$(A/\hbar)^2T_{1e}$ and E_a from the apparent temperature variation of T_{2M}. The k_1 values are per water molecule assuming them all to be equivalent in a species.

Discussion

In Figure 4 are plotted water exchange results for a variety of species measured by our group using ^{17}O nmr techniques. The data for NCS^- complexes of Ni(II) would fit the line at 25° were the $Ni(NCS)_3(H_2O)_3^-$ species the correct one. The activation enthalpies are lower in general for Cl^- and NCS^- species[7,8] (8 and 6 kcal/mol, respectively). For the others the values are near 10 kcal/mol. There appears to be a general, somewhat regular, labilization of the remaining water molecules upon successive substitution in the aquo ion. The activation parameters appear to vary somewhat nonsystematically. Part of the increased rate does seem to involve the entropy factor. Scalar coupling constants (^{17}O) are quite similar for all species. No doubt both electronic and solvation effects are involved in the observed results, but it is difficult to see a clear explanation at this time.

It is most interesting to note that Rablen and Gordon[3] have found that terpyridyl does not produce the effects mentioned above and in fact causes only a small change in the water lability. Dr. M. Grant in this laboratory has completed a study of the aquo $Ni(dipyridyl)^{2+}$ and $Ni(dipyridyl)_2^{2+}$ systems and finds results similar to those of Rablen. It is tempting to ascribe these results to possible back π bonding effects where aromatic rings are involved.

Some comments on the validity and meaning of the nmr studies may be in order. When one replaces all of the water by using excess ligand, no line broadening effects or shifts are observed in the concentration ranges employed. This fact rules out possible contributions to the observed rates from outer-sphere complexes or by water substitution on the fully formed complex. Earlier work in this laboratory on Cl^- and NCS^- showed, indeed, that the results could not be accounted for by processes in which each ligand always replaced the other ("coupled" processes).

The observed activation parameters are somewhat dependent on the absolute values of ΔH for formation of the complexes and these may not always be reliable. The effects observed so far are fairly small and basically hard to account for.

Acknowledgments. We wish to thank the Washington State University Research Committee for funds enabling purchase of the ^{17}O.

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(8) R. B. Jordan, H. W. Dodgen, and J. P. Hunt, *ibid.*, 5, 1906 (1966).

Structural Studies of Pentacoordinate Silicon. VI. Cyclobis(benzamidodimethylsilane)

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Abstract: The crystal and molecular structure of 2,2,4,4-tetramethyl-3-benzoyl-6-phenyl-2,4-disila-1,3,5-oxadiazine, $C_{18}H_{22}N_2O_2Si_2$, has been determined by a single-crystal three-dimensional X-ray diffraction study. This compound crystallizes in the centrosymmetric space group Pbca with lattice parameters $a = 10.543 \pm 0.005$, $b = 8.281 \pm 0.003$, and $c = 43.443 \pm 0.020$ Å ($Z = 8$). The intensity data were collected on a Picker automatic diffractometer (Cu Kα radiation) and the structure was solved by iterative application of Sayre's equation. All but methyl hydrogens were located by difference synthesis. Full matrix least-squares refinement of atom positions, hydrogen isotropic thermal parameters, and anisotropic thermal parameters for all other atoms converged at a final $R_1 = 6.1\%$ for 2376 reflections above background. The structure suggests that the Si atom bonded to oxygen is incipiently pentacoordinate *via* an interaction with the exocyclic carbonyl group. The Si···O distance is 2.613 ± 0.003 Å, substantially less than the sum of the Si and O van der Waals radii, 3.35 Å. Distortion of the bond angles provides additional evidence for this interaction. The heterocyclic ring is essentially planar, with a maximum deviation from the least-squares plane of 0.13 Å. The structural features are discussed in relation to the tautomerizations observed for disilaoxadiazines.

