55.88; H, 10.32; N, 1.86; Found: C, 56.11; H, 10.38; N, 1.89. EI-MS, m/e: 751(M-1), 736, 692, 662, 606, 462, 404, 330, 316, 253.

2,8,9-Tris(hydroxymethyl)-5-bora-1-aza-4,6,11-trioxatricyclo[3.3.3.0^{1,5}]-undecane, ("one-boron compound"), 67. ***Method A*****:** Under nitrogen, the mixture of tertiary amine **36** (100 mg, 0.420 mmol) and H_3BO_3 (25.8 mg, 0.420 mmol) in DMF (3.00 mL) was heated (oil bath 165−175 °C) for 3 - 5 h. Solvent was removed in a gentle stream of N_2 providing white solid product. The product was further purified by washed with hot THF and then keeping on the vacuum line for 2 days to give the title compound **67** (101 mg, 97.0%) mp: 222–223.5 °C. ^{1}H NMR (400 MHz, DMSO–d_6) δ_H: 4.50 (3 H, t, OH), 3.73-3.79 (6 H, m, CH_2), 3.57 (3 H, q, CH_2), 3.44 (3 H, t, CH_2), 3.31-3.37 (3 H, m, CH). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 64.2, 62.0, 57.2; Anal. Calcd for $C_9H_{18}NO_6B$: C, 43.73; H, 7.37; N, 5.67. Found: C, 43.88; H, 7.28; N, 5.55. EI-MS, m/e: 247 (M^+), 246, 208, 148, 44. A crystal 0.156 mm × 0.160 mm × 1.540 mm was selected for X-ray crystallography with 0.71073 Å (Mo Kα) radiation: monoclinic a = 16.9503(11) Å, b = 16.9503(11) Å, c = 14.8701(10) Å, $\alpha = \beta = \gamma = 90.00°$; Z = 16, 2651 reflections were collected, 2615 independent, $-22 \leq h \leq 22$, $-22 \leq k \leq 22$, $-19 \leq l \leq 19$.The structure was solved by direct methods with refinement by full-matrix least squares on F^2, Goodness-of-fit 1.056, resulting in final R indices of R1 = 0.0316, wR2 = 0.0804 ($I > 2\sigma(I)$), R1 = 0.0319, wR2 = 0.0807 (all data). Full details are given in Appendix 2.

Method B: Tertiary amine **36** (0.478 g, 2.00 mmol) and H_3BO_3 (0.310 g, 5.00 mmol) were mixed together and ground thoroughly with a mortar and pestle. First the mixture became wet, and grinding was continued until it became very dry. THF (60 mL) was added and refluxed for 2 h. The mixture was filtered (hot) to give white solid product **67** (0.482 g, 97.6%).

Reaction of 67 with pyridine. Under N_2, at rt, the mixture of compound **67** (50.0 mg) and pyridine (3.00 mL) was stirred overnight. Compound **67** didn't dissolve in pyridine. Then the mixture was heated to reflux for 3-4 h. The solid still didn't dissolve in pyridine. After filtration, the solvent was removed to give some white solid. NMR showed it still was compound **67**. So 1-B compound didn't react with pyridine.

1,7-Dibora-11-aza-2,6,8,14,15,17-hexaoxatetracyclo[8.4.2.2.^{7,12}0^{4,11}]octadecane, ("two-boron compound"), 69. Under N_2, the solution of tertiary amine **36** (200 mg, 0.840 mmol) and boric acid (104 mg, 1.68 mmol) in DMF (10 mL) was heated (oil bath 145 – 155 °C) for 4-6 h (A stream of nitrogen was used to carefully to blow off some water drops which formed on flask neck). After 3 h heating, some solid was formed. The solvent was removed (the best way is to use nitrogen to blow off DMF) to give white solid (234 mg). It does not dissolve in most organic solvents and is very moisture sensitive, hydrolyzing to the one-boron compound, mp > 260 °C.

Two-boron·pyridine compound, 71. ***Method A*****:** Under N_2, compound **69** (60.0 mg) was added to pyridine (2.50 mL). At rt, stirred for 4 - 5 h and then the solvent was slowly blown off by nitrogen to give white crystalline compound **71** (85.1 mg, 87.5%) This white crystal is very moisture-sensitive, hydrolyzing to **67**. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.79 (2 H, dd, pyridine), 8.08 (1 H, tt, pyridine), 7.64 (2 H, m, pyridine), 4.15 (3 H, m, CH_2), 3.95 (3 H, m, CH_2), 3.62-3.75 (9 H, m, CH_2, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 143.9, 141.7, 125.5, 63.9, 63.6, 57.3; mp > 40 °C (dec.). A crystal 0.34 × 0.16 × 0.16 mm was selected for X-ray crystallography with 0.71073 Å radiation: monoclinic a = 11.5031(8) Å, b = 11.6639(8) Å, c = 12.9997(9) Å, α = 97.56(3)°, β = 92.13(3)°, γ = 117.95(3)°; Z = 4; 7490 reflections were collected, 4658 independent, $-15 \leq h \leq 15$, $-15 \leq k \leq 15$, $-17 \leq l \leq 17$. Full-matrix least- squares refinement on F^2, data-to-parameter ratio = 17.3, Goodness-of-fit = 1.092, R1 = 0.0762, wR2 = 0.2046 ($I > 2\sigma (I)$), R1 = 0.1132, wR2 = 0.2235 (all data). The structure revealed the compound had crystallized as a pyridine adduct. Full details are given in Appendix 3.

Method B**:** Under N_2, a solution of tertiary amine **36** (100 mg, 0.420 mmol) and pyr·BH_3 (0.11 mL, 0.84 mmol, 8 M) in DMF was stirred overnight at rt. The solvent was slowly blown off by nitrogen to give white crystal 2 B•pyridine **71**(154 mg, 89 %) directly.

2Ph•2Si compound, 74. Phenyl triethoxysilane (0.606 mL, 2.52 mmol) was added to the solution of tertiary amine **36** (100 mg, 0.420 mmol) in DMF (2.50 mL). Under N_2, the solution was heated (oil bath 135-145 °C) for 4-6 h (or TLC may be used to follow the reaction). The solvent was removed under reduced pressure and the residue was purified by recrystallization from xylene to afford white solid compound **74** (159 mg, 84%).^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.69 (4 H, m, Ph), 7.39 (6 H, m, Ph), 3.81 (6 H, dd, CH_2), 3.74 (6 H, t, CH_2), 3.50 (3 H, m, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 134.3, 131.9, 130.5, 128.0, 61.1, 57.6; Anal. Calcd for $C_{21}H_{25}NSi_2O_6$: C, 56.86; H, 5.68; N, 3.16. Found: C, 56.90; H, 5.85; N, 3.17. A crystal 0.325 mm × 0.290 mm × 0.280 mm was selected for X-ray crystallography with 0.71073 Å (Mo Kα) radiation: monoclinic, a = 10.483(2) Å, b = 11.489(2) Å, c = 17.440(4) Å, α = 90.00°, β = 101.86(3)°, γ = 90.00°; Z = 4; 4672 reflections were collected, 3223 independent, $-13 \le h \le 13$, $-15 \le k \le 15$, $-23 \le l \le 22$. Full-matrix least-squares refinement on F^2, data-to-parameter ratio = 17.2, Goodness-of-fit = 1.819, R1 = 0.1253, wR2 = 0.2892 (all data), R1 = 0.0977, wR2 = 0.2747 ($I > 2\sigma(I)$). The complete details are given in Appendix 4.

"One-phenyl-one-silicon" (1Ph-1Si) compound, 75. The solution of tertiary amine **36** (200 mg, 0.820 mmol) and phenyl triethoxysilane (0.820 mL, 3.36 mmol) in DMF (5 mL) was heated (oil bath 130-145 °C). TLC was used to follow the reaction. The reaction was stopped immediately when the spot of 1Ph-1Si **75** was detected (acetone solvent, $KMnO_4$ as visualization reagent) on TLC plate. The solvent was removed under reduced pressure and the residue was purified by column chromatography with ethyl acetate and acetone as eluent to give 2Ph•2Si **74** (40 mg) and 1Ph•1Si (148 mg, 40%). ^{1}H NMR (400 HMz, $CDCl_3$) δ_H: 7.69 (2 H, m, Ph), 7.34 (3 H, m, Ph), 4.18 (3 H, br, OH), 3.58-3.78 (12 H, m, CH_2), 3.42 (3 H, m, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 134.3, 134.2, 129.9, 127.9, 61.8, 61.1, 57.0; Anal. Calcd for $C_{15}H_{23}NSiO_6$: C, 52.77; H, 6.79; N, 4.10; Found: C, 52.39; H, 6.83; N, 4.08.

"Two-methyl-two-silicon" (2Me-2Si) compound, 76. Tertiary amine 36 (100 mg, 0.420 mmol) was added to a solution of methyl triethoxysilane (0.500 mL) and DMF (2.50 mL). The mixture was heated (oil bath 95-120 °C) for 7-9 h until TLC indicated no starting tertiary amine 36. The solvent was removed under reduced pressure to afford white solid compound 76 (122 mg, 91.0%). This was further purified by recrystallization with hexanes, mp > 325 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 3.63 (6 H, dd, CH_2), 3.55 (6 H, t, CH_2), 3.29 (3 H, m, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 60.8, 57.2, -4.9; Anal. Calcd for $C_{11}H_{21}NSiO_6$: C, 41.36; H, 6.63; N, 4.38. Found: C, 41.51; H, 6.71; N, 4.39; EI-MS, m/e, 319 (M^+), 298, 284, 257. A crystal 0.183 mm × 0.138 mm × 0.113 mm was selected for X-ray crystallography with 0.71073 Å (Mo Kα) radiation: monoclinic, a = 10.2030(6) Å, b = 11.1393(7) Å, c = 26.179(2) Å, α = 90.0000(10)°, β = 98.2610(10)°, γ = 90.0000(10)°; Z = 8; 7280 reflections were collected, 4542 independent, $-13 \leq h \leq 13$, $-14 \leq k \leq 14$, $-34 \leq l \leq 34$. Full-matrix least-squares refinement on F^2, data-to-parameter ratio = 17.2, Goodness-of-fit = 1.053, R1 = 0.1389, wR2 = 0.3176 (all data), R1 = 0.1010, wR2 = 0.2919 ($I > 2\sigma(I)$). The complete details are given in Appendix 5.

One-methyl-one-silicon (1Me-1Si) compound, 77. The solution of tertiary amine **36** (200 mg, 0.840 mmol) and $MeSi(OEt)_3$ (0.680 mL, 3.40 mmol) in DMF (6 mL) was heated (oil bath 120-135 °C). The reaction was followed by TLC. After 4 h, the spot of 2Me-2Si **76** compound was detected on the TLC plate. The solvent was removed under reduced pressure to give some sticky residue. This residue was purified as follows: hexanes (55 mL) was added to the residue and refluxed for 5-10 minutes, filtered (hot), filtrate was evaporated to give 2Me-2Si **76** (87 mg). The solid (insoluble in hexanes) was purified by column chromatography to give 1Me•1Si **77** (89 mg, 39%) and tertiary amine **36** (60 mg) (acetone and methanol as solvent). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 4.69 (3 H, br, OH), 3.51-3.67 (12 H, m, CH_2), 3.34 (3 H, m, CH), 0.10 (3 H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 61.6, 60.9, 57.0, -4.5; Anal. Calcd for $C_{10}H_{21}NSiO_6$: C, 42.99; H, 7.58; N, 5.01; Found: C, 42.91; H, 7.39; N, 5.58.

Attempts to synthesize two-hydrogen-two-silicon compound 85. ***Method A:*** Under nitrogen, the solution of tertiary amine **36** (100 mg, 0.420 mmol) and triethoxysilane (154 μL, 0.840 mmol) in DMF (3 mL) was heated (oil bath 110-130 °C) for 6-8 h, at which time TLC (ethyl acetate as solvent) indicated no tertiary amine remained and also some white solid was formed. The reaction was halted, the solvent was removed under reduced pressure to give a white solid. This solid was washed DMF, benzene, acetone and then put on vacuum for 4 days to give white solid (120 mg). It didn't dissolve in any solvent (H_2O, DMF, DMSO, alcohols, $CHCl_3$, acetone, acetonitrile, ethyl acetate, trifluoroacetic acid).

***Method B*:** Under N_2, the solution of **67** compound (100 mg, 0.410 mmol) and triethoxysilane (149 μL, 0.820 mmol) in DMF (3 mL) was heated (oil bath 80-110 °C). The reaction was followed by TLC. After about 4 h, no **67** compound was detected on TLC plate. The solvent was removed under reduced pressure to give white solid. This solid was dissolved in xylene, filtered and the xylene was removed to give 2H•2Si **85** (102 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 4.22 (2 H, s, HSi), 3.69 (6 H, dd, CH_2), 3.58 (6 H, t, CH_2), 3.34 (3 H, tt, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 60.5, 57.4.

Reaction of tertiary amine 36 with tetraethoxysilane. Under N_2, the solution of tertiary amine **36** (100 mg, 0.420 mmol) and tetraethoxysilane (0.500 ml, 2.24 mmol) in

DMF (3 mL) was heated (oil bath 135-145 °C) overnight. Some white precipitate was formed. The precipitate was filtered and filter cake was washed with water, benzene and acetone to give white solid 0.1 g. This white solid didn't dissolved in any solvent. The elemental analysis results were: C, 21.65; H, 4.69; N, 2.47.

Reaction of tertiary amine 36 with $SiCl_4$. The solution of tertiary amine **36** (100 mg, 0.420 mmol) in DMF (3 mL) was cooled to -5 °C, then silicon tetrachloride (96.5 μL, 0.840 mmol) was added dropwise. The reaction mixture was warmed gradually to room temperature and an initially formed precipitate dissolved. The reaction was stirred for 4 h at rt (after 1.5 h, the solution became cloudy and some precipitate was formed again). The reaction mixture was filtered to give 120 mg of a white solid. This was dissolved in H_2O (15 mL) and filtered. The filtrate was concentrated under reduced pressure to give white solid (91.7 mg). This was recrystallized from methanol to give white crystal. ^{1}H NMR (400 MHz, D_2O) δ_H: 3.99 (1 H, m, CH; 2 H, m, CH_2), 3.90 (2 H, q, CH_2), 2.68 (2 H, t, OH); ^{13}C NMR (100 MHz, D_2O) δ_C; 63.5, 57.6. The X-ray crystal structure showed it was tertiary amine HCl salt **36·HCl**. A crystal 0.278 mm x 0.165 mm x 0.280 mm was selected for X-ray crystallography with 0.71073 Å (Mo Kα) radiation: monoclinic a = 6.8972(4) Å, b = 8.2335(5) Å, c = 11.2422(7) Å, α = 92.2850(10)°, β = 102.8470(10)°, γ = 91.2820(10)°; Z = 2; 3019 reflections were collected, 2805 independent, $-9 \leq h \leq 9$, $-10 \leq k \leq 10$, $-14 \leq l \leq 14$. Full-matrix least-squares refinement on F^2, data-to-parameter ratio = 12.4, Goodness-of-fit = 1.068, R1 = 0.0313, wR2 = 0.0842 (all data), R1 = 0.0297, wR2 = 0.0831 ($I > 2\sigma(I)$). Full details are given in Appendix 6.

Protected tertiary amine, 86. At 0 °C, trimethylsilyl chloride (0.480 mL, 3.78 mmol) was added to a stirred solution of tertiary amine **36** (100 mg, 0.420 mmol) and imidazole (260 mg, 3.78 mmol) in DMF (10 mL). The mixture was stirred at 0 °C for 1 h and stirred for 4 h at rt. Water (20 mL) was added to the reaction solution at 0 °C. The reaction mixture was extracted with ether (3 × 20 mL) and the organic layer was washed with brine (2 × 15 mL), dried with sodium sulfate and evaporated. The residue was purified by column chromatography on silica gel using hexane:ethyl acetate (20:1) as the eluent to give 230 mg (82%) of compound **86** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 3.60 (12 H, d, CH_2), 3.06 (3 H, m, CH), 0.15 (54 H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 62.9, 58.1, -0.3; Anal. Cacld for $C_{27}H_{69}NO_6Si_6$: C, 48.23; H, 10.34; N, 2.08; Found: C, 48.51; H 10.56; N, 2.21.

Reaction of tertiary amine 36 with aluminum isopropoxide. This reaction was tried several times under the following conditions (in all reactions the molar ratio of tertiary amine **36** and aluminum isopropoxide was 1:2): (a) benzene as solvent, the mixture was refluxed for 6-8 h. (b) DMF as solvent, the mixture was heated (oil bath 125-135 °C) for 6-8 h. (c) 1:1 benzene and DMF (v/v) as solvent, the solution was stirred overnight at rt. Under these conditions, all gave a white precipitate, mp> 260 ^{0}C. This white precipitate didn't dissolve in any organic solvent (DMF, DMSO, alcohols, $CHCl_3$, acetone, acetonitrile, ethyl acetate). It just dissolved in hot water and was hydrolyzed to tertiary amine **36**.

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APPENDICES

APPENDIX 1

CRYSTAL STRUCTURE DATA FOR COMPOUND 36

data_pbca (tertiary amine)

```
_audit_creation_method            SHELXL-97
_chemical_name_systematic


_chemical_name_common             ?
_chemical_melting_point           ?
_chemical_formula_moiety          ?
_chemical_formula_sum
 'C9 H15 N O6'
_chemical_formula_weight          233.22

loop_
 _atom_type_symbol
 _atom_type_description
 _atom_type_scat_dispersion_real
 _atom_type_scat_dispersion_imag
 _atom_type_scat_source
 'C'  'C'   0.0033   0.0016
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'H'  'H'   0.0000   0.0000
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'N'  'N'   0.0061   0.0033
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'O'  'O'   0.0106   0.0060
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

_symmetry_cell_setting            ?
_symmetry_space_group_name_H-M    ?

loop_
 _symmetry_equiv_pos_as_xyz
 'x, y, z'
 '-x+1/2, -y, z+1/2'
 '-x, y+1/2, -z+1/2'
 'x+1/2, -y+1/2, -z'
 '-x, -y, -z'
 'x-1/2, y, -z-1/2'
 'x, -y-1/2, z-1/2'
 '-x-1/2, y-1/2, z'

_cell_length_a                    10.915(2)
_cell_length_b                    8.9100(18)
_cell_length_c                    23.635(5)
_cell_angle_alpha                 90.00
_cell_angle_beta                  90.00
_cell_angle_gamma                 90.00
_cell_volume                      2298.6(8)
_cell_formula_units_Z             8
_cell_measurement_temperature     193(2)
_cell_measurement_reflns_used     ?
```

```
_cell_measurement_theta_min       ?
_cell_measurement_theta_max       ?

_exptl_crystal_description        ?
_exptl_crystal_colour             ?
_exptl_crystal_size_max           0.39
_exptl_crystal_size_mid           0.32
_exptl_crystal_size_min           0.20
_exptl_crystal_density_meas       ?
_exptl_crystal_density_diffrn     1.348
_exptl_crystal_density_method     'not measured'
_exptl_crystal_F_000              992
_exptl_absorpt_coefficient_mu     0.114
_exptl_absorpt_correction_type    ?
_exptl_absorpt_correction_T_min   ?
_exptl_absorpt_correction_T_max   ?
_exptl_absorpt_process_details    ?

_exptl_special_details
;
 ?
;

_diffrn_ambient_temperature       193(2)
_diffrn_radiation_wavelength      0.71073
_diffrn_radiation_type            MoK\a
_diffrn_radiation_source          'fine-focus sealed tube'
_diffrn_radiation_monochromator   graphite
_diffrn_measurement_device_type   ?
_diffrn_measurement_method        ?
_diffrn_detector_area_resol_mean  ?
_diffrn_standards_number          ?
_diffrn_standards_interval_count  ?
_diffrn_standards_interval_time   ?
_diffrn_standards_decay_%         ?
_diffrn_reflns_number             21931
_diffrn_reflns_av_R_equivalents   0.0239
_diffrn_reflns_av_sigmaI/netI     0.0136
_diffrn_reflns_limit_h_min        -14
_diffrn_reflns_limit_h_max        14
_diffrn_reflns_limit_k_min        -11
_diffrn_reflns_limit_k_max        11
_diffrn_reflns_limit_l_min        -31
_diffrn_reflns_limit_l_max        30
_diffrn_reflns_theta_min          1.72
_diffrn_reflns_theta_max          28.32
_reflns_number_total              2858
_reflns_number_gt                 2682
_reflns_threshold_expression      >2sigma(I)

_computing_data_collection        ?
_computing_cell_refinement        ?
```

```
_computing_data_reduction         ?
_computing_structure_solution     'SHELXS-97 (Sheldrick,
1990)'
_computing_structure_refinement   'SHELXL-97 (Sheldrick,
1997)'
_computing_molecular_graphics     ?
_computing_publication_material   ?

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted
R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors
R are based
 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-
factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.
R-factors based
 on F^2^ are statistically about twice as large as those
based on F, and R-
 factors based on ALL data will be even larger.
;

_refine_ls_structure_factor_coef  Fsqd
_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0650P)^2^+0.5358P] where
P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      direct
_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     mixed
_refine_ls_extinction_method      SHELXL
_refine_ls_extinction_coef        0.0235(19)
_refine_ls_extinction_expression
 'Fc^*^=kFc[1+0.001xFc^2^\l^3^/sin(2\q)]^-1/4^'
_refine_ls_number_reflns          2858
_refine_ls_number_parameters      170
_refine_ls_number_restraints      0
_refine_ls_R_factor_all           0.0378
_refine_ls_R_factor_gt            0.0361
_refine_ls_wR_factor_ref          0.1032
_refine_ls_wR_factor_gt           0.1009
_refine_ls_goodness_of_fit_ref    1.026
_refine_ls_restrained_S_all       1.026
_refine_ls_shift/su_max           0.001
_refine_ls_shift/su_mean          0.000

loop_
```

```
 _atom_site_label
 _atom_site_type_symbol
 _atom_site_fract_x
 _atom_site_fract_y
 _atom_site_fract_z
 _atom_site_U_iso_or_equiv
 _atom_site_adp_type
 _atom_site_occupancy
 _atom_site_symmetry_multiplicity
 _atom_site_calc_flag
 _atom_site_refinement_flags
 _atom_site_disorder_assembly
 _atom_site_disorder_group
O3 O 0.54781(7) 0.02502(8) 0.29744(3) 0.02818(18) Uani 1 1 d
. . .
N1 N 0.54025(7) 0.31619(9) 0.37092(3) 0.01954(18) Uani 1 1 d
. . .
O5 O 0.79707(6) 0.22275(9) 0.46848(3) 0.02734(18) Uani 1 1 d
. . .
O2 O 0.70558(7) 0.47638(8) 0.29885(3) 0.03115(19) Uani 1 1 d
. . .
O6 O 0.23938(7) 0.41860(9) 0.43489(3) 0.0320(2) Uani 1 1 d .
. .
O1 O 0.57161(7) 0.63151(9) 0.37812(3) 0.03117(19) Uani 1 1 d
. . .
O4 O 0.49101(7) -0.00440(8) 0.40596(3) 0.03160(19) Uani 1 1
d . . .
C9 C 0.70469(8) 0.31217(10) 0.44233(4) 0.0238(2) Uani 1 1 d
. . .
H9A H 0.7443 0.3895 0.4185 0.029 Uiso 1 1 calc R . .
H9B H 0.6570 0.3644 0.4720 0.029 Uiso 1 1 calc R . .
C8 C 0.54598(8) 0.10566(10) 0.44156(4) 0.0224(2) Uani 1 1 d
. . .
H8A H 0.6024 0.0563 0.4686 0.027 Uiso 1 1 calc R . .
H8B H 0.4818 0.1583 0.4635 0.027 Uiso 1 1 calc R . .
C7 C 0.44848(8) 0.40750(10) 0.39898(4) 0.02057(19) Uani 1 1
d . . .
H7A H 0.4702 0.4086 0.4401 0.025 Uiso 1 1 calc R . .
C6 C 0.61682(7) 0.21878(9) 0.40556(3) 0.01820(18) Uani 1 1 d
. . .
H6A H 0.6689 0.1593 0.3789 0.022 Uiso 1 1 calc R . .
C5 C 0.53957(8) 0.30275(10) 0.30952(4) 0.02108(19) Uani 1 1
d . . .
H5A H 0.4875 0.3874 0.2956 0.025 Uiso 1 1 calc R . .
C4 C 0.66648(9) 0.32921(11) 0.28415(4) 0.0246(2) Uani 1 1 d
. . .
H4A H 0.7251 0.2542 0.2991 0.030 Uiso 1 1 calc R . .
H4B H 0.6631 0.3187 0.2425 0.030 Uiso 1 1 calc R . .
C3 C 0.31751(8) 0.34618(11) 0.39490(4) 0.0253(2) Uani 1 1 d
. . .
H3A H 0.2855 0.3627 0.3562 0.030 Uiso 1 1 calc R . .
H3B H 0.3181 0.2368 0.4022 0.030 Uiso 1 1 calc R . .
```

```
C2 C 0.45118(9) 0.57150(11) 0.37894(4) 0.0267(2) Uani 1 1 d
. . .
H2A H 0.4159 0.5775 0.3404 0.032 Uiso 1 1 calc R . .
H2B H 0.3995 0.6330 0.4044 0.032 Uiso 1 1 calc R . .
C1 C 0.48189(9) 0.16001(11) 0.28532(4) 0.0263(2) Uani 1 1 d
. . .
H1A H 0.3978 0.1502 0.3006 0.032 Uiso 1 1 calc R . .
H1B H 0.4752 0.1710 0.2438 0.032 Uiso 1 1 calc R . .
H1 H 0.6136(15) 0.5766(18) 0.3567(6) 0.043(4) Uiso 1 1 d . .
.
H2 H 0.7841(16) 0.4846(17) 0.2956(7) 0.044(4) Uiso 1 1 d . .
.
H3 H 0.5303(14) 0.0024(16) 0.3317(7) 0.039(4) Uiso 1 1 d . .
.
H4 H 0.4234(16) -0.0281(18) 0.4183(7) 0.047(4) Uiso 1 1 d .
. .
H5 H 0.8444(16) 0.1926(17) 0.4418(7) 0.048(4) Uiso 1 1 d . .
.
H6 H 0.2589(17) 0.3829(19) 0.4660(8) 0.055(4) Uiso 1 1 d . .
.

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 _atom_site_aniso_U_22
 _atom_site_aniso_U_33
 _atom_site_aniso_U_23
 _atom_site_aniso_U_13
 _atom_site_aniso_U_12
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0.0008(3)
N1 0.0184(3) 0.0241(4) 0.0162(3) -0.0003(3) -0.0005(2)
0.0048(3)
O5 0.0211(3) 0.0373(4) 0.0237(3) 0.0024(3) -0.0056(2)
0.0018(3)
O2 0.0240(4) 0.0257(4) 0.0437(4) 0.0003(3) 0.0061(3) -
0.0019(3)
O6 0.0219(3) 0.0467(5) 0.0275(4) 0.0037(3) 0.0055(3)
0.0099(3)
O1 0.0267(4) 0.0252(4) 0.0416(4) -0.0062(3) 0.0022(3) -
0.0024(3)
O4 0.0305(4) 0.0321(4) 0.0321(4) -0.0050(3) 0.0046(3) -
0.0139(3)
C9 0.0216(4) 0.0242(4) 0.0255(4) -0.0015(3) -0.0062(3) -
0.0006(3)
C8 0.0217(4) 0.0237(4) 0.0220(4) 0.0014(3) -0.0003(3) -
0.0030(3)
C7 0.0174(4) 0.0239(4) 0.0204(4) -0.0016(3) 0.0002(3)
0.0029(3)
C6 0.0162(4) 0.0199(4) 0.0185(4) 0.0002(3) -0.0013(3)
0.0000(3)
```

```
C5 0.0199(4) 0.0255(4) 0.0178(4) -0.0007(3) -0.0012(3)
0.0012(3)
C4 0.0247(4) 0.0270(4) 0.0222(4) 0.0001(3) 0.0040(3) -
0.0003(3)
C3 0.0174(4) 0.0327(5) 0.0257(4) -0.0004(4) 0.0016(3)
0.0010(3)
C2 0.0222(4) 0.0248(4) 0.0329(5) -0.0006(4) 0.0001(3)
0.0035(3)
C1 0.0217(4) 0.0333(5) 0.0239(4) -0.0068(4) -0.0037(3) -
0.0005(4)

_geom_special_details
;
 All esds (except the esd in the dihedral angle between two
l.s. planes)
 are estimated using the full covariance matrix.  The cell
esds are taken
 into account individually in the estimation of esds in
distances, angles
 and torsion angles; correlations between esds in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell esds is used for estimating esds
involving l.s. planes.
;

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 _geom_bond_atom_site_label_2
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 _geom_bond_publ_flag
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O3 H3 0.855(17) . ?
N1 C7 1.4509(11) . ?
N1 C5 1.4561(11) . ?
N1 C6 1.4566(10) . ?
O5 C9 1.4262(11) . ?
O5 H5 0.858(18) . ?
O2 C4 1.4221(12) . ?
O2 H2 0.864(18) . ?
O6 C3 1.4273(11) . ?
O6 H6 0.829(18) . ?
O1 C2 1.4192(12) . ?
O1 H1 0.839(16) . ?
O4 C8 1.4247(11) . ?
O4 H4 0.821(18) . ?
C9 C6 1.5387(12) . ?
C9 H9A 0.9900 . ?
C9 H9B 0.9900 . ?
C8 C6 1.5290(12) . ?
```

```
C8 H8A 0.9900 . ?
C8 H8B 0.9900 . ?
C7 C3 1.5335(12) . ?
C7 C2 1.5364(14) . ?
C7 H7A 1.0000 . ?
C6 H6A 1.0000 . ?
C5 C4 1.5278(13) . ?
C5 C1 1.5301(13) . ?
C5 H5A 1.0000 . ?
C4 H4A 0.9900 . ?
C4 H4B 0.9900 . ?
C3 H3A 0.9900 . ?
C3 H3B 0.9900 . ?
C2 H2A 0.9900 . ?
C2 H2B 0.9900 . ?
C1 H1A 0.9900 . ?
C1 H1B 0.9900 . ?

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 _geom_angle_atom_site_label_2
 _geom_angle_atom_site_label_3
 _geom_angle
 _geom_angle_site_symmetry_1
 _geom_angle_site_symmetry_3
 _geom_angle_publ_flag
C1 O3 H3 106.0(10) . . ?
C7 N1 C5 119.87(7) . . ?
C7 N1 C6 118.25(7) . . ?
C5 N1 C6 120.93(7) . . ?
C9 O5 H5 106.4(11) . . ?
C4 O2 H2 110.7(10) . . ?
C3 O6 H6 105.1(12) . . ?
C2 O1 H1 107.1(11) . . ?
C8 O4 H4 110.2(11) . . ?
O5 C9 C6 112.54(7) . . ?
O5 C9 H9A 109.1 . . ?
C6 C9 H9A 109.1 . . ?
O5 C9 H9B 109.1 . . ?
C6 C9 H9B 109.1 . . ?
H9A C9 H9B 107.8 . . ?
O4 C8 C6 109.75(7) . . ?
O4 C8 H8A 109.7 . . ?
C6 C8 H8A 109.7 . . ?
O4 C8 H8B 109.7 . . ?
C6 C8 H8B 109.7 . . ?

H8A C8 H8B 108.2 . . ?
N1 C7 C3 114.52(7) . . ?
N1 C7 C2 112.28(7) . . ?
C3 C7 C2 109.72(7) . . ?
N1 C7 H7A 106.6 . . ?
```

```
C3 C7 H7A 106.6 . . ?
C2 C7 H7A 106.6 . . ?
N1 C6 C8 114.54(7) . . ?
N1 C6 C9 110.66(7) . . ?
C8 C6 C9 110.94(7) . . ?
N1 C6 H6A 106.7 . . ?
C8 C6 H6A 106.7 . . ?
C9 C6 H6A 106.7 . . ?
N1 C5 C4 111.95(7) . . ?
N1 C5 C1 116.30(8) . . ?
C4 C5 C1 110.77(7) . . ?
N1 C5 H5A 105.6 . . ?
C4 C5 H5A 105.6 . . ?
C1 C5 H5A 105.6 . . ?
O2 C4 C5 108.58(8) . . ?
O2 C4 H4A 110.0 . . ?
C5 C4 H4A 110.0 . . ?
O2 C4 H4B 110.0 . . ?
C5 C4 H4B 110.0 . . ?
H4A C4 H4B 108.4 . . ?
O6 C3 C7 110.75(8) . . ?
O6 C3 H3A 109.5 . . ?
C7 C3 H3A 109.5 . . ?
O6 C3 H3B 109.5 . . ?
C7 C3 H3B 109.5 . . ?
H3A C3 H3B 108.1 . . ?
O1 C2 C7 112.35(8) . . ?
O1 C2 H2A 109.1 . . ?
C7 C2 H2A 109.1 . . ?
O1 C2 H2B 109.1 . . ?
C7 C2 H2B 109.1 . . ?
H2A C2 H2B 107.9 . . ?
O3 C1 C5 114.65(7) . . ?
O3 C1 H1A 108.6 . . ?
C5 C1 H1A 108.6 . . ?
O3 C1 H1B 108.6 . . ?
C5 C1 H1B 108.6 . . ?
H1A C1 H1B 107.6 . . ?

_diffrn_measured_fraction_theta_max    0.998
_diffrn_reflns_theta_full              28.32
_diffrn_measured_fraction_theta_full   0.998
_refine_diff_density_max    0.360
_refine_diff_density_min   -0.166
_refine_diff_density_rms    0.047
```