A recent series of X-ray diffraction studies[1-5] has demonstrated the presence of expanded-octet bonding in stable organosilicon compounds and thus provided support for the extracoordinate intermediates believed to form during displacement reactions at silicon.[6] Pentacoordinate silicon has been directly established in dimethylsilylamine pentamer,[7] in bis(*o*-phenylenedioxy)phenylsiliconate,[3] and in several triptych compounds,[1,2,4,5] all of which assume essentially a trigonal bipyramid geometry.

Valence shell expansion of silicon has also been pro-

(1) J. W. Turley and F. P. Boer, *J. Amer. Chem. Soc.*, 90, 4026 (1968).

(2) F. P. Boer, J. W. Turley, and J. J. Flynn, *ibid.*, 90, 5102 (1968).

(3) F. P. Boer, J. J. Flynn, and J. W. Turley, *ibid.*, 90, 6973 (1968).

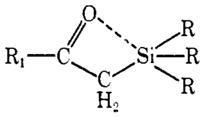
(4) J. W. Turley and F. P. Boer, *ibid.*, 91, 4129 (1969).

(5) F. P. Boer and J. W. Turley, *ibid.*, 91, 4134 (1969).

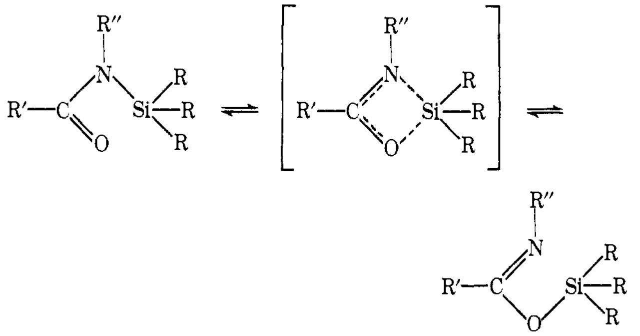
(6) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

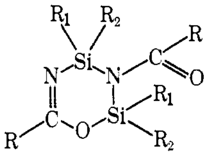
(7) R. Rudman, W. C. Hamilton, S. Novick, and T. D. Goldfarb, *J. Amer. Chem. Soc.*, 89, 5157 (1967).

posed in β-silyl ketones and in silylamides. Musker and Ashby[8] have suggested that perturbation of the carbonyl group by silicon 3d orbitals is the principal cause of the observed intensification of n–π* transitions in β-silyl ketones



and further proposed that "this interaction may be of general importance in providing a pathway for decomposition of organosilanes." The structural properties of silylamides are not well understood, but spectroscopic results have been cited[9,10] in favor of both the tautomeric N-silylamide and O-silylimino ether structures. During investigations designed to resolve some of the controversy over these compounds, Klebe[11] synthesized several derivatives of a novel dimeric silylamide, 2,4-disila-1,3,5-oxadiazine (I)





I

by reaction of organodichlorosilanes with N-unsubstituted amides. These substances, which have the interesting property of containing simultaneously both canonical forms of the silylamide function, have furthermore been shown to undergo two distinct temperature-dependent isomerizations closely related to the amide–imino ether tautomerism mentioned above. The suggestions were made that these rearrangements, which are thought to proceed through transition states involving extracoordinate silicon, might be facilitated by incipient pentacoordination in the ground state; and that the high reactivity of silylamides toward protonic reagents might correlate with structures in which silicon has such a pentacoordinate geometry, whereas the less reactive silylamines have normal tetragonal configurations.[11]

The present single-crystal X-ray diffraction investigation of cyclobis(benzamidodimethylsilane) (I, $R_1 = R_2 = CH_3$ and $R = C_6H_5$) was undertaken to determine the geometry of coordination at silicon and its potential role in the disilaoxadiazine tautomerism. This system affords a unique opportunity to determine directly the structure of a model compound undergoing a unimolecular displacement reaction at silicon in which incipient pentacoordination may appear in the ground state.

Experimental Section

A sample of cyclobis(benzamidodimethylsilane), mp 126–127°, was prepared by Klebe's method,[11] and colorless single crystals of needle-like habit were grown from heptane. A crystal of approximate dimensions 0.29 × 0.15 × 0.92 mm was sealed in a 0.3-mm glass capillary tube. To avoid hydrolysis of the sample, all of these experimental manipulations were performed in a dry N_2 atmosphere.