APPENDIX 2

CRYSTAL STRUCTURE DATA FOR COMPOUND 67

```
data_face(one boron)

_audit_creation_method            SHELXL-97
_chemical_name_systematic
;
 ?
;
_chemical_name_common             ?
_chemical_melting_point           ?
_chemical_formula_moiety          ?
_chemical_formula_sum
 'C9 H18 B N O6'
_chemical_formula_weight          247.05

loop_
 _atom_type_symbol
 _atom_type_description
 _atom_type_scat_dispersion_real
 _atom_type_scat_dispersion_imag
 _atom_type_scat_source
 'C'  'C'   0.0033   0.0016
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'H'  'H'   0.0000   0.0000
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'N'  'N'   0.0061   0.0033
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'O'  'O'   0.0106   0.0060
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'B'  'B'   0.0013   0.0007
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

_symmetry_cell_setting            ?
_symmetry_space_group_name_H-M    ?

loop_
 _symmetry_equiv_pos_as_xyz
 'x, y, z'
 '-x+1/2, -y+1/2, z+1/2'
 '-y, x+1/2, z+1/4'
 'y+1/2, -x, z+3/4'
 'x, -y, z+1/2'
 '-x+1/2, y+1/2, z'
 '-y, -x+1/2, z+3/4'
 'y+1/2, x, z+1/4'
 'x+1/2, y+1/2, z+1/2'
 '-x+1, -y+1, z+1'
 '-y+1/2, x+1, z+3/4'
```

```
 'y+1, -x+1/2, z+5/4'
 'x+1/2, -y+1/2, z+1'
 '-x+1, y+1, z+1/2'
 '-y+1/2, -x+1, z+5/4'
 'y+1, x+1/2, z+3/4'

_cell_length_a                    16.9503(11)
_cell_length_b                    16.9503(11)
_cell_length_c                    14.8701(10)
_cell_angle_alpha                 90.00
_cell_angle_beta                  90.00
_cell_angle_gamma                 90.00
_cell_volume                      4272.4(5)
_cell_formula_units_Z             16
_cell_measurement_temperature     193(2)
_cell_measurement_reflns_used     ?
_cell_measurement_theta_min       ?
_cell_measurement_theta_max       ?

_exptl_crystal_description        ?
_exptl_crystal_colour             ?
_exptl_crystal_size_max           1.540
_exptl_crystal_size_mid           0.160
_exptl_crystal_size_min           0.156
_exptl_crystal_density_meas       ?
_exptl_crystal_density_diffrn     1.536
_exptl_crystal_density_method     'not measured'
_exptl_crystal_F_000              2112
_exptl_absorpt_coefficient_mu     0.126
_exptl_absorpt_correction_type    ?
_exptl_absorpt_correction_T_min   ?
_exptl_absorpt_correction_T_max   ?
_exptl_absorpt_process_details    ?

_exptl_special_details
;
 ?
;

_diffrn_ambient_temperature       193(2)
_diffrn_radiation_wavelength      0.71073
_diffrn_radiation_type            MoK\a
_diffrn_radiation_source          'fine-focus sealed tube'
_diffrn_radiation_monochromator   graphite
_diffrn_measurement_device_type   ?
_diffrn_measurement_method        ?
_diffrn_detector_area_resol_mean  ?
_diffrn_standards_number          ?
_diffrn_standards_interval_count  ?
_diffrn_standards_interval_time   ?
_diffrn_standards_decay_%         ?
_diffrn_reflns_number             20614
```

```
_diffrn_reflns_av_R_equivalents   0.0257
_diffrn_reflns_av_sigmaI/netI     0.0201
_diffrn_reflns_limit_h_min        -22
_diffrn_reflns_limit_h_max        22
_diffrn_reflns_limit_k_min        -22
_diffrn_reflns_limit_k_max        22
_diffrn_reflns_limit_l_min        -19
_diffrn_reflns_limit_l_max        19
_diffrn_reflns_theta_min          2.40
_diffrn_reflns_theta_max          28.32
_reflns_number_total              2651
_reflns_number_gt                 2615
_reflns_threshold_expression      >2sigma(I)

_computing_data_collection        ?
_computing_cell_refinement        ?
_computing_data_reduction         ?
_computing_structure_solution     'SHELXS-97 (Sheldrick,
1990)'
_computing_structure_refinement   'SHELXL-97 (Sheldrick,
1997)'
_computing_molecular_graphics     ?
_computing_publication_material   ?

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted
R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors
R are based
 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-
factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.
R-factors based
 on F^2^ are statistically about twice as large as those
based on F, and R-
 factors based on ALL data will be even larger.
;

_refine_ls_structure_factor_coef  Fsqd
_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0673P)^2^+0.2442P] where
P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      direct
_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     mixed
_refine_ls_extinction_method      none
```

```
_refine_ls_extinction_coef        ?
_refine_ls_abs_structure_details
 'Flack H D (1983), Acta Cryst. A39, 876-881'
_refine_ls_abs_structure_Flack    0.6(5)
_refine_ls_number_reflns          2651
_refine_ls_number_parameters      226
_refine_ls_number_restraints      1
_refine_ls_R_factor_all           0.0319
_refine_ls_R_factor_gt            0.0316
_refine_ls_wR_factor_ref          0.0807
_refine_ls_wR_factor_gt           0.0804
_refine_ls_goodness_of_fit_ref    1.056
_refine_ls_restrained_S_all       1.056
_refine_ls_shift/su_max           0.002
_refine_ls_shift/su_mean          0.000

loop_
 _atom_site_label
 _atom_site_type_symbol
 _atom_site_fract_x
 _atom_site_fract_y
 _atom_site_fract_z
 _atom_site_U_iso_or_equiv
 _atom_site_adp_type
 _atom_site_occupancy
 _atom_site_symmetry_multiplicity
 _atom_site_calc_flag
 _atom_site_refinement_flags
 _atom_site_disorder_assembly
 _atom_site_disorder_group
B1 B 0.09550(7) 0.36668(7) 0.33552(8) 0.0217(2) Uani 1 1 d .
. .
N1 N 0.03293(5) 0.28950(5) 0.32844(6) 0.01637(16) Uani 1 1 d
. . .
O1 O 0.06661(5) 0.41124(5) 0.41000(6) 0.02660(18) Uani 1 1 d
. . .
O2 O 0.08735(5) 0.40382(5) 0.24837(5) 0.02675(19) Uani 1 1 d
. . .
O3 O 0.17149(5) 0.33075(5) 0.34936(6) 0.02599(19) Uani 1 1 d
. . .
O4 O -0.14732(6) 0.29248(6) 0.47798(7) 0.0315(2) Uani 1 1 d
. . .
H4 H -0.1544(13) 0.2521(13) 0.5075(17) 0.039(5) Uiso 1 1 d .
. .
O5 O -0.06881(6) 0.25192(5) 0.10899(6) 0.0298(2) Uani 1 1 d
. . .
H5 H -0.0683(13) 0.2093(14) 0.0717(16) 0.048(5) Uiso 1 1 d .
. .
O6 O 0.04810(5) 0.14230(5) 0.46764(5) 0.02376(18) Uani 1 1 d
. . .
H6 H 0.0056(17) 0.1249(13) 0.4795(16) 0.048(6) Uiso 1 1 d .
. .
```

```
C4 C -0.01544(7) 0.39457(6) 0.41842(8) 0.0244(2) Uani 1 1 d
. . .
H4A H -0.0471(11) 0.4198(11) 0.3727(13) 0.031(4) Uiso 1 1 d
. . .
H4B H -0.0342(10) 0.4120(10) 0.4730(13) 0.026(4) Uiso 1 1 d
. . .
C5 C 0.05972(7) 0.34632(7) 0.18537(7) 0.0244(2) Uani 1 1 d .
. .
H5A H 0.0408(11) 0.3733(11) 0.1374(13) 0.031(4) Uiso 1 1 d .
. .
H5B H 0.1026(10) 0.3123(10) 0.1672(12) 0.025(4) Uiso 1 1 d .
. .
C6 C 0.15896(6) 0.25481(7) 0.38828(8) 0.0240(2) Uani 1 1 d .
. .
H6A H 0.1476(11) 0.2580(11) 0.4525(14) 0.030(4) Uiso 1 1 d .
. .
H6B H 0.2023(12) 0.2249(12) 0.3785(15) 0.038(4) Uiso 1 1 d .
. .
C7 C -0.02155(6) 0.30497(6) 0.40683(7) 0.01882(19) Uani 1 1
d . . .
H7 H -0.0010(9) 0.2807(8) 0.4561(10) 0.012(3) Uiso 1 1 d . .
.
C8 C -0.00365(6) 0.30088(6) 0.23701(7) 0.01886(19) Uani 1 1
d . . .
H8 H -0.0442(9) 0.3374(9) 0.2457(12) 0.019(3) Uiso 1 1 d . .
.
C9 C 0.08895(5) 0.22051(6) 0.33631(7) 0.01901(19) Uani 1 1 d
. . .
H9 H 0.1074(9) 0.2111(9) 0.2762(11) 0.019(3) Uiso 1 1 d . .
.
C10 C -0.10551(6) 0.27417(7) 0.39802(8) 0.0234(2) Uani 1 1 d
. . .
H10A H -0.1068(11) 0.2190(11) 0.3899(13) 0.030(4) Uiso 1 1 d
. . .
H10B H -0.1327(12) 0.2985(12) 0.3485(15) 0.038(5) Uiso 1 1 d
. . .
C11 C -0.03248(6) 0.22639(6) 0.19060(7) 0.0217(2) Uani 1 1 d
. . .
H11A H 0.0117(10) 0.1936(9) 0.1803(12) 0.024(4) Uiso 1 1 d .
. .
H11B H -0.0717(10) 0.1984(10) 0.2259(12) 0.025(3) Uiso 1 1 d
. . .
C12 C 0.05740(6) 0.14282(6) 0.37226(7) 0.0207(2) Uani 1 1 d
. . .
H12A H 0.0098(12) 0.1272(10) 0.3429(14) 0.034(4) Uiso 1 1 d
. . .
H12B H 0.0945(10) 0.1030(10) 0.3542(11) 0.029(4) Uiso 1 1 d
. . .

loop_
 _atom_site_aniso_label
 _atom_site_aniso_U_11
```

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 _atom_site_aniso_U_22
 _atom_site_aniso_U_33
 _atom_site_aniso_U_23
 _atom_site_aniso_U_13
 _atom_site_aniso_U_12
B1 0.0222(5) 0.0205(5) 0.0223(5) 0.0017(4) 0.0001(4) -
0.0063(4)
N1 0.0170(3) 0.0165(3) 0.0156(4) 0.0022(3) 0.0011(3)
0.0000(3)
O1 0.0288(4) 0.0243(4) 0.0267(4) -0.0039(3) -0.0006(3) -
0.0056(3)
O2 0.0347(4) 0.0223(4) 0.0232(4) 0.0049(3) -0.0005(3) -
0.0092(3)
O3 0.0192(3) 0.0276(4) 0.0311(4) 0.0057(3) 0.0010(3) -
0.0059(3)
O4 0.0326(4) 0.0284(4) 0.0335(4) 0.0077(3) 0.0157(4)
0.0070(3)
O5 0.0393(5) 0.0302(4) 0.0200(4) -0.0019(3) -0.0072(3)
0.0037(3)
O6 0.0233(4) 0.0268(4) 0.0211(4) 0.0040(3) 0.0014(3) -
0.0046(3)
C4 0.0272(5) 0.0223(4) 0.0237(5) -0.0017(4) 0.0022(4)
0.0011(3)
C5 0.0283(5) 0.0267(5) 0.0184(5) 0.0037(4) 0.0012(4) -
0.0064(4)
C6 0.0185(4) 0.0270(5) 0.0264(5) 0.0052(4) -0.0013(4) -
0.0018(4)
C7 0.0204(4) 0.0202(4) 0.0159(4) 0.0015(3) 0.0034(3)
0.0013(3)
C8 0.0208(4) 0.0193(4) 0.0164(4) 0.0025(3) -0.0006(3) -
0.0004(3)
C9 0.0179(4) 0.0190(4) 0.0202(5) 0.0024(3) 0.0011(3)
0.0019(3)
C10 0.0206(4) 0.0241(5) 0.0254(5) 0.0027(4) 0.0046(4) -
0.0002(3)
C11 0.0241(5) 0.0210(4) 0.0199(4) -0.0003(4) -0.0026(4) -
0.0009(4)
C12 0.0231(4) 0.0175(4) 0.0215(5) 0.0022(3) 0.0002(4)
0.0007(3)

_geom_special_details
;
 All esds (except the esd in the dihedral angle between two
l.s. planes)
 are estimated using the full covariance matrix.  The cell
esds are taken
 into account individually in the estimation of esds in
distances, angles
 and torsion angles; correlations between esds in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
```

```
 treatment of cell esds is used for estimating esds
involving l.s. planes.
;

loop_
 _geom_bond_atom_site_label_1
 _geom_bond_atom_site_label_2
 _geom_bond_distance
 _geom_bond_site_symmetry_2
 _geom_bond_publ_flag
B1 O1 1.4272(15) . ?
B1 O3 1.4396(14) . ?
B1 O2 1.4473(14) . ?
B1 N1 1.6875(13) . ?
N1 C8 1.5067(12) . ?
N1 C7 1.5101(12) . ?
N1 C9 1.5109(12) . ?
O1 C4 1.4246(14) . ?
O2 C5 1.4306(14) . ?
O3 C6 1.4273(13) . ?
O4 C10 1.4186(13) . ?
O4 H4 0.82(2) . ?
O5 C11 1.4281(13) . ?
O5 H5 0.91(2) . ?
O6 C12 1.4270(13) . ?
O6 H6 0.80(3) . ?
C4 C7 1.5321(15) . ?
C4 H4A 0.97(2) . ?
C4 H4B 0.920(19) . ?
C5 C8 1.5285(14) . ?
C5 H5A 0.91(2) . ?
C5 H5B 0.967(17) . ?
C6 C9 1.5308(14) . ?
C6 H6A 0.98(2) . ?
C6 H6B 0.90(2) . ?
C7 C10 1.5216(14) . ?
C7 H7 0.910(14) . ?
C8 C11 1.5196(14) . ?
C8 H8 0.934(16) . ?
C9 C12 1.5186(13) . ?
C9 H9 0.961(17) . ?
C10 H10A 0.944(19) . ?
C10 H10B 0.96(2) . ?
C11 H11A 0.946(17) . ?
C11 H11B 0.971(17) . ?
C12 H12A 0.95(2) . ?
C12 H12B 0.962(17) . ?

loop_
 _geom_angle_atom_site_label_1
 _geom_angle_atom_site_label_2
 _geom_angle_atom_site_label_3
```

```
 _geom_angle
 _geom_angle_site_symmetry_1
 _geom_angle_site_symmetry_3
 _geom_angle_publ_flag
O1 B1 O3 114.84(10) . . ?
O1 B1 O2 115.59(9) . . ?
O3 B1 O2 113.42(9) . . ?
O1 B1 N1 104.06(8) . . ?
O3 B1 N1 104.08(8) . . ?
O2 B1 N1 102.79(8) . . ?
C8 N1 C7 115.00(8) . . ?
C8 N1 C9 115.32(7) . . ?
C7 N1 C9 117.32(7) . . ?
C8 N1 B1 102.45(7) . . ?
C7 N1 B1 101.63(7) . . ?
C9 N1 B1 101.55(7) . . ?
C4 O1 B1 107.35(8) . . ?
C5 O2 B1 108.74(8) . . ?
C6 O3 B1 107.84(8) . . ?
C10 O4 H4 109.8(16) . . ?
C11 O5 H5 105.8(14) . . ?
C12 O6 H6 108.7(18) . . ?
O1 C4 C7 104.64(8) . . ?
O1 C4 H4A 113.2(11) . . ?
C7 C4 H4A 108.8(11) . . ?
O1 C4 H4B 110.5(10) . . ?
C7 C4 H4B 113.2(10) . . ?
H4A C4 H4B 106.6(15) . . ?
O2 C5 C8 104.15(8) . . ?
O2 C5 H5A 106.7(12) . . ?
C8 C5 H5A 113.7(12) . . ?
O2 C5 H5B 110.1(11) . . ?
C8 C5 H5B 111.6(10) . . ?
H5A C5 H5B 110.3(17) . . ?
O3 C6 C9 104.66(8) . . ?
O3 C6 H6A 112.1(11) . . ?
C9 C6 H6A 111.2(11) . . ?
O3 C6 H6B 108.6(13) . . ?
C9 C6 H6B 109.6(13) . . ?
H6A C6 H6B 110.4(18) . . ?
N1 C7 C10 116.48(8) . . ?
N1 C7 C4 102.57(8) . . ?
C10 C7 C4 114.39(8) . . ?
N1 C7 H7 108.0(9) . . ?
C10 C7 H7 105.8(9) . . ?
C4 C7 H7 109.4(8) . . ?
N1 C8 C11 115.83(8) . . ?
N1 C8 C5 103.22(8) . . ?
C11 C8 C5 114.62(9) . . ?
N1 C8 H8 105.3(11) . . ?
C11 C8 H8 112.1(10) . . ?
C5 C8 H8 104.6(10) . . ?
```

```
N1 C9 C12 118.49(8) . . ?
N1 C9 C6 103.44(8) . . ?
C12 C9 C6 115.13(9) . . ?
N1 C9 H9 105.2(9) . . ?
C12 C9 H9 107.3(9) . . ?
C6 C9 H9 106.3(10) . . ?
O4 C10 C7 108.67(9) . . ?
O4 C10 H10A 108.2(12) . . ?

C7 C10 H10A 111.9(11) . . ?
O4 C10 H10B 108.0(12) . . ?
C7 C10 H10B 111.5(12) . . ?
H10A C10 H10B 108.4(17) . . ?
O5 C11 C8 105.83(8) . . ?
O5 C11 H11A 112.4(11) . . ?
C8 C11 H11A 108.0(10) . . ?
O5 C11 H11B 108.2(10) . . ?
C8 C11 H11B 112.4(10) . . ?
H11A C11 H11B 110.0(15) . . ?
O6 C12 C9 113.21(9) . . ?
O6 C12 H12A 111.1(12) . . ?
C9 C12 H12A 112.1(11) . . ?
O6 C12 H12B 110.2(10) . . ?
C9 C12 H12B 106.3(10) . . ?
H12A C12 H12B 103.3(15) . . ?

_diffrn_measured_fraction_theta_max    0.999
_diffrn_reflns_theta_full              28.32
_diffrn_measured_fraction_theta_full   0.999
_refine_diff_density_max    0.274
_refine_diff_density_min   -0.227
_refine_diff_density_rms    0.053
```

APPENDIX 3

CRYSTAL STRUCTURE DATA FOR COMPOUND 71

```
data_p-1 (2 boron + pyridine)

_audit_creation_method            SHELXL-97
_chemical_name_systematic
;
 ?
;
_chemical_name_common             ?
_chemical_melting_point           ?
_chemical_formula_moiety          ?
_chemical_formula_sum
 'C14 H20 B2 N2 O6'
_chemical_formula_weight          333.94

loop_
 _atom_type_symbol
 _atom_type_description
 _atom_type_scat_dispersion_real
 _atom_type_scat_dispersion_imag
 _atom_type_scat_source
 'C'  'C'   0.0033   0.0016
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'H'  'H'   0.0000   0.0000
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 'B'  'B'   0.0013   0.0007
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 'O'  'O'   0.0106   0.0060
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_symmetry_space_group_name_H-M    ?

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 'x, y, z'
 '-x, -y, -z'

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_cell_length_b                    11.6639(8)
_cell_length_c                    12.9997(9)
_cell_angle_alpha                 97.56(3)
_cell_angle_beta                  92.13(3)
_cell_angle_gamma                 117.95(3)
_cell_volume                      1517.55(18)
_cell_formula_units_Z             4
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_exptl_special_details
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;

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_computing_data_reduction         ?
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1990)'
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1997)'
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_computing_publication_material   ?

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted
R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors
R are based
 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-
factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.
R-factors based
 on F^2^ are statistically about twice as large as those
based on F, and R-
 factors based on ALL data will be even larger.
;

_refine_ls_structure_factor_coef  Fsqd
_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.1065P)^2^+0.5031P] where
P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      direct
_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
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_refine_ls_wR_factor_ref          0.2235
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_refine_ls_goodness_of_fit_ref    1.092
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O12 O 0.54794(18) 0.65314(18) 0.11245(15) 0.0360(5) Uani 1 1
d . . .
O11 O 0.65986(19) 0.88823(19) 0.17156(15) 0.0360(5) Uani 1 1
d . . .
O10 O 0.70195(18) 0.7971(2) 0.00664(15) 0.0378(5) Uani 1 1 d
. . .
O9 O 1.00268(19) 0.8396(2) 0.35091(16) 0.0432(5) Uani 1 1 d
. . .
O8 O 1.06281(19) 0.7803(2) 0.18288(16) 0.0399(5) Uani 1 1 d
. . .
N3 N 0.8404(2) 0.7594(2) 0.19485(16) 0.0277(5) Uani 1 1 d .
. .
O7 O 0.9052(2) 0.6110(2) 0.26928(17) 0.0430(5) Uani 1 1 d .
. .
C22 C 0.8905(3) 0.7920(3) 0.0917(2) 0.0313(6) Uani 1 1 d . .
.
H22A H 0.8637 0.7070 0.0440 0.038 Uiso 1 1 calc R . .
N4 N 0.4918(2) 0.7953(2) 0.02290(18) 0.0341(5) Uani 1 1 d .
. .
C16 C 0.7248(3) 0.6241(3) 0.1924(2) 0.0344(6) Uani 1 1 d . .
.
H16A H 0.6856 0.6260 0.2596 0.041 Uiso 1 1 calc R . .
C19 C 0.8373(3) 0.8700(3) 0.2664(2) 0.0326(6) Uani 1 1 d . .
.
H19A H 0.9022 0.9540 0.2447 0.039 Uiso 1 1 calc R . .
C17 C 0.6139(3) 0.5770(3) 0.1051(2) 0.0374(6) Uani 1 1 d . .
.
H17A H 0.6508 0.5805 0.0373 0.045 Uiso 1 1 calc R . .
H17B H 0.5492 0.4841 0.1068 0.045 Uiso 1 1 calc R . .
C21 C 1.0407(3) 0.8598(3) 0.1185(2) 0.0365(6) Uani 1 1 d . .
.
H21A H 1.0853 0.8633 0.0544 0.044 Uiso 1 1 calc R . .
H21B H 1.0742 0.9506 0.1565 0.044 Uiso 1 1 calc R . .
C20 C 0.7059(3) 0.8709(3) 0.2669(2) 0.0335(6) Uani 1 1 d . .
.
H20A H 0.6387 0.7866 0.2848 0.040 Uiso 1 1 calc R . .
H20B H 0.7153 0.9425 0.3223 0.040 Uiso 1 1 calc R . .
C23 C 0.8404(3) 0.8693(3) 0.0372(2) 0.0343(6) Uani 1 1 d . .
.
H23A H 0.8609 0.9518 0.0846 0.041 Uiso 1 1 calc R . .
H23B H 0.8870 0.8934 -0.0254 0.041 Uiso 1 1 calc R . .
C18 C 0.8956(3) 0.8640(3) 0.3715(2) 0.0406(7) Uani 1 1 d . .
.
H18A H 0.9270 0.9483 0.4198 0.049 Uiso 1 1 calc R . .
```

```
H18B H 0.8283 0.7924 0.4036 0.049 Uiso 1 1 calc R . .
B4 B 0.6121(3) 0.7830(3) 0.0838(2) 0.0316(6) Uani 1 1 d . .
.
C24 C 0.5052(3) 0.8463(3) -0.0640(2) 0.0445(7) Uani 1 1 d .
. .
H24A H 0.5859 0.8738 -0.0945 0.053 Uiso 1 1 calc R . .
C15 C 0.7909(3) 0.5375(3) 0.1964(3) 0.0438(7) Uani 1 1 d . .
.
H15A H 0.7304 0.4538 0.2191 0.053 Uiso 1 1 calc R . .
H15B H 0.8154 0.5172 0.1267 0.053 Uiso 1 1 calc R . .
B3 B 0.9661(3) 0.7465(3) 0.2561(3) 0.0356(7) Uani 1 1 d . .
.
C28 C 0.3782(3) 0.7571(3) 0.0655(3) 0.0491(8) Uani 1 1 d . .
.
H28A H 0.3694 0.7220 0.1284 0.059 Uiso 1 1 calc R . .
C26 C 0.2869(3) 0.8194(3) -0.0681(3) 0.0546(9) Uani 1 1 d .
. .
H26A H 0.2160 0.8274 -0.1000 0.065 Uiso 1 1 calc R . .
C27 C 0.2741(3) 0.7671(4) 0.0211(3) 0.0581(10) Uani 1 1 d .
. .
H27A H 0.1938 0.7379 0.0523 0.070 Uiso 1 1 calc R . .
C25 C 0.4038(4) 0.8602(4) -0.1111(3) 0.0553(9) Uani 1 1 d .
. .
H25A H 0.4152 0.8979 -0.1729 0.066 Uiso 1 1 calc R . .
O6 O 0.3389(2) 0.6937(2) 0.35640(19) 0.0544(6) Uani 1 1 d .
. .
N1 N 0.1580(2) 0.3929(2) 0.31308(17) 0.0306(5) Uani 1 1 d .
. .
O5 O 0.2453(2) 0.6069(2) 0.50763(18) 0.0601(7) Uani 1 1 d .
. .
N2 N 0.4702(2) 0.7917(2) 0.52717(18) 0.0362(5) Uani 1 1 d .
. .
O3 O 0.1175(2) 0.1759(2) 0.22368(18) 0.0512(6) Uani 1 1 d .
. .
O4 O 0.4259(2) 0.5761(2) 0.4439(2) 0.0571(7) Uani 1 1 d . .
.
O2 O 0.0227(2) 0.2907(2) 0.14279(18) 0.0572(6) Uani 1 1 d .
. .
O1 O -0.0609(2) 0.1977(2) 0.2980(2) 0.0559(6) Uani 1 1 d . .
.
B2 B 0.3609(3) 0.6539(3) 0.4527(2) 0.0329(7) Uani 1 1 d . .
.
C14 C 0.4302(3) 0.8693(3) 0.5838(2) 0.0440(7) Uani 1 1 d . .
.
H14A H 0.3384 0.8427 0.5818 0.053 Uiso 1 1 calc R . .
C10 C 0.5988(3) 0.8291(3) 0.5304(2) 0.0444(7) Uani 1 1 d . .
.
H10A H 0.6266 0.7746 0.4895 0.053 Uiso 1 1 calc R . .
C9 C 0.2189(3) 0.6293(3) 0.2958(2) 0.0437(7) Uani 1 1 d . .
.
H9A H 0.2218 0.6816 0.2409 0.052 Uiso 1 1 calc R . .
H9B H 0.1503 0.6281 0.3401 0.052 Uiso 1 1 calc R . .
```

```
C7 C 0.0531(3) 0.4228(3) 0.1668(3) 0.0484(8) Uani 1 1 d . .
.
H7A H -0.0214 0.4298 0.1971 0.058 Uiso 1 1 calc R . .
H7B H 0.0692 0.4631 0.1028 0.058 Uiso 1 1 calc R . .
C4 C 0.2536(3) 0.2631(3) 0.2417(3) 0.0493(8) Uani 1 1 d . .
.
H4A H 0.2861 0.3002 0.1780 0.059 Uiso 1 1 calc R . .
H4B H 0.3022 0.2166 0.2610 0.059 Uiso 1 1 calc R . .
C8 C 0.1756(3) 0.4924(3) 0.2443(3) 0.0482(8) Uani 1 1 d . .
.
H8A H 0.2494 0.4983 0.2030 0.058 Uiso 1 1 calc R . .
C2 C 0.0867(3) 0.3947(3) 0.4056(3) 0.0491(8) Uani 1 1 d . .
.
H2A H 0.0338 0.4383 0.3869 0.059 Uiso 1 1 calc R . .
C6 C 0.4083(3) 0.4863(3) 0.3568(3) 0.0458(8) Uani 1 1 d . .
.
H6A H 0.4727 0.4537 0.3670 0.055 Uiso 1 1 calc R . .
H6B H 0.4311 0.5334 0.2965 0.055 Uiso 1 1 calc R . .
C13 C 0.5205(3) 0.9867(3) 0.6447(3) 0.0492(8) Uani 1 1 d . .
.
H13A H 0.4914 1.0416 0.6832 0.059 Uiso 1 1 calc R . .
C5 C 0.2751(3) 0.3706(3) 0.3288(3) 0.0438(7) Uani 1 1 d . .
.
H5A H 0.2593 0.3271 0.3919 0.053 Uiso 1 1 calc R . .
C12 C 0.6529(3) 1.0233(3) 0.6491(3) 0.0507(8) Uani 1 1 d . .
.
H12A H 0.7162 1.1027 0.6921 0.061 Uiso 1 1 calc R . .
C3 C 0.1661(3) 0.4757(3) 0.5067(2) 0.0462(8) Uani 1 1 d . .
.
H3A H 0.1041 0.4658 0.5598 0.055 Uiso 1 1 calc R . .
H3B H 0.2226 0.4383 0.5289 0.055 Uiso 1 1 calc R . .
C11 C 0.6927(3) 0.9442(3) 0.5909(3) 0.0524(8) Uani 1 1 d . .
.
H11A H 0.7840 0.9685 0.5924 0.063 Uiso 1 1 calc R . .
C1 C -0.0146(4) 0.2548(4) 0.4029(3) 0.0603(10) Uani 1 1 d .
. .
H1A H 0.0252 0.2074 0.4355 0.072 Uiso 1 1 calc R . .
H1B H -0.0886 0.2503 0.4418 0.072 Uiso 1 1 calc R . .
B1 B 0.0463(3) 0.2494(3) 0.2367(3) 0.0423(8) Uani 1 1 d . .
.

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 _atom_site_aniso_U_33
 _atom_site_aniso_U_23
 _atom_site_aniso_U_13
 _atom_site_aniso_U_12
O12 0.0281(10) 0.0321(10) 0.0457(11) 0.0024(8) -0.0031(8)
0.0142(8)
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O11	0.0371(11)	0.0366(11)	0.0370(11)	0.0004(8)	-0.0024(8)	0.0218(9)
O10	0.0311(10)	0.0517(12)	0.0333(10)	0.0061(9)	0.0015(8)	0.0225(9)
O9	0.0352(11)	0.0547(13)	0.0401(11)	0.0031(10)	-0.0074(9)	0.0238(10)
O8	0.0306(10)	0.0516(12)	0.0460(12)	0.0166(10)	0.0042(9)	0.0243(9)
N3	0.0260(11)	0.0257(11)	0.0310(11)	0.0050(9)	0.0019(9)	0.0120(9)
O7	0.0385(11)	0.0423(12)	0.0524(13)	0.0157(10)	-0.0017(9)	0.0213(10)
C22	0.0298(13)	0.0377(15)	0.0296(13)	0.0062(11)	0.0042(10)	0.0186(12)
N4	0.0278(12)	0.0360(13)	0.0389(13)	0.0028(10)	-0.0005(9)	0.0168(10)
C16	0.0304(14)	0.0280(13)	0.0418(15)	0.0057(11)	-0.0009(11)	0.0118(11)
C19	0.0322(14)	0.0316(14)	0.0308(14)	-0.0022(11)	-0.0018(11)	0.0148(11)
C17	0.0317(14)	0.0269(14)	0.0478(17)	0.0010(12)	-0.0056(12)	0.0114(11)
C21	0.0291(14)	0.0453(16)	0.0412(16)	0.0136(13)	0.0065(12)	0.0210(13)
C20	0.0324(14)	0.0371(15)	0.0309(14)	-0.0009(11)	0.0003(11)	0.0184(12)
C23	0.0298(14)	0.0438(16)	0.0351(14)	0.0121(12)	0.0065(11)	0.0208(12)
C18	0.0348(15)	0.0490(18)	0.0351(15)	0.0006(13)	-0.0038(12)	0.0198(14)
B4	0.0253(14)	0.0373(16)	0.0342(16)	0.0036(13)	-0.0010(12)	0.0175(13)
C24	0.0401(16)	0.060(2)	0.0423(17)	0.0108(15)	0.0030(13)	0.0308(15)
C15	0.0387(16)	0.0339(16)	0.059(2)	0.0116(14)	-0.0030(14)	0.0172(13)
B3	0.0286(15)	0.0419(18)	0.0387(17)	0.0093(14)	-0.0040(13)	0.0188(14)
C28	0.0389(17)	0.055(2)	0.067(2)	0.0229(17)	0.0146(15)	0.0294(15)
C26	0.0400(18)	0.053(2)	0.073(2)	-0.0034(18)	-0.0120(16)	0.0297(16)
C27	0.0339(17)	0.054(2)	0.095(3)	0.023(2)	0.0113(17)	0.0255(16)
C25	0.059(2)	0.075(2)	0.0452(19)	0.0146(17)	-0.0004(16)	0.042(2)
O6	0.0560(14)	0.0335(11)	0.0624(15)	0.0051(10)	-0.0239(11)	0.0151(10)
N1	0.0302(11)	0.0273(11)	0.0342(12)	0.0011(9)	-0.0037(9)	0.0152(9)
O5	0.0619(15)	0.0450(13)	0.0492(14)	-0.0048(11)	0.0144(12)	0.0083(12)

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N2 0.0376(13) 0.0306(12) 0.0341(12) 0.0016(10) -0.0032(10)
0.0127(10)
O3 0.0479(13) 0.0364(12) 0.0605(14) -0.0111(10) -0.0048(11)
0.0186(10)
O4 0.0470(13) 0.0461(13) 0.0744(16) -0.0168(11) -0.0211(11)
0.0279(11)
O2 0.0607(15) 0.0415(13) 0.0551(14) -0.0040(10) -0.0248(12)
0.0179(11)
O1 0.0412(13) 0.0377(12) 0.0671(16) -0.0066(11) 0.0012(11)
0.0053(10)
B2 0.0354(16) 0.0266(15) 0.0347(16) 0.0019(12) 0.0000(13)
0.0144(13)
C14 0.0425(17) 0.0361(16) 0.0489(18) -0.0029(13) -0.0058(14)
0.0183(14)
C10 0.0388(17) 0.0408(17) 0.0463(18) 0.0014(13) 0.0019(13)
0.0147(14)
C9 0.0559(19) 0.0331(15) 0.0406(16) 0.0060(12) -0.0092(14)
0.0211(14)
C7 0.059(2) 0.0453(18) 0.0440(18) -0.0070(14) -0.0186(15)
0.0327(16)
C4 0.054(2) 0.0422(18) 0.054(2) -0.0085(15) -0.0102(15)
0.0311(16)
C8 0.0539(19) 0.0373(17) 0.0468(18) 0.0090(14) -0.0170(15)
0.0176(15)
C2 0.0428(17) 0.0405(17) 0.0490(19) -0.0028(14) 0.0126(14)
0.0096(14)
C6 0.0375(16) 0.0447(17) 0.0567(19) -0.0092(14) -0.0079(14)
0.0263(14)
C13 0.058(2) 0.0352(16) 0.0512(19) -0.0055(14) -0.0060(15)
0.0234(15)
C5 0.0384(16) 0.0385(16) 0.0568(19) -0.0052(14) -0.0042(14)
0.0242(14)
C12 0.056(2) 0.0301(16) 0.0499(19) -0.0001(14) -0.0128(15)
0.0103(14)
C3 0.0449(17) 0.0408(17) 0.0379(16) 0.0038(13) 0.0071(13)
0.0089(14)
C11 0.0378(17) 0.0437(19) 0.059(2) 0.0031(15) -0.0032(15)
0.0076(14)
C1 0.048(2) 0.049(2) 0.059(2) 0.0085(17) 0.0076(17)
0.0023(16)
B1 0.0397(18) 0.0318(17) 0.0454(19) -0.0071(14) -0.0117(15)
0.0136(14)

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 All esds (except the esd in the dihedral angle between two
l.s. planes)
 are estimated using the full covariance matrix.  The cell
esds are taken
 into account individually in the estimation of esds in
distances, angles
```

```
 and torsion angles; correlations between esds in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell esds is used for estimating esds
involving l.s. planes.
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O12 B4 1.449(4) . ?
O11 C20 1.406(3) . ?
O11 B4 1.436(4) . ?
O10 C23 1.418(3) . ?
O10 B4 1.436(4) . ?
O9 C18 1.415(4) . ?
O9 B3 1.435(4) . ?
O8 C21 1.427(3) . ?
O8 B3 1.436(4) . ?
N3 C22 1.503(3) . ?
N3 C19 1.503(3) . ?
N3 C16 1.508(3) . ?
N3 B3 1.703(4) . ?
O7 C15 1.414(4) . ?
O7 B3 1.436(4) . ?
C22 C23 1.508(4) . ?
C22 C21 1.528(4) . ?
C22 H22A 1.0000 . ?
N4 C24 1.327(4) . ?
N4 C28 1.336(4) . ?
N4 B4 1.642(4) . ?
C16 C17 1.513(4) . ?
C16 C15 1.527(4) . ?
C16 H16A 1.0000 . ?
C19 C20 1.516(4) . ?
C19 C18 1.525(4) . ?
C19 H19A 1.0000 . ?
C17 H17A 0.9900 . ?
C17 H17B 0.9900 . ?
C21 H21A 0.9900 . ?
C21 H21B 0.9900 . ?
C20 H20A 0.9900 . ?
C20 H20B 0.9900 . ?
C23 H23A 0.9900 . ?
C23 H23B 0.9900 . ?
C18 H18A 0.9900 . ?
C18 H18B 0.9900 . ?
```

```
C24 C25 1.382(4) . ?
C24 H24A 0.9500 . ?
C15 H15A 0.9900 . ?
C15 H15B 0.9900 . ?
C28 C27 1.371(5) . ?
C28 H28A 0.9500 . ?
C26 C27 1.362(5) . ?
C26 C25 1.369(5) . ?
C26 H26A 0.9500 . ?
C27 H27A 0.9500 . ?
C25 H25A 0.9500 . ?
O6 C9 1.372(4) . ?
O6 B2 1.445(4) . ?
N1 C2 1.484(4) . ?
N1 C5 1.499(4) . ?
N1 C8 1.501(4) . ?
N1 B1 1.700(4) . ?
O5 C3 1.364(4) . ?
O5 B2 1.438(4) . ?
N2 C10 1.328(4) . ?
N2 C14 1.346(4) . ?
N2 B2 1.645(4) . ?
O3 C4 1.399(4) . ?
O3 B1 1.437(4) . ?
O4 C6 1.375(4) . ?
O4 B2 1.418(4) . ?
O2 C7 1.398(4) . ?
O2 B1 1.431(4) . ?
O1 C1 1.400(4) . ?
O1 B1 1.423(5) . ?
C14 C13 1.379(4) . ?
C14 H14A 0.9500 . ?
C10 C11 1.374(5) . ?
C10 H10A 0.9500 . ?
C9 C8 1.482(4) . ?
C9 H9A 0.9900 . ?
C9 H9B 0.9900 . ?
C7 C8 1.505(4) . ?
C7 H7A 0.9900 . ?
C7 H7B 0.9900 . ?
C4 C5 1.492(4) . ?
C4 H4A 0.9900 . ?
C4 H4B 0.9900 . ?
C8 H8A 1.0000 . ?
C2 C1 1.490(5) . ?
C2 C3 1.493(4) . ?
C2 H2A 1.0000 . ?
C6 C5 1.480(4) . ?
C6 H6A 0.9900 . ?
C6 H6B 0.9900 . ?
C13 C12 1.372(5) . ?
C13 H13A 0.9500 . ?
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C5 H5A 1.0000 . ?
C12 C11 1.368(5) . ?
C12 H12A 0.9500 . ?
C3 H3A 0.9900 . ?
C3 H3B 0.9900 . ?
C11 H11A 0.9500 . ?
C1 H1A 0.9900 . ?
C1 H1B 0.9900 . ?