A preliminary alignment on the long (*b*) axis was carried out on a Weissenberg camera, and the reciprocal lattice was surveyed for systematic absences. The crystal was then carefully centered on a Picker automatic four-circle diffractometer. Lattice constants were calculated from a least-squares refinement of the setting angles of 11 reflections with Cu Kα radiation (λ 1.5418 Å). The parameters of the orthorhombic cell, $a = 10.543 \pm 0.005$, $b = 8.281 \pm 0.003$, and $c = 43.443 \pm 0.020$ Å, give a calculated density of 1.243 g cm^{-3} for $Si_2O_2N_2C_{18}H_{22}$ with $Z = 8$. Attempts to determine an experimental density failed because of the rapid hydrolysis of the crystals in the conventional solvents. However, the mass spectrum, which showed a molecular ion peak at 354, is consistent with the assumed formula. The space group Pbca was established uniquely by the absence of 0*kl* reflections for *k* odd, *h*0*l* for *l* odd, *hk*0 for *h* odd.

The intensity data were collected using the θ–2θ scan mode of the diffractometer with Ni filtered Cu Kα radiation. The take-off angle of the tube was 3°, and a counter aperture 6.0 × 6.0 mm was placed 30 cm from the crystal. Scan angles ranging between 2.0 and 2.8° of 2θ were measured at a speed of 2°/min, and two stationary-crystal–stationary-counter background counts of 15 sec were taken at each end of the scan. The reciprocal lattice was recorded out to the instrumental limit ($\sin\theta = 0.909$) and a total of 3255 of the 4348 independent reflections in the Cu Kα sphere was measured. An error

$$\sigma(I) = [(0.03I)^2 + N_0 + k^2N_b]^{1/2}$$

was assigned to the net intensity $I = N_0 - kN_b$ of each reflection in order to establish the weights $w(F) = 4F^2/\sigma^2(F^2)$ for subsequent least-squares refinement, where the quantity $\Sigma w(|F_o| - |F_c|)^2$ was minimized. Here N_0 is the gross count, N_b is the background count, and k is the ratio of scan time to background time. Reflections for which $I < 0$ or $\sigma(I)/I > 0.25$ were considered to be absent and were not used in the refinement. A correction was made for Lorentz and polarization effects, but absorption corrections were neglected. The Cu Kα linear absorption coefficient of 17.5 cm^{-1} indicates that transmission factors vary between 0.60 and 0.77. Finally, an absolute scale factor and overall temperature factor were computed by Wilson's method.

Solution and Refinement of the Structure

A set of normalized structure factors (*E*'s) was calculated for the three-dimensional set of intensities. The signs of 388 reflections for which $|E| > 1.5$ were determined using the multiple-solution program of Long,[12] which solves the phase problem by reiterative application of the Sayre equation[13]

$$s(E_a) = s(\sum_{a=b+c} E_b E_c)$$

where s means "sign of" and **a**, **b**, **c** are vectors representing the reflection indices *hkl*. The size of the problem is indicated by the total of 44,176 terms which had to be assembled and the 780 sec of central processing time required on a CDC 6600 computer. The correct solution, which assumed positive signs for 5.2.1, 1.1.34, 3.4.12, 5.2.21, 3.2.1, and 2.2.33 and a negative sign for

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(8) W. K. Musker and R. W. Ashby, *J. Org. Chem.*, **31**, 4237 (1966).

(9) J. Pump and E. G. Rochow, *Chem. Ber.*, **97**, 627 (1964).

(10) See ref 11 and references therein.

(11) J. F. Klebe, *J. Amer. Chem. Soc.*, **90**, 5246 (1968).

(12) R. E. Long, Ph.D. Thesis, University of California at Los Angeles, 1965.

(13) D. Sayre, *Acta Cryst.*, **5**, 60 (1952).