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 _geom_angle_atom_site_label_3
 _geom_angle
 _geom_angle_site_symmetry_1
 _geom_angle_site_symmetry_3
 _geom_angle_publ_flag
C17 O12 B4 119.0(2) . . ?
C20 O11 B4 119.2(2) . . ?
C23 O10 B4 119.5(2) . . ?
C18 O9 B3 109.0(2) . . ?
C21 O8 B3 107.8(2) . . ?
C22 N3 C19 115.2(2) . . ?
C22 N3 C16 116.2(2) . . ?
C19 N3 C16 116.0(2) . . ?
C22 N3 B3 101.68(19) . . ?
C19 N3 B3 102.4(2) . . ?
C16 N3 B3 101.88(19) . . ?
C15 O7 B3 109.1(2) . . ?
N3 C22 C23 116.2(2) . . ?
N3 C22 C21 102.8(2) . . ?
C23 C22 C21 114.6(2) . . ?
N3 C22 H22A 107.6 . . ?
C23 C22 H22A 107.6 . . ?
C21 C22 H22A 107.6 . . ?
C24 N4 C28 119.1(3) . . ?
C24 N4 B4 122.6(2) . . ?
C28 N4 B4 118.2(2) . . ?
N3 C16 C17 116.5(2) . . ?
N3 C16 C15 103.2(2) . . ?
C17 C16 C15 115.5(2) . . ?
N3 C16 H16A 107.0 . . ?
C17 C16 H16A 107.1 . . ?
C15 C16 H16A 107.0 . . ?
N3 C19 C20 117.0(2) . . ?
N3 C19 C18 102.8(2) . . ?
C20 C19 C18 115.2(2) . . ?
N3 C19 H19A 107.1 . . ?
C20 C19 H19A 107.1 . . ?
C18 C19 H19A 107.1 . . ?
O12 C17 C16 112.6(2) . . ?
O12 C17 H17A 109.1 . . ?
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```
C16 C17 H17A 109.1 . . ?
O12 C17 H17B 109.1 . . ?
C16 C17 H17B 109.1 . . ?
H17A C17 H17B 107.8 . . ?
O8 C21 C22 104.7(2) . . ?
O8 C21 H21A 110.8 . . ?
C22 C21 H21A 110.8 . . ?
O8 C21 H21B 110.8 . . ?
C22 C21 H21B 110.8 . . ?
H21A C21 H21B 108.9 . . ?
O11 C20 C19 114.2(2) . . ?
O11 C20 H20A 108.7 . . ?
C19 C20 H20A 108.7 . . ?
O11 C20 H20B 108.7 . . ?
C19 C20 H20B 108.7 . . ?
H20A C20 H20B 107.6 . . ?
O10 C23 C22 112.1(2) . . ?
O10 C23 H23A 109.2 . . ?
C22 C23 H23A 109.2 . . ?
O10 C23 H23B 109.2 . . ?
C22 C23 H23B 109.2 . . ?
H23A C23 H23B 107.9 . . ?
O9 C18 C19 106.2(2) . . ?
O9 C18 H18A 110.5 . . ?
C19 C18 H18A 110.5 . . ?
O9 C18 H18B 110.5 . . ?
C19 C18 H18B 110.5 . . ?
H18A C18 H18B 108.7 . . ?
O10 B4 O11 115.8(2) . . ?
O10 B4 O12 114.0(2) . . ?
O11 B4 O12 113.6(2) . . ?
O10 B4 N4 103.7(2) . . ?
O11 B4 N4 103.4(2) . . ?
O12 B4 N4 104.4(2) . . ?
N4 C24 C25 121.2(3) . . ?
N4 C24 H24A 119.4 . . ?
C25 C24 H24A 119.4 . . ?
O7 C15 C16 105.9(2) . . ?
O7 C15 H15A 110.6 . . ?
C16 C15 H15A 110.6 . . ?
O7 C15 H15B 110.6 . . ?
C16 C15 H15B 110.6 . . ?
H15A C15 H15B 108.7 . . ?
O9 B3 O7 115.0(3) . . ?
O9 B3 O8 115.4(3) . . ?
O7 B3 O8 114.4(3) . . ?
O9 B3 N3 103.0(2) . . ?
O7 B3 N3 103.3(2) . . ?
O8 B3 N3 103.3(2) . . ?
N4 C28 C27 122.0(3) . . ?
N4 C28 H28A 119.0 . . ?
C27 C28 H28A 119.0 . . ?
```

```
C27 C26 C25 118.8(3) . . ?
C27 C26 H26A 120.6 . . ?
C25 C26 H26A 120.6 . . ?
C26 C27 C28 119.3(3) . . ?
C26 C27 H27A 120.3 . . ?
C28 C27 H27A 120.3 . . ?
C26 C25 C24 119.6(3) . . ?
C26 C25 H25A 120.2 . . ?
C24 C25 H25A 120.2 . . ?
C9 O6 B2 122.0(2) . . ?
C2 N1 C5 116.5(2) . . ?
C2 N1 C8 116.4(3) . . ?
C5 N1 C8 114.6(2) . . ?
C2 N1 B1 101.7(2) . . ?
C5 N1 B1 102.0(2) . . ?
C8 N1 B1 102.1(2) . . ?
C3 O5 B2 121.3(3) . . ?
C10 N2 C14 119.3(3) . . ?
C10 N2 B2 120.5(2) . . ?
C14 N2 B2 120.2(2) . . ?
C4 O3 B1 109.2(2) . . ?
C6 O4 B2 124.0(2) . . ?
C7 O2 B1 108.4(2) . . ?
C1 O1 B1 109.0(2) . . ?
O4 B2 O5 116.2(3) . . ?
O4 B2 O6 114.4(3) . . ?
O5 B2 O6 111.9(3) . . ?
O4 B2 N2 103.4(2) . . ?
O5 B2 N2 104.8(2) . . ?
O6 B2 N2 104.4(2) . . ?
N2 C14 C13 121.0(3) . . ?
N2 C14 H14A 119.5 . . ?
C13 C14 H14A 119.5 . . ?
N2 C10 C11 122.0(3) . . ?
N2 C10 H10A 119.0 . . ?
C11 C10 H10A 119.0 . . ?
O6 C9 C8 117.1(3) . . ?
O6 C9 H9A 108.0 . . ?
C8 C9 H9A 108.0 . . ?
O6 C9 H9B 108.0 . . ?
C8 C9 H9B 108.0 . . ?
H9A C9 H9B 107.3 . . ?
O2 C7 C8 107.7(3) . . ?
O2 C7 H7A 110.2 . . ?
C8 C7 H7A 110.2 . . ?
O2 C7 H7B 110.2 . . ?
C8 C7 H7B 110.2 . . ?
H7A C7 H7B 108.5 . . ?
O3 C4 C5 107.6(3) . . ?
O3 C4 H4A 110.2 . . ?
C5 C4 H4A 110.2 . . ?
O3 C4 H4B 110.2 . . ?
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```
C5 C4 H4B 110.2 . . ?
H4A C4 H4B 108.5 . . ?
C9 C8 N1 117.6(3) . . ?
C9 C8 C7 119.3(3) . . ?
N1 C8 C7 103.7(2) . . ?
C9 C8 H8A 104.9 . . ?
N1 C8 H8A 104.9 . . ?
C7 C8 H8A 104.9 . . ?
N1 C2 C1 105.0(3) . . ?
N1 C2 C3 118.3(3) . . ?
C1 C2 C3 119.4(3) . . ?
N1 C2 H2A 104.0 . . ?
C1 C2 H2A 104.0 . . ?
C3 C2 H2A 104.0 . . ?
O4 C6 C5 117.4(3) . . ?
O4 C6 H6A 107.9 . . ?
C5 C6 H6A 107.9 . . ?
O4 C6 H6B 108.0 . . ?
C5 C6 H6B 108.0 . . ?
H6A C6 H6B 107.2 . . ?
C12 C13 C14 119.3(3) . . ?
C12 C13 H13A 120.4 . . ?
C14 C13 H13A 120.4 . . ?
C6 C5 C4 119.8(3) . . ?
C6 C5 N1 118.8(2) . . ?
C4 C5 N1 104.9(2) . . ?
C6 C5 H5A 103.7 . . ?
C4 C5 H5A 103.7 . . ?
N1 C5 H5A 103.7 . . ?
C11 C12 C13 119.3(3) . . ?
C11 C12 H12A 120.4 . . ?
C13 C12 H12A 120.4 . . ?
O5 C3 C2 117.0(3) . . ?
O5 C3 H3A 108.1 . . ?
C2 C3 H3A 108.1 . . ?
O5 C3 H3B 108.1 . . ?
C2 C3 H3B 108.1 . . ?
H3A C3 H3B 107.3 . . ?
C12 C11 C10 119.1(3) . . ?
C12 C11 H11A 120.4 . . ?
C10 C11 H11A 120.4 . . ?
O1 C1 C2 107.6(3) . . ?
O1 C1 H1A 110.2 . . ?
C2 C1 H1A 110.2 . . ?
O1 C1 H1B 110.2 . . ?
C2 C1 H1B 110.2 . . ?
H1A C1 H1B 108.5 . . ?
O1 B1 O2 117.0(3) . . ?
O1 B1 O3 114.5(3) . . ?
O2 B1 O3 113.3(3) . . ?
O1 B1 N1 103.4(2) . . ?
O2 B1 N1 103.3(2) . . ?
```

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O3 B1 N1 103.0(2) . . ?

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_diffrn_reflns_theta_full              28.30
_diffrn_measured_fraction_theta_full   0.990
_refine_diff_density_max    1.301
_refine_diff_density_min   -0.561
_refine_diff_density_rms    0.065
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APPENDIX 4

CRYSTAL STRUCTURE DATA FOR COMPOUND 74

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data_final(2Ph,2Si)

_audit_creation_method            SHELXL-97
_chemical_name_systematic
;
 ?
;
_chemical_name_common             ?
_chemical_melting_point           ?
_chemical_formula_moiety          ?
_chemical_formula_sum
 'C21 H25 N O6 Si2'
_chemical_formula_weight          443.60

loop_
 _atom_type_symbol
 _atom_type_description
 _atom_type_scat_dispersion_real
 _atom_type_scat_dispersion_imag
 _atom_type_scat_source
 'C'  'C'   0.0033   0.0016
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'H'  'H'   0.0000   0.0000
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'N'  'N'   0.0061   0.0033
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'O'  'O'   0.0106   0.0060
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'Si'  'Si'   0.0817   0.0704
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

_symmetry_cell_setting            ?
_symmetry_space_group_name_H-M    ?

loop_
 _symmetry_equiv_pos_as_xyz
 'x, y, z'
 '-x, y+1/2, -z+1/2'
 '-x, -y, -z'
 'x, -y-1/2, z-1/2'

_cell_length_a                    10.483(2)
_cell_length_b                    11.489(2)
_cell_length_c                    17.440(4)
_cell_angle_alpha                 90.00
_cell_angle_beta                  101.86(3)
_cell_angle_gamma                 90.00
_cell_volume                      2055.7(7)
_cell_formula_units_Z             4
_cell_measurement_temperature     193(2)
_cell_measurement_reflns_used     ?
_cell_measurement_theta_min       ?
```

```
_cell_measurement_theta_max       ?

_exptl_crystal_description        ?
_exptl_crystal_colour             ?
_exptl_crystal_size_max           0.325
_exptl_crystal_size_mid           0.290
_exptl_crystal_size_min           0.280
_exptl_crystal_density_meas       ?
_exptl_crystal_density_diffrn     1.433
_exptl_crystal_density_method     'not measured'
_exptl_crystal_F_000              936
_exptl_absorpt_coefficient_mu     0.212
_exptl_absorpt_correction_type    ?
_exptl_absorpt_correction_T_min   ?
_exptl_absorpt_correction_T_max   ?
_exptl_absorpt_process_details    ?

_exptl_special_details
;
 ?
;

_diffrn_ambient_temperature       193(2)
_diffrn_radiation_wavelength      0.71073
_diffrn_radiation_type            MoK\a
_diffrn_radiation_source          'fine-focus sealed tube'
_diffrn_radiation_monochromator   graphite
_diffrn_measurement_device_type   ?
_diffrn_measurement_method        ?
_diffrn_detector_area_resol_mean  ?
_diffrn_standards_number          ?
_diffrn_standards_interval_count  ?
_diffrn_standards_interval_time   ?
_diffrn_standards_decay_%         ?
_diffrn_reflns_number             16579
_diffrn_reflns_av_R_equivalents   0.0689
_diffrn_reflns_av_sigmaI/netI     0.0632
_diffrn_reflns_limit_h_min        -13
_diffrn_reflns_limit_h_max        13
_diffrn_reflns_limit_k_min        -15
_diffrn_reflns_limit_k_max        15
_diffrn_reflns_limit_l_min        -23
_diffrn_reflns_limit_l_max        22
_diffrn_reflns_theta_min          2.39
_diffrn_reflns_theta_max          28.36
_reflns_number_total              4672
_reflns_number_gt                 3223
_reflns_threshold_expression      >2sigma(I)

_computing_data_collection        ?
_computing_cell_refinement        ?
_computing_data_reduction         ?
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```
_computing_structure_solution     'SHELXS-97 (Sheldrick,
1990)'
_computing_structure_refinement   'SHELXL-97 (Sheldrick,
1997)'
_computing_molecular_graphics     ?
_computing_publication_material   ?

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted
R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors
R are based
 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-
factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.
R-factors based
 on F^2^ are statistically about twice as large as those
based on F, and R-
 factors based on ALL data will be even larger.
;

_refine_ls_structure_factor_coef  Fsqd
_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.1000P)^2^+0.0000P] where
P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      direct
_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     mixed
_refine_ls_extinction_method      none
_refine_ls_extinction_coef        ?
_refine_ls_number_reflns          4672
_refine_ls_number_parameters      271
_refine_ls_number_restraints      0
_refine_ls_R_factor_all           0.1253
_refine_ls_R_factor_gt            0.0977
_refine_ls_wR_factor_ref          0.2892
_refine_ls_wR_factor_gt           0.2747
_refine_ls_goodness_of_fit_ref    1.819
_refine_ls_restrained_S_all       1.819
_refine_ls_shift/su_max           0.185
_refine_ls_shift/su_mean          0.026

loop_

 _atom_site_label
 _atom_site_type_symbol
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 _atom_site_fract_y
 _atom_site_fract_z
 _atom_site_U_iso_or_equiv
 _atom_site_adp_type
 _atom_site_occupancy
 _atom_site_symmetry_multiplicity
 _atom_site_calc_flag
 _atom_site_refinement_flags
 _atom_site_disorder_assembly
 _atom_site_disorder_group
Si1 Si 0.48882(9) 0.55136(10) 0.22916(5) 0.0266(3) Uani 1 1
d . . .
Si2 Si 0.83179(9) 0.61170(10) 0.53180(5) 0.0274(3) Uani 1 1
d . . .
O6 O 0.8433(3) 0.4768(3) 0.50714(18) 0.0461(8) Uani 1 1 d .
. .
O1 O 0.3960(3) 0.6020(3) 0.28613(16) 0.0447(9) Uani 1 1 d .
. .
O3 O 0.5467(3) 0.4240(3) 0.25279(17) 0.0478(9) Uani 1 1 d .
. .
N1 N 0.6531(3) 0.5809(3) 0.37369(18) 0.0276(7) Uani 1 1 d .
. .
O5 O 0.6835(3) 0.6390(3) 0.54200(16) 0.0458(9) Uani 1 1 d .
. .
O2 O 0.5979(3) 0.6443(3) 0.21421(17) 0.0473(9) Uani 1 1 d .
. .
C10 C 0.3772(4) 0.5344(4) 0.1321(2) 0.0294(8) Uani 1 1 d . .
.
C16 C 0.9398(3) 0.6346(4) 0.6289(2) 0.0297(9) Uani 1 1 d . .
.
O4 O 0.8786(3) 0.7007(3) 0.47127(16) 0.0449(8) Uani 1 1 d .
. .
C6 C 0.8721(3) 0.6778(4) 0.3897(2) 0.0339(10) Uani 1 1 d . .
.
H6A H 0.9166 0.6034 0.3838 0.041 Uiso 1 1 calc R . .
H6B H 0.9179 0.7404 0.3672 0.041 Uiso 1 1 calc R . .
C19 C 1.0988(4) 0.6674(4) 0.7770(2) 0.0391(10) Uani 1 1 d .
. .
H19A H 1.1526 0.6786 0.8274 0.047 Uiso 1 1 calc R . .
C7 C 0.5905(4) 0.3807(4) 0.3307(2) 0.0306(8) Uani 1 1 d . .
.
H7A H 0.6247 0.3007 0.3284 0.037 Uiso 1 1 calc R . .
H7B H 0.5160 0.3773 0.3575 0.037 Uiso 1 1 calc R . .
C8 C 0.6972(4) 0.4586(4) 0.3774(2) 0.0396(10) Uani 1 1 d . .
.
H8A H 0.7742 0.4541 0.3518 0.047 Uiso 1 1 calc R . .
C9 C 0.7391(4) 0.4116(4) 0.4602(2) 0.0308(9) Uani 1 1 d . .
.
H9A H 0.6633 0.4125 0.4859 0.037 Uiso 1 1 calc R . .
H9B H 0.7672 0.3297 0.4575 0.037 Uiso 1 1 calc R . .
```

```
C4 C 0.7277(4) 0.6544(4) 0.2573(2) 0.0350(10) Uani 1 1 d . .
.
H4A H 0.7704 0.7216 0.2374 0.042 Uiso 1 1 calc R . .
H4B H 0.7770 0.5833 0.2497 0.042 Uiso 1 1 calc R . .
C21 C 0.9342(4) 0.5594(4) 0.6908(2) 0.0345(10) Uani 1 1 d .
. .
H21A H 0.8747 0.4961 0.6826 0.041 Uiso 1 1 calc R . .
C15 C 0.2534(4) 0.4864(4) 0.1262(2) 0.0331(9) Uani 1 1 d . .
.
H15A H 0.2267 0.4615 0.1724 0.040 Uiso 1 1 calc R . .
C5 C 0.7306(4) 0.6712(4) 0.3449(2) 0.0362(10) Uani 1 1 d . .
.
H5A H 0.6888 0.7479 0.3512 0.043 Uiso 1 1 calc R . .
C3 C 0.5894(3) 0.6950(4) 0.4811(2) 0.0335(9) Uani 1 1 d . .
.
H3A H 0.6281 0.7666 0.4640 0.040 Uiso 1 1 calc R . .
H3B H 0.5122 0.7177 0.5021 0.040 Uiso 1 1 calc R . .
C20 C 1.0138(4) 0.5750(5) 0.7640(2) 0.0398(11) Uani 1 1 d .
. .
H20A H 1.0095 0.5219 0.8051 0.048 Uiso 1 1 calc R . .
C18 C 1.1059(4) 0.7445(4) 0.7165(2) 0.0393(10) Uani 1 1 d .
. .
H18A H 1.1646 0.8083 0.7252 0.047 Uiso 1 1 calc R . .
C2 C 0.5475(4) 0.6154(4) 0.4117(2) 0.0358(10) Uani 1 1 d . .
.
H2A H 0.5126 0.5428 0.4315 0.043 Uiso 1 1 calc R . .
C13 C 0.2068(5) 0.5121(5) -0.0134(3) 0.0474(12) Uani 1 1 d .
. .
H13A H 0.1499 0.5036 -0.0631 0.057 Uiso 1 1 calc R . .
C11 C 0.4118(4) 0.5744(5) 0.0634(2) 0.0410(11) Uani 1 1 d .
. .
H11A H 0.4941 0.6105 0.0659 0.049 Uiso 1 1 calc R . .
C1 C 0.4354(3) 0.6714(4) 0.3526(2) 0.0333(9) Uani 1 1 d . .
.
H1A H 0.3604 0.6841 0.3780 0.040 Uiso 1 1 calc R . .
H1B H 0.4638 0.7482 0.3366 0.040 Uiso 1 1 calc R . .
C17 C 1.0268(4) 0.7274(4) 0.6435(2) 0.0347(9) Uani 1 1 d . .
.
H17A H 1.0319 0.7803 0.6024 0.042 Uiso 1 1 calc R . .
C14 C 0.1682(4) 0.4740(4) 0.0543(2) 0.0407(11) Uani 1 1 d .
. .
H14A H 0.0847 0.4400 0.0513 0.049 Uiso 1 1 calc R . .
C12 C 0.3273(5) 0.5618(5) -0.0080(2) 0.0509(13) Uani 1 1 d .
. .
H12A H 0.3530 0.5880 -0.0542 0.061 Uiso 1 1 calc R . .

loop_
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 _atom_site_aniso_U_22
 _atom_site_aniso_U_33
 _atom_site_aniso_U_23
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 _atom_site_aniso_U_13
 _atom_site_aniso_U_12
Si1 0.0248(5) 0.0307(7) 0.0233(5) 0.0025(4) 0.0028(4)
0.0006(4)
Si2 0.0234(5) 0.0339(8) 0.0240(5) -0.0006(4) 0.0026(4) -
0.0018(4)
O6 0.0384(17) 0.050(2) 0.0441(17) 0.0014(15) -0.0054(13) -
0.0031(14)
O1 0.0301(14) 0.065(3) 0.0354(15) -0.0146(14) -0.0009(12)
0.0077(14)
O3 0.066(2) 0.037(2) 0.0325(15) -0.0032(13) -0.0101(14)
0.0041(16)
N1 0.0258(15) 0.0233(19) 0.0377(17) 0.0059(13) 0.0160(13)
0.0013(13)
O5 0.0367(15) 0.066(3) 0.0335(15) -0.0006(14) 0.0033(12)
0.0062(15)
O2 0.0335(15) 0.068(3) 0.0372(15) 0.0146(15) 0.0007(12) -
0.0106(15)
C10 0.0298(18) 0.030(2) 0.0275(17) 0.0039(15) 0.0030(14)
0.0027(15)
C16 0.0232(16) 0.036(2) 0.0298(17) -0.0046(16) 0.0050(13)
0.0014(15)
O4 0.0426(17) 0.055(2) 0.0350(15) -0.0009(14) 0.0043(12) -
0.0131(15)
C6 0.0244(17) 0.050(3) 0.0278(17) 0.0022(17) 0.0069(13) -
0.0067(16)
C19 0.0270(18) 0.055(3) 0.0327(19) -0.0077(19) 0.0005(15)
0.0002(18)
C7 0.0371(19) 0.024(2) 0.0263(17) 0.0012(14) -0.0032(14) -
0.0006(16)
C8 0.036(2) 0.042(3) 0.039(2) 0.0012(18) 0.0041(16) -
0.0029(18)
C9 0.0324(19) 0.027(2) 0.0305(18) 0.0017(15) 0.0003(14) -
0.0043(16)
C4 0.0258(17) 0.050(3) 0.0295(18) 0.0048(17) 0.0063(14) -
0.0090(17)
C21 0.0302(19) 0.044(3) 0.0289(18) -0.0011(17) 0.0040(15) -
0.0039(17)
C15 0.0294(18) 0.036(3) 0.0331(19) 0.0020(16) 0.0035(14)
0.0040(16)
C5 0.0318(19) 0.040(3) 0.037(2) 0.0043(18) 0.0090(15) -
0.0036(17)
C3 0.0245(17) 0.043(3) 0.0318(18) -0.0046(17) 0.0033(14)
0.0068(16)
C20 0.032(2) 0.061(3) 0.0260(18) 0.0002(18) 0.0047(15) -
0.0007(19)
C18 0.0288(19) 0.046(3) 0.041(2) -0.0134(19) 0.0036(16) -
0.0067(18)
C2 0.0309(19) 0.043(3) 0.0331(19) -0.0005(17) 0.0066(15)
0.0033(17)
C13 0.045(2) 0.057(3) 0.033(2) 0.000(2) -0.0104(18) 0.003(2)
```

```
C11 0.036(2) 0.053(3) 0.0318(19) 0.0104(19) 0.0017(16) -
0.005(2)
C1 0.0242(17) 0.047(3) 0.0284(17) -0.0010(17) 0.0038(13)
0.0065(16)
C17 0.0305(18) 0.037(3) 0.0357(19) -0.0026(17) 0.0047(15)
0.0021(17)
C14 0.032(2) 0.047(3) 0.038(2) 0.0021(19) -0.0035(16)
0.0040(18)
C12 0.058(3) 0.068(4) 0.0254(19) 0.014(2) 0.0046(18) -
0.001(3)

_geom_special_details
;
 All esds (except the esd in the dihedral angle between two
l.s. planes)
 are estimated using the full covariance matrix.  The cell
esds are taken
 into account individually in the estimation of esds in
distances, angles
 and torsion angles; correlations between esds in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell esds is used for estimating esds
involving l.s. planes.
;

loop_
 _geom_bond_atom_site_label_1
 _geom_bond_atom_site_label_2
 _geom_bond_distance
 _geom_bond_site_symmetry_2
 _geom_bond_publ_flag
Si1 O3 1.606(4) . ?
Si1 O2 1.624(3) . ?

Si1 O1 1.634(3) . ?
Si1 C10 1.859(4) . ?
Si2 O4 1.616(3) . ?
Si2 O6 1.619(4) . ?
Si2 O5 1.631(3) . ?
Si2 C16 1.851(4) . ?
O6 C9 1.435(5) . ?
O1 C1 1.397(5) . ?
O3 C7 1.431(4) . ?
N1 C2 1.458(5) . ?
N1 C8 1.477(6) . ?
N1 C5 1.467(5) . ?
O5 C3 1.444(5) . ?
O2 C4 1.417(4) . ?
C10 C11 1.400(5) . ?
C10 C15 1.394(5) . ?
```

```
C16 C17 1.392(6) . ?
C16 C21 1.393(6) . ?
O4 C6 1.435(4) . ?
C6 C5 1.530(5) . ?
C19 C20 1.374(7) . ?
C19 C18 1.392(6) . ?
C7 C8 1.529(6) . ?
C8 C9 1.519(5) . ?
C4 C5 1.535(5) . ?
C21 C20 1.385(5) . ?
C15 C14 1.389(5) . ?
C3 C2 1.507(6) . ?
C18 C17 1.383(5) . ?
C2 C1 1.536(5) . ?
C13 C12 1.372(7) . ?
C13 C14 1.396(6) . ?
C11 C12 1.379(6) . ?

loop_
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 _geom_angle_atom_site_label_2
 _geom_angle_atom_site_label_3
 _geom_angle
 _geom_angle_site_symmetry_1
 _geom_angle_site_symmetry_3
 _geom_angle_publ_flag
O3 Si1 O2 113.51(19) . . ?
O3 Si1 O1 114.17(18) . . ?
O2 Si1 O1 113.0(2) . . ?
O3 Si1 C10 105.80(17) . . ?
O2 Si1 C10 104.78(16) . . ?
O1 Si1 C10 104.39(16) . . ?
O4 Si2 O6 112.49(18) . . ?
O4 Si2 O5 111.96(18) . . ?
O6 Si2 O5 109.73(18) . . ?
O4 Si2 C16 107.25(17) . . ?
O6 Si2 C16 108.29(18) . . ?
O5 Si2 C16 106.88(16) . . ?
C9 O6 Si2 124.2(3) . . ?
C1 O1 Si1 126.6(2) . . ?
C7 O3 Si1 126.2(3) . . ?
C2 N1 C8 119.9(3) . . ?
C2 N1 C5 119.2(4) . . ?
C8 N1 C5 119.9(3) . . ?
C3 O5 Si2 121.8(3) . . ?
C4 O2 Si1 126.8(3) . . ?
C11 C10 C15 117.9(3) . . ?
C11 C10 Si1 121.3(3) . . ?
C15 C10 Si1 120.8(3) . . ?
C17 C16 C21 117.6(3) . . ?
C17 C16 Si2 122.1(3) . . ?
C21 C16 Si2 120.4(3) . . ?
```

```
C6 O4 Si2 125.0(3) . . ?
O4 C6 C5 111.0(3) . . ?
C20 C19 C18 120.0(4) . . ?
O3 C7 C8 111.0(3) . . ?
N1 C8 C9 113.9(4) . . ?
N1 C8 C7 110.3(3) . . ?
C9 C8 C7 109.6(4) . . ?
O6 C9 C8 113.3(3) . . ?
O2 C4 C5 111.0(3) . . ?
C20 C21 C16 121.4(4) . . ?
C14 C15 C10 121.6(4) . . ?
N1 C5 C6 114.0(3) . . ?
N1 C5 C4 110.6(3) . . ?
C6 C5 C4 109.4(3) . . ?
O5 C3 C2 111.3(4) . . ?
C19 C20 C21 120.0(4) . . ?
C17 C18 C19 119.5(4) . . ?
N1 C2 C3 114.0(3) . . ?
N1 C2 C1 110.9(3) . . ?
C3 C2 C1 110.0(4) . . ?
C12 C13 C14 119.7(4) . . ?
C12 C11 C10 120.4(4) . . ?
O1 C1 C2 111.9(4) . . ?
C18 C17 C16 121.6(4) . . ?
C15 C14 C13 119.2(4) . . ?
C13 C12 C11 121.2(4) . . ?

_diffrn_measured_fraction_theta_max    0.911
_diffrn_reflns_theta_full              28.36
_diffrn_measured_fraction_theta_full   0.911
_refine_diff_density_max    1.397
_refine_diff_density_min   -0.448
_refine_diff_density_rms    0.103
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APPENDIX 5

CRYSTAL STRUCTURE DATA FOR COMPOUND 76

```
data_p21n (2Me 2Si)

_audit_creation_method            SHELXL-97
_chemical_name_systematic
;
 ?
;
_chemical_name_common             ?
_chemical_melting_point           ?
_chemical_formula_moiety          ?
_chemical_formula_sum
 'C11 H21 N O6 Si2'
_chemical_formula_weight          319.47

loop_
 _atom_type_symbol
 _atom_type_description
 _atom_type_scat_dispersion_real
 _atom_type_scat_dispersion_imag
 _atom_type_scat_source
 'C'  'C'   0.0033   0.0016
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'H'  'H'   0.0000   0.0000
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'N'  'N'   0.0061   0.0033
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'O'  'O'   0.0106   0.0060
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'Si'  'Si'   0.0817   0.0704
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

_symmetry_cell_setting            ?
_symmetry_space_group_name_H-M    ?

loop_
 _symmetry_equiv_pos_as_xyz
 'x, y, z'
 '-x+1/2, y+1/2, -z+1/2'
 '-x, -y, -z'
 'x-1/2, -y-1/2, z-1/2'

_cell_length_a                    10.2030(6)
_cell_length_b                    11.1393(7)
_cell_length_c                    26.179(2)
_cell_angle_alpha                 90.0000(10)
_cell_angle_beta                  98.2610(10)
_cell_angle_gamma                 90.0000(10)
_cell_volume                      2944.5(3)
_cell_formula_units_Z             8
_cell_measurement_temperature     193(2)
_cell_measurement_reflns_used     ?
_cell_measurement_theta_min       ?
```

```
_cell_measurement_theta_max       ?

_exptl_crystal_description        ?
_exptl_crystal_colour             ?
_exptl_crystal_size_max           0.183
_exptl_crystal_size_mid           0.138
_exptl_crystal_size_min           0.113
_exptl_crystal_density_meas       ?
_exptl_crystal_density_diffrn     1.441
_exptl_crystal_density_method     'not measured'
_exptl_crystal_F_000              1360
_exptl_absorpt_coefficient_mu     0.265
_exptl_absorpt_correction_type    ?
_exptl_absorpt_correction_T_min   ?
_exptl_absorpt_correction_T_max   ?
_exptl_absorpt_process_details    ?

_exptl_special_details
;
 ?
;

_diffrn_ambient_temperature       193(2)
_diffrn_radiation_wavelength      0.71073
_diffrn_radiation_type            MoK\a
_diffrn_radiation_source          'fine-focus sealed tube'
_diffrn_radiation_monochromator   graphite
_diffrn_measurement_device_type   ?
_diffrn_measurement_method        ?
_diffrn_detector_area_resol_mean  ?
_diffrn_standards_number          ?
_diffrn_standards_interval_count  ?
_diffrn_standards_interval_time   ?
_diffrn_standards_decay_%         ?
_diffrn_reflns_number             29407
_diffrn_reflns_av_R_equivalents   0.0527
_diffrn_reflns_av_sigmaI/netI     0.0523
_diffrn_reflns_limit_h_min        -13
_diffrn_reflns_limit_h_max        13
_diffrn_reflns_limit_k_min        -14
_diffrn_reflns_limit_k_max        14
_diffrn_reflns_limit_l_min        -34
_diffrn_reflns_limit_l_max        34
_diffrn_reflns_theta_min          1.57
_diffrn_reflns_theta_max          28.30
_reflns_number_total              7280
_reflns_number_gt                 4542
_reflns_threshold_expression      >2sigma(I)

_computing_data_collection        ?
_computing_cell_refinement        ?
_computing_data_reduction         ?
```

```
_computing_structure_solution     'SHELXS-97 (Sheldrick,
1990)'
_computing_structure_refinement   'SHELXL-97 (Sheldrick,
1997)'
_computing_molecular_graphics     ?
_computing_publication_material   ?

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted
R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors
R are based
 on F, with F set to zero for negative F^2^. The threshold
expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-
factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.
R-factors based
 on F^2^ are statistically about twice as large as those
based on F, and R-
 factors based on ALL data will be even larger.
;

_refine_ls_structure_factor_coef  Fsqd
_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.1833P)^2^+4.1469P] where
P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      direct
_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     mixed
_refine_ls_extinction_method      none
_refine_ls_extinction_coef        ?
_refine_ls_number_reflns          7280
_refine_ls_number_parameters      361
_refine_ls_number_restraints      0
_refine_ls_R_factor_all           0.1389
_refine_ls_R_factor_gt            0.1010
_refine_ls_wR_factor_ref          0.3176
_refine_ls_wR_factor_gt           0.2919
_refine_ls_goodness_of_fit_ref    1.053
_refine_ls_restrained_S_all       1.053
_refine_ls_shift/su_max           0.019
_refine_ls_shift/su_mean          0.002

loop_
 _atom_site_label
 _atom_site_type_symbol
 _atom_site_fract_x
```

```
 _atom_site_fract_y
 _atom_site_fract_z
 _atom_site_U_iso_or_equiv
 _atom_site_adp_type
 _atom_site_occupancy
 _atom_site_symmetry_multiplicity
 _atom_site_calc_flag
 _atom_site_refinement_flags
 _atom_site_disorder_assembly
 _atom_site_disorder_group
Si1 Si 0.17214(12) 0.02308(12) 0.21167(5) 0.0360(3) Uani 1 1
d . . .
Si2 Si 0.72677(12) -0.00490(12) 0.30450(5) 0.0358(3) Uani 1
1 d . . .
Si3 Si 0.43038(13) 0.77084(14) -0.04806(5) 0.0403(4) Uani 1
1 d . . .
Si4 Si 0.98766(12) 0.76011(12) 0.04252(5) 0.0355(3) Uani 1 1
d . . .
N1 N 0.4448(3) 0.0087(3) 0.25741(13) 0.0279(8) Uani 1 1 d .
. .
N2 N 0.7135(3) 0.7642(3) -0.00160(13) 0.0299(8) Uani 1 1 d .
. .
O1 O 0.2481(4) 0.1264(4) 0.18562(17) 0.0623(12) Uani 1 1 d .
. .
O2 O 0.1770(3) 0.0413(5) 0.27364(15) 0.0622(12) Uani 1 1 d .
. .
O3 O 0.2226(4) -0.1134(4) 0.20063(17) 0.0573(11) Uani 1 1 d
. . .
O4 O 0.7127(4) 0.0979(4) 0.26035(19) 0.0664(12) Uani 1 1 d .
. .
O5 O 0.6405(4) 0.0274(4) 0.35035(16) 0.0633(12) Uani 1 1 d .
. .
O6 O 0.6833(4) -0.1359(4) 0.28068(16) 0.0594(11) Uani 1 1 d
. . .
O7 O 0.5157(3) 0.8396(4) -0.08778(13) 0.0480(9) Uani 1 1 d .
. .
O8 O 0.4440(3) 0.8398(4) 0.00739(13) 0.0478(9) Uani 1 1 d .
. .
O9 O 0.4741(3) 0.6305(3) -0.04018(15) 0.0490(9) Uani 1 1 d .
. .
O10 O 0.9801(3) 0.8301(4) -0.01240(14) 0.0481(9) Uani 1 1 d
. . .
O11 O 0.9081(3) 0.8304(3) 0.08328(13) 0.0462(9) Uani 1 1 d .
. .
O12 O 0.9405(3) 0.6212(3) 0.03409(14) 0.0444(8) Uani 1 1 d .
. .
C1 C 0.3662(5) 0.1879(4) 0.2072(2) 0.0451(12) Uani 1 1 d . .
.
H1A H 0.3490 0.2344 0.2378 0.054 Uiso 1 1 calc R . .
H1B H 0.3923 0.2450 0.1815 0.054 Uiso 1 1 calc R . .
C2 C 0.4795(5) 0.0995(5) 0.2231(2) 0.0458(12) Uani 1 1 d . .
.
```

```
H2A H 0.5011 0.0592 0.1912 0.055 Uiso 1 1 calc R . .
C3 C 0.6019(5) 0.1738(5) 0.2467(2) 0.0496(13) Uani 1 1 d . .
.
H3A H 0.6228 0.2343 0.2214 0.060 Uiso 1 1 calc R . .
H3B H 0.5818 0.2168 0.2777 0.060 Uiso 1 1 calc R . .
C4 C 0.2709(4) -0.0005(5) 0.31373(18) 0.0403(11) Uani 1 1 d
. . .
H4A H 0.2674 -0.0893 0.3145 0.048 Uiso 1 1 calc R . .
H4B H 0.2483 0.0296 0.3470 0.048 Uiso 1 1 calc R . .
C5 C 0.4122(5) 0.0390(5) 0.3082(2) 0.0476(12) Uani 1 1 d . .
.
H5A H 0.4159 0.1284 0.3116 0.057 Uiso 1 1 calc R . .
C6 C 0.5092(5) -0.0130(5) 0.35209(18) 0.0445(12) Uani 1 1 d
. . .
H6A H 0.4819 0.0106 0.3855 0.053 Uiso 1 1 calc R . .
H6B H 0.5068 -0.1017 0.3499 0.053 Uiso 1 1 calc R . .
C7 C 0.3558(4) -0.1447(4) 0.19404(19) 0.0377(10) Uani 1 1 d
. . .
H7A H 0.3826 -0.0978 0.1651 0.045 Uiso 1 1 calc R . .
H7B H 0.3598 -0.2310 0.1854 0.045 Uiso 1 1 calc R . .
C8 C 0.4516(5) -0.1186(4) 0.2436(2) 0.0419(11) Uani 1 1 d .
. .
H8A H 0.4254 -0.1684 0.2723 0.050 Uiso 1 1 calc R . .
C9 C 0.5917(5) -0.1551(5) 0.2346(2) 0.0433(12) Uani 1 1 d .
. .
H9A H 0.5924 -0.2408 0.2247 0.052 Uiso 1 1 calc R . .
H9B H 0.6186 -0.1069 0.2061 0.052 Uiso 1 1 calc R . .
C10 C -0.0026(5) 0.0323(6) 0.1839(2) 0.0521(14) Uani 1 1 d .
. .
H10A H -0.0364 0.1127 0.1899 0.078 Uiso 1 1 calc R . .
H10B H -0.0533 -0.0276 0.2003 0.078 Uiso 1 1 calc R . .
H10C H -0.0118 0.0168 0.1467 0.078 Uiso 1 1 calc R . .
C11 C 0.9005(5) -0.0113(6) 0.3335(2) 0.0523(14) Uani 1 1 d .
. .
H11A H 0.9556 -0.0297 0.3068 0.079 Uiso 1 1 calc R . .
H11B H 0.9120 -0.0739 0.3600 0.079 Uiso 1 1 calc R . .
H11C H 0.9270 0.0664 0.3492 0.079 Uiso 1 1 calc R . .
C12 C 0.6324(5) 0.9069(5) -0.07160(19) 0.0426(11) Uani 1 1 d
. . .
H12A H 0.6136 0.9684 -0.0463 0.051 Uiso 1 1 calc R . .
H12B H 0.6595 0.9489 -0.1017 0.051 Uiso 1 1 calc R . .
C13 C 0.7460(4) 0.8267(4) -0.04697(17) 0.0358(10) Uani 1 1 d
. . .
H13A H 0.7618 0.7646 -0.0730 0.043 Uiso 1 1 calc R . .
C14 C 0.8715(5) 0.9014(5) -0.0352(2) 0.0449(12) Uani 1 1 d .
. .
H14A H 0.8929 0.9375 -0.0676 0.054 Uiso 1 1 calc R . .
H14B H 0.8566 0.9675 -0.0114 0.054 Uiso 1 1 calc R . .
C15 C 0.5370(5) 0.8112(5) 0.05159(18) 0.0445(12) Uani 1 1 d
. . .
H15A H 0.5261 0.7260 0.0609 0.053 Uiso 1 1 calc R . .
H15B H 0.5190 0.8613 0.0810 0.053 Uiso 1 1 calc R . .
```

```
C16 C 0.6790(5) 0.8321(4) 0.04195(17) 0.0358(10) Uani 1 1 d
. . .
H16A H 0.6865 0.9190 0.0333 0.043 Uiso 1 1 calc R . .
C17 C 0.7761(5) 0.8093(5) 0.09097(18) 0.0424(11) Uani 1 1 d
. . .
H17A H 0.7539 0.8624 0.1188 0.051 Uiso 1 1 calc R . .
H17B H 0.7672 0.7252 0.1021 0.051 Uiso 1 1 calc R . .
C18 C 0.6032(5) 0.5846(4) -0.0434(2) 0.0419(11) Uani 1 1 d .
. .
H18A H 0.6282 0.6058 -0.0775 0.050 Uiso 1 1 calc R . .
H18B H 0.6014 0.4960 -0.0409 0.050 Uiso 1 1 calc R . .
C19 C 0.7069(4) 0.6338(4) -0.00112(19) 0.0371(10) Uani 1 1 d
. . .
H19A H 0.6809 0.6091 0.0328 0.045 Uiso 1 1 calc R . .
C20 C 0.8414(5) 0.5775(5) -0.0050(2) 0.0432(12) Uani 1 1 d .
. .
H20A H 0.8349 0.4892 -0.0018 0.052 Uiso 1 1 calc R . .
H20B H 0.8669 0.5957 -0.0392 0.052 Uiso 1 1 calc R . .
C21 C 0.2559(5) 0.7748(7) -0.0765(2) 0.0630(17) Uani 1 1 d .
. .
H21A H 0.2025 0.7340 -0.0535 0.095 Uiso 1 1 calc R . .
H21B H 0.2449 0.7342 -0.1100 0.095 Uiso 1 1 calc R . .
H21C H 0.2269 0.8585 -0.0812 0.095 Uiso 1 1 calc R . .
C22 C 1.1627(5) 0.7566(5) 0.0708(2) 0.0476(12) Uani 1 1 d .
. .
H22A H 1.1721 0.7150 0.1041 0.071 Uiso 1 1 calc R . .
H22B H 1.1960 0.8389 0.0759 0.071 Uiso 1 1 calc R . .
H22C H 1.2138 0.7141 0.0474 0.071 Uiso 1 1 calc R . .

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 _atom_site_aniso_U_22
 _atom_site_aniso_U_33
 _atom_site_aniso_U_23
 _atom_site_aniso_U_13
 _atom_site_aniso_U_12
Si1 0.0271(6) 0.0414(7) 0.0392(7) -0.0087(5) 0.0035(5)
0.0020(5)
Si2 0.0261(6) 0.0444(8) 0.0368(7) -0.0007(5) 0.0044(5)
0.0006(5)
Si3 0.0289(6) 0.0531(8) 0.0378(7) -0.0038(6) 0.0018(5)
0.0083(6)
Si4 0.0283(6) 0.0432(7) 0.0339(7) 0.0006(5) 0.0008(5)
0.0024(5)
N1 0.0331(19) 0.0226(17) 0.0297(18) -0.0029(13) 0.0105(15) -
0.0023(13)
N2 0.0331(19) 0.0299(18) 0.0274(18) 0.0008(14) 0.0065(14)
0.0065(14)
O1 0.036(2) 0.070(3) 0.077(3) 0.030(2) -0.0032(19)
0.0022(18)
```

```
O2 0.0292(18) 0.114(4) 0.045(2) 0.000(2) 0.0096(16) -
0.001(2)
O3 0.044(2) 0.053(2) 0.071(3) -0.023(2) -0.0029(18)
0.0006(17)
O4 0.037(2) 0.069(3) 0.092(3) 0.031(2) 0.007(2) -0.0032(19)
O5 0.036(2) 0.101(3) 0.052(2) -0.013(2) 0.0043(17) -0.008(2)
O6 0.049(2) 0.063(3) 0.063(3) -0.011(2) -0.0062(18)
0.0194(19)
O7 0.0379(18) 0.065(2) 0.0383(19) 0.0071(17) -0.0028(14)
0.0101(17)
O8 0.0336(17) 0.069(2) 0.0412(19) -0.0058(17) 0.0054(14)
0.0152(17)
O9 0.0331(18) 0.052(2) 0.060(2) -0.0044(17) 0.0012(16) -
0.0004(15)
O10 0.0333(17) 0.066(2) 0.044(2) 0.0132(18) 0.0036(14) -
0.0018(17)
O11 0.0399(18) 0.056(2) 0.0410(19) -0.0122(16) 0.0010(15)
0.0046(16)
O12 0.0338(17) 0.0439(19) 0.052(2) -0.0022(15) -0.0049(15)
0.0119(14)
C1 0.038(3) 0.032(2) 0.065(3) 0.010(2) 0.006(2) 0.009(2)
C2 0.038(3) 0.042(3) 0.057(3) 0.011(2) 0.008(2) -0.001(2)
C3 0.031(2) 0.037(3) 0.080(4) 0.013(3) 0.003(2) -0.003(2)
C4 0.029(2) 0.061(3) 0.032(2) -0.008(2) 0.0075(18) -0.004(2)
C5 0.041(3) 0.059(3) 0.045(3) -0.009(2) 0.013(2) -0.005(2)
C6 0.031(2) 0.074(4) 0.028(2) -0.006(2) 0.0051(18) -0.008(2)
C7 0.035(2) 0.037(2) 0.040(2) -0.0117(19) -0.0011(19)
0.0048(18)
C8 0.044(3) 0.039(3) 0.042(3) -0.002(2) 0.004(2) 0.002(2)
C9 0.040(3) 0.045(3) 0.043(3) -0.012(2) -0.002(2) 0.015(2)
C10 0.034(3) 0.065(4) 0.056(3) -0.013(3) 0.000(2) 0.003(2)
C11 0.033(3) 0.074(4) 0.050(3) -0.001(3) 0.003(2) 0.000(2)
C12 0.042(3) 0.049(3) 0.036(2) 0.011(2) 0.000(2) 0.008(2)
C13 0.035(2) 0.044(3) 0.028(2) 0.0033(19) 0.0052(18)
0.0037(19)
C14 0.039(3) 0.052(3) 0.042(3) 0.014(2) 0.001(2) -0.003(2)
C15 0.040(3) 0.064(3) 0.030(2) -0.002(2) 0.010(2) 0.015(2)
C16 0.040(2) 0.037(2) 0.031(2) -0.0018(18) 0.0061(18)
0.0083(19)
C17 0.037(2) 0.061(3) 0.028(2) -0.002(2) 0.0023(19) 0.007(2)
C18 0.034(2) 0.035(2) 0.054(3) -0.007(2) -0.001(2)
0.0030(19)
C19 0.034(2) 0.031(2) 0.044(3) -0.0030(19) 0.0016(19)
0.0029(18)
C20 0.032(2) 0.042(3) 0.053(3) -0.014(2) -0.003(2) 0.010(2)
C21 0.030(3) 0.095(5) 0.062(4) -0.011(3) -0.003(2) 0.013(3)
C22 0.031(2) 0.060(3) 0.048(3) 0.002(2) -0.006(2) -0.002(2)

_geom_special_details
;
 All esds (except the esd in the dihedral angle between two
l.s. planes)
```

```
 are estimated using the full covariance matrix.  The cell
esds are taken
 into account individually in the estimation of esds in
distances, angles
 and torsion angles; correlations between esds in cell
parameters are only
 used when they are defined by crystal symmetry.  An
approximate (isotropic)
 treatment of cell esds is used for estimating esds
involving l.s. planes.
;

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 _geom_bond_site_symmetry_2
 _geom_bond_publ_flag
Si1 O1 1.594(4) . ?
Si1 O2 1.629(4) . ?
Si1 O3 1.644(4) . ?
Si1 C10 1.829(5) . ?
Si2 O4 1.619(4) . ?
Si2 O6 1.624(4) . ?
Si2 O5 1.627(4) . ?
Si2 C11 1.826(5) . ?
Si3 O9 1.630(4) . ?
Si3 O8 1.631(4) . ?
Si3 O7 1.638(4) . ?
Si3 C21 1.829(5) . ?
Si4 O12 1.626(4) . ?
Si4 O10 1.628(4) . ?
Si4 O11 1.631(4) . ?
Si4 C22 1.833(5) . ?
N1 C2 1.431(6) . ?
N1 C5 1.457(6) . ?
N1 C8 1.468(6) . ?
N2 C16 1.453(5) . ?
N2 C19 1.455(6) . ?
N2 C13 1.456(5) . ?
O1 C1 1.430(6) . ?
O2 C4 1.396(6) . ?
O3 C7 1.437(6) . ?
O4 C3 1.416(6) . ?
O5 C6 1.421(6) . ?
O6 C9 1.432(6) . ?
O7 C12 1.420(6) . ?
O8 C15 1.423(6) . ?
O9 C18 1.427(6) . ?
O10 C14 1.423(6) . ?
O11 C17 1.410(6) . ?
O12 C20 1.417(6) . ?
```

```
C1 C2 1.529(7) . ?
C2 C3 1.551(7) . ?
C4 C5 1.533(7) . ?
C5 C6 1.518(7) . ?
C7 C8 1.535(7) . ?
C8 C9 1.537(7) . ?
C12 C13 1.530(6) . ?
C13 C14 1.521(7) . ?
C15 C16 1.524(7) . ?
C16 C17 1.526(6) . ?
C18 C19 1.520(6) . ?
C19 C20 1.526(6) . ?

loop_
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 _geom_angle_atom_site_label_2
 _geom_angle_atom_site_label_3
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 _geom_angle_site_symmetry_1
 _geom_angle_site_symmetry_3
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O1 Si1 O2 112.9(2) . . ?
O1 Si1 O3 114.1(2) . . ?
O2 Si1 O3 109.0(2) . . ?
O1 Si1 C10 107.2(3) . . ?
O2 Si1 C10 106.1(2) . . ?
O3 Si1 C10 107.1(2) . . ?
O4 Si2 O6 111.7(2) . . ?
O4 Si2 O5 111.6(3) . . ?
O6 Si2 O5 109.6(2) . . ?
O4 Si2 C11 107.8(2) . . ?
O6 Si2 C11 108.6(2) . . ?
O5 Si2 C11 107.3(2) . . ?
O9 Si3 O8 110.6(2) . . ?
O9 Si3 O7 111.6(2) . . ?
O8 Si3 O7 111.1(2) . . ?
O9 Si3 C21 107.9(3) . . ?
O8 Si3 C21 107.7(2) . . ?
O7 Si3 C21 107.8(3) . . ?
O12 Si4 O10 111.1(2) . . ?
O12 Si4 O11 112.4(2) . . ?
O10 Si4 O11 112.5(2) . . ?
O12 Si4 C22 106.7(2) . . ?
O10 Si4 C22 106.6(2) . . ?
O11 Si4 C22 107.1(2) . . ?
C2 N1 C5 121.3(4) . . ?
C2 N1 C8 120.3(4) . . ?
C5 N1 C8 118.3(4) . . ?
C16 N2 C19 119.7(4) . . ?
C16 N2 C13 120.1(4) . . ?
C19 N2 C13 120.1(4) . . ?
C1 O1 Si1 127.6(4) . . ?
```

```
C4 O2 Si1 128.8(3) . . ?
C7 O3 Si1 124.8(3) . . ?
C3 O4 Si2 126.0(4) . . ?
C6 O5 Si2 124.5(3) . . ?
C9 O6 Si2 124.5(3) . . ?
C12 O7 Si3 123.8(3) . . ?
C15 O8 Si3 125.4(3) . . ?
C18 O9 Si3 125.0(3) . . ?
C14 O10 Si4 125.0(3) . . ?
C17 O11 Si4 126.1(3) . . ?
C20 O12 Si4 126.3(3) . . ?
O1 C1 C2 111.1(4) . . ?
N1 C2 C1 112.4(4) . . ?
N1 C2 C3 112.6(4) . . ?
C1 C2 C3 107.4(4) . . ?
O4 C3 C2 110.5(4) . . ?
O2 C4 C5 112.8(4) . . ?
N1 C5 C6 113.1(4) . . ?
N1 C5 C4 111.1(4) . . ?
C6 C5 C4 109.8(4) . . ?
O5 C6 C5 111.7(4) . . ?
O3 C7 C8 110.6(4) . . ?
N1 C8 C7 110.1(4) . . ?
N1 C8 C9 111.8(4) . . ?
C7 C8 C9 108.3(4) . . ?
O6 C9 C8 109.9(4) . . ?
O7 C12 C13 111.7(4) . . ?
N2 C13 C14 112.4(4) . . ?
N2 C13 C12 112.0(4) . . ?
C14 C13 C12 109.3(4) . . ?
O10 C14 C13 111.2(4) . . ?
O8 C15 C16 111.7(4) . . ?
N2 C16 C15 113.2(4) . . ?
N2 C16 C17 111.9(4) . . ?
C15 C16 C17 110.7(4) . . ?
O11 C17 C16 111.8(4) . . ?
O9 C18 C19 112.3(4) . . ?
N2 C19 C18 112.5(4) . . ?
N2 C19 C20 111.5(4) . . ?
C18 C19 C20 110.0(4) . . ?
O12 C20 C19 111.5(4) . . ?

_diffrn_measured_fraction_theta_max    0.994
_diffrn_reflns_theta_full              28.30
_diffrn_measured_fraction_theta_full   0.994
_refine_diff_density_max    2.035
_refine_diff_density_min   -0.475
_refine_diff_density_rms    0.134
```

APPENDIX 6

CRYSTAL STRUCTURE DATA FOR COMPOUND 36•HCl

dta-1 (tert-amine HCl)

```
_audit_creation_method            SHELXL-97
_chemical_name_systematic
;
 ?
;
_chemical_name_common             ?
_chemical_melting_point           ?
_chemical_formula_moiety          ?
_chemical_formula_sum
 'C9 H22 Cl N O6 Si0'
_chemical_formula_weight          275.73

loop_
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 _atom_type_description
 _atom_type_scat_dispersion_real
 _atom_type_scat_dispersion_imag
 _atom_type_scat_source
 'C'  'C'   0.0033   0.0016
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'N'  'N'   0.0061   0.0033
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'O'  'O'   0.0106   0.0060
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'Si'  'Si'   0.0817   0.0704
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'Cl'  'Cl'   0.1484   0.1585
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'H'  'H'   0.0000   0.0000
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

_symmetry_cell_setting            ?
_symmetry_space_group_name_H-M    ?

loop_
 _symmetry_equiv_pos_as_xyz
 'x, y, z'
 '-x, -y, -z'

_cell_length_a                    6.8927(4)
_cell_length_b                    8.2335(5)
_cell_length_c                    11.2422(7)
_cell_angle_alpha                 92.2850(10)
_cell_angle_beta                  102.8470(10)
_cell_angle_gamma                 91.2820(10)
_cell_volume                      621.22(6)
_cell_formula_units_Z             2
_cell_measurement_temperature     193(2)
_cell_measurement_reflns_used     ?
_cell_measurement_theta_min       ?
_cell_measurement_theta_max       ?

_exptl_crystal_description        ?
_exptl_crystal_colour             ?
_exptl_crystal_size_max           0.280
_exptl_crystal_size_mid           0.278
```

```
_exptl_crystal_size_min           0.165
_exptl_crystal_density_meas       ?
_exptl_crystal_density_diffrn     1.474
_exptl_crystal_density_method     'not measured'
_exptl_crystal_F_000              296
_exptl_absorpt_coefficient_mu     0.325
_exptl_absorpt_correction_type    ?
_exptl_absorpt_correction_T_min   ?
_exptl_absorpt_correction_T_max   ?
_exptl_absorpt_process_details    ?

_exptl_special_details
;
 ?
;

_diffrn_ambient_temperature       193(2)
_diffrn_radiation_wavelength      0.71073
_diffrn_radiation_type            MoK\a
_diffrn_radiation_source          'fine-focus sealed tube'
_diffrn_radiation_monochromator   graphite
_diffrn_measurement_device_type   ?
_diffrn_measurement_method        ?
_diffrn_detector_area_resol_mean  ?
_diffrn_standards_number          ?
_diffrn_standards_interval_count  ?
_diffrn_standards_interval_time   ?
_diffrn_standards_decay_%         ?
_diffrn_reflns_number             6210
_diffrn_reflns_av_R_equivalents   0.0215
_diffrn_reflns_av_sigmaI/netI     0.0293
_diffrn_reflns_limit_h_min        -9
_diffrn_reflns_limit_h_max        9
_diffrn_reflns_limit_k_min        -10
_diffrn_reflns_limit_k_max        10
_diffrn_reflns_limit_l_min        -14
_diffrn_reflns_limit_l_max        14
_diffrn_reflns_theta_min          1.86
_diffrn_reflns_theta_max          28.32
_reflns_number_total              3019
_reflns_number_gt                 2805
_reflns_threshold_expression      >2sigma(I)

_computing_data_collection        ?
_computing_cell_refinement        ?
_computing_data_reduction         ?
_computing_structure_solution     'SHELXS-97 (Sheldrick, 1990)'
_computing_structure_refinement   'SHELXL-97 (Sheldrick, 1997)'
_computing_molecular_graphics     ?
_computing_publication_material   ?

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR
and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and
is
 not relevant to the choice of reflections for refinement.  R-factors
based
 on F^2^ are statistically about twice as large as those based on F, and
R-
```

```
 factors based on ALL data will be even larger.
;

_refine_ls_structure_factor_coef  Fsqd
_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0499P)^2^+0.0984P] where P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      direct
_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     mixed
_refine_ls_extinction_method      SHELXL
_refine_ls_extinction_coef        0.079(7)
_refine_ls_extinction_expression
 'Fc^*^=kFc[1+0.001xFc^2^\l^3^/sin(2\q)]^-1/4^'
_refine_ls_number_reflns          3019
_refine_ls_number_parameters      243
_refine_ls_number_restraints      0
_refine_ls_R_factor_all           0.0313
_refine_ls_R_factor_gt            0.0297
_refine_ls_wR_factor_ref          0.0842
_refine_ls_wR_factor_gt           0.0831
_refine_ls_goodness_of_fit_ref    1.068
_refine_ls_restrained_S_all       1.068
_refine_ls_shift/su_max           0.004
_refine_ls_shift/su_mean          0.001

loop_
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 _atom_site_type_symbol
 _atom_site_fract_x
 _atom_site_fract_y
 _atom_site_fract_z
 _atom_site_U_iso_or_equiv
 _atom_site_adp_type
 _atom_site_occupancy
 _atom_site_symmetry_multiplicity
 _atom_site_calc_flag
 _atom_site_refinement_flags
 _atom_site_disorder_assembly
 _atom_site_disorder_group
Cl1 Cl 0.50100(4) 0.61215(3) 0.81232(2) 0.02694(11) Uani 1 1 d . . .
O3 O 0.16907(12) 0.17535(9) 1.00167(7) 0.02465(18) Uani 1 1 d . . .
O6 O -0.46385(11) 0.23196(11) 0.56263(8) 0.02730(18) Uani 1 1 d . . .
O5 O -0.36887(10) -0.10950(9) 0.67299(7) 0.02287(17) Uani 1 1 d . . .
O4 O -0.44110(11) 0.23670(11) 0.85110(8) 0.02757(19) Uani 1 1 d . . .
N1 N -0.12595(12) 0.17035(9) 0.73757(7) 0.01493(17) Uani 1 1 d . . .
O2 O 0.06068(12) 0.51167(9) 0.68675(7) 0.02457(18) Uani 1 1 d . . .
O1 O 0.21374(12) -0.00145(10) 0.63643(7) 0.02525(18) Uani 1 1 d . . .
C9 C -0.03559(14) 0.00343(11) 0.75922(8) 0.01628(19) Uani 1 1 d . . .
C8 C -0.09609(14) 0.28573(11) 0.85029(8) 0.01631(19) Uani 1 1 d . . .
C7 C -0.10335(14) 0.24943(12) 0.62035(8) 0.01748(19) Uani 1 1 d . . .
C6 C 0.11417(14) 0.30835(12) 0.92611(9) 0.0189(2) Uani 1 1 d . . .
C5 C 0.18339(14) -0.00913(12) 0.75760(9) 0.0200(2) Uani 1 1 d . . .
C4 C -0.16324(14) -0.12016(12) 0.66876(9) 0.0201(2) Uani 1 1 d . . .
C3 C 0.08093(15) 0.35770(12) 0.62932(9) 0.0203(2) Uani 1 1 d . . .
C2 C -0.24513(15) 0.23409(12) 0.92470(9) 0.0204(2) Uani 1 1 d . . .
C1 C -0.29538(15) 0.33850(13) 0.57124(10) 0.0230(2) Uani 1 1 d . . .
H81 H -0.1305(18) 0.3884(16) 0.8199(11) 0.015(3) Uiso 1 1 d . . .
H11 H -0.309(2) 0.4276(18) 0.6270(13) 0.025(3) Uiso 1 1 d . . .
H91 H -0.0506(17) -0.0190(14) 0.8366(11) 0.012(3) Uiso 1 1 d . . .
H71 H -0.0960(19) 0.1609(16) 0.5639(12) 0.019(3) Uiso 1 1 d . . .
```

```
H21 H -0.228(2) 0.3043(17) 0.9953(13) 0.026(3) Uiso 1 1 d . . .
H62 H 0.211(2) 0.3211(16) 0.8748(13) 0.026(3) Uiso 1 1 d . . .
H32 H 0.200(2) 0.3086(17) 0.6724(12) 0.026(3) Uiso 1 1 d . . .
H42 H -0.1180(19) -0.2238(17) 0.6897(12) 0.020(3) Uiso 1 1 d . . .
H71 H 0.092(2) 0.3724(17) 0.5434(13) 0.027(3) Uiso 1 1 d . . .
H1 H -0.257(2) 0.1446(17) 0.7215(12) 0.022(3) Uiso 1 1 d . . .
H61 H 0.113(2) 0.4085(16) 0.9768(12) 0.021(3) Uiso 1 1 d . . .
H41 H -0.155(2) -0.1014(16) 0.5864(12) 0.022(3) Uiso 1 1 d . . .
H22 H -0.2252(19) 0.1265(17) 0.9487(12) 0.019(3) Uiso 1 1 d . . .
H52 H 0.265(2) 0.0719(17) 0.8119(13) 0.027(3) Uiso 1 1 d . . .
H51 H 0.218(2) -0.1138(18) 0.7879(13) 0.026(3) Uiso 1 1 d . . .
H12 H -0.289(2) 0.3786(18) 0.4915(13) 0.029(3) Uiso 1 1 d . . .
H6' H -0.496(2) 0.1937(19) 0.4931(16) 0.035(4) Uiso 1 1 d . . .
H3' H 0.268(3) 0.203(2) 1.0470(16) 0.038(4) Uiso 1 1 d . . .
H5' H -0.393(3) -0.185(2) 0.7160(16) 0.046(5) Uiso 1 1 d . . .
H1' H 0.332(3) 0.020(2) 0.6446(15) 0.043(4) Uiso 1 1 d . . .
H2' H 0.171(3) 0.546(2) 0.7132(17) 0.051(5) Uiso 1 1 d . . .
H4' H -0.463(3) 0.331(2) 0.8397(16) 0.047(5) Uiso 1 1 d . . .

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Cl1 0.02280(15) 0.02405(15) 0.03115(16) 0.00152(10) 0.00037(10) -
0.00305(10)
O3 0.0229(4) 0.0254(4) 0.0218(4) 0.0040(3) -0.0034(3) -0.0037(3)
O6 0.0178(4) 0.0384(4) 0.0232(4) 0.0027(3) -0.0006(3) -0.0043(3)
O5 0.0166(3) 0.0217(4) 0.0294(4) 0.0014(3) 0.0038(3) -0.0038(3)
O4 0.0161(4) 0.0266(4) 0.0407(5) 0.0013(3) 0.0081(3) -0.0016(3)
N1 0.0128(4) 0.0154(4) 0.0162(4) -0.0005(3) 0.0028(3) -0.0010(3)
O2 0.0209(4) 0.0183(3) 0.0332(4) -0.0009(3) 0.0041(3) -0.0029(3)
O1 0.0174(4) 0.0343(4) 0.0248(4) -0.0026(3) 0.0069(3) 0.0013(3)
C9 0.0161(4) 0.0143(4) 0.0180(4) 0.0002(3) 0.0032(3) -0.0002(3)
C8 0.0164(4) 0.0152(4) 0.0174(4) -0.0019(3) 0.0044(3) -0.0010(3)
C7 0.0171(4) 0.0190(4) 0.0160(4) 0.0013(3) 0.0029(3) -0.0005(3)
C6 0.0179(4) 0.0175(4) 0.0199(4) -0.0013(3) 0.0019(4) -0.0024(3)
C5 0.0160(4) 0.0205(5) 0.0223(5) -0.0009(4) 0.0018(3) 0.0018(3)
C4 0.0171(4) 0.0177(4) 0.0247(5) -0.0038(4) 0.0041(4) -0.0019(3)
C3 0.0191(5) 0.0199(5) 0.0224(5) 0.0020(4) 0.0060(4) -0.0011(4)
C2 0.0193(5) 0.0204(5) 0.0231(5) -0.0017(4) 0.0088(4) -0.0016(4)
C1 0.0184(5) 0.0251(5) 0.0233(5) 0.0046(4) -0.0005(4) 0.0005(4)

_geom_special_details
;
 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are
taken
 into account individually in the estimation of esds in distances,
angles
 and torsion angles; correlations between esds in cell parameters are
only
 used when they are defined by crystal symmetry.  An approximate
(isotropic)
 treatment of cell esds is used for estimating esds involving l.s.
planes.
;

loop_
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O6 C1 1.4230(13) . ?
O6 H6' 0.812(17) . ?
O5 C4 1.4332(12) . ?
O5 H5' 0.838(19) . ?
O4 C2 1.4196(13) . ?
O4 H4' 0.802(19) . ?
N1 C8 1.5264(12) . ?
N1 C9 1.5276(11) . ?
N1 C7 1.5297(12) . ?
N1 H1 0.903(14) . ?
O2 C3 1.4234(12) . ?
O2 H2' 0.79(2) . ?
O1 C5 1.4270(12) . ?
O1 H1' 0.815(19) . ?
C9 C5 1.5193(13) . ?
C9 C4 1.5243(13) . ?
C9 H91 0.924(12) . ?
C8 C6 1.5125(13) . ?
C8 C2 1.5254(13) . ?
C8 H81 0.940(13) . ?
C7 C3 1.5177(13) . ?
C7 C1 1.5314(13) . ?
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C6 H62 0.978(14) . ?
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C4 H41 0.958(14) . ?
C3 H32 0.962(14) . ?
C3 H71 0.997(14) . ?
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C1 H11 0.966(14) . ?
C1 H12 0.978(15) . ?

loop_
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C1 O6 H6' 108.2(11) . . ?
C4 O5 H5' 106.4(12) . . ?
C2 O4 H4' 105.6(13) . . ?
C8 N1 C9 115.46(7) . . ?
C8 N1 C7 115.15(7) . . ?
C9 N1 C7 116.08(7) . . ?
C8 N1 H1 103.2(8) . . ?
C9 N1 H1 101.6(9) . . ?
C7 N1 H1 102.2(8) . . ?
C3 O2 H2' 105.6(13) . . ?
C5 O1 H1' 105.3(12) . . ?
C5 C9 C4 111.24(8) . . ?
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C5 C9 N1 116.80(8) . . ?
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N1 C9 H91 103.7(7) . . ?
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C6 C8 N1 116.63(8) . . ?
C2 C8 N1 107.74(7) . . ?
C6 C8 H81 105.3(8) . . ?
C2 C8 H81 108.4(8) . . ?
N1 C8 H81 105.2(7) . . ?
C3 C7 N1 116.52(8) . . ?
C3 C7 C1 112.12(8) . . ?
N1 C7 C1 107.38(8) . . ?
C3 C7 H71 107.1(8) . . ?
N1 C7 H71 105.3(8) . . ?
C1 C7 H71 108.0(8) . . ?
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O3 C6 H62 108.7(8) . . ?
C8 C6 H62 111.6(8) . . ?
O3 C6 H61 110.0(8) . . ?
C8 C6 H61 105.2(8) . . ?
H62 C6 H61 109.8(11) . . ?
O1 C5 C9 111.22(8) . . ?
O1 C5 H52 111.2(9) . . ?
C9 C5 H52 111.9(8) . . ?
O1 C5 H51 109.5(8) . . ?
C9 C5 H51 104.4(8) . . ?
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O5 C4 C9 110.73(8) . . ?
O5 C4 H42 110.1(8) . . ?
C9 C4 H42 107.8(8) . . ?
O5 C4 H41 106.7(8) . . ?
C9 C4 H41 111.7(8) . . ?
H42 C4 H41 109.8(11) . . ?
O2 C3 C7 111.09(8) . . ?
O2 C3 H32 109.4(8) . . ?
C7 C3 H32 112.4(8) . . ?
O2 C3 H71 109.7(8) . . ?
C7 C3 H71 105.6(8) . . ?
H32 C3 H71 108.5(11) . . ?
O4 C2 C8 109.46(8) . . ?
O4 C2 H21 112.3(8) . . ?
C8 C2 H21 108.7(8) . . ?
O4 C2 H22 106.4(8) . . ?
C8 C2 H22 110.9(8) . . ?
H21 C2 H22 109.1(12) . . ?
O6 C1 C7 110.21(8) . . ?
O6 C1 H11 106.7(8) . . ?
C7 C1 H11 110.1(8) . . ?
O6 C1 H12 111.3(8) . . ?
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1
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