5.4.16, gave a consistency index

$$C = \frac{\langle |E_a \sum_{a=b+c} E_b E_c| \rangle}{\langle |E_a| \sum_{a=b+c} |E_b||E_c| \rangle}$$

of 0.779 after six cycles. An E-map calculated[14] from this solution showed the skeleton of the heavier (Si, O, N, C) atoms clearly. All but five phases, 2.2.3, 4.3.3, 3.3.5, 4.5.22, and 1.3.37, were subsequently shown to be correct. One cycle of full matrix least-squares refinement[15,16] on the positions of the 24 atoms found in the E-map reduced

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

from 0.25 to 0.17. In this calculation oxygen scattering factors were assumed for atoms O(1) and N(1), which had not yet been positively identified. Integration over the peaks in the electron density map[14] based on these calculated phases gave total electron populations of 6.94 and 7.70 electrons, respectively, for the atoms henceforth labeled as N(1) and O(1). These identifications are consistent with the final bond distances. R_1 was reduced to 0.11 and

$$R_2 = \left\{ \frac{\sum w[F_o - F_o]^2}{\sum w F_o^2} \right\}^{1/2}$$

to 0.15 after one further cycle in which atomic positions and isotropic temperature factors were varied. A difference map was now calculated,[14] which clearly revealed all but methyl hydrogens at reasonable bond distances. An additional cycle of isotropic refinement including the hydrogens[17] gave R_1 = 0.10 and R_2 = 0.13. Three cycles of least squares, in which all atomic positions, heavy atom anisotropic thermal parameters, and hydrogen isotropic temperature factors were simultaneously varied, converged to final discrepancy indices R_1 = 0.061 and R_2 = 0.081 for the 2376 reflections above background. The mean shift of position parameters in the final cycle was 0.01σ, with a maximum (hydrogen) shift of 0.17σ. A final difference map revealed some residual electron density (as high as 0.16 e Å^{-3}) in the regions occupied by the methyl hydrogens, which appear to be disordered.

Atomic parameters and their estimated standard deviations are given in Table I, while bond distances and angles, together with standard deviations computed[18] from the variance–covariance matrix obtained in the final least-squares cycle, are listed in Table II. The root-mean-square components of thermal displacement along the principal axes, as defined by the anisotropic thermal parameters, are compiled in Table III. The directions of thermal motion may be inferred from Figure 1, in which the three-dimensional structure of the molecule is shown using ellipsoids to represent the anisotropic thermal motion.[19] A table of observed and calculated structure factors is available to the interested reader.[20]

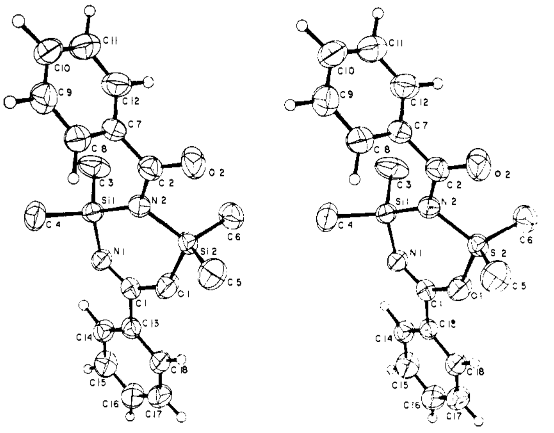

Figure 1. Three-dimensional view of the molecular structure of cyclobis(benzamidodimethylsilane), showing ellipsoids of thermal motion.

Description and Discussion of the Structure

The results confirm that the compound $C_{18}H_{22}N_2O_2Si_2$ is indeed cyclobis(benzamidodimethylsilane), and thus establish directly the existence of the new heterocycle 2,4-disila-1,3,5-oxadiazine. An interaction between the exocyclic carbonyl and silicon is indicated by our experimental Si(2)–O(2) distance of 2.613 ± 0.003 Å, which is 0.74 Å less than the sum of the respective van der Waals radii,[21] about 3.35 Å. This distance is, nevertheless, well outside the range (1.61–1.81 Å) reported for silicon–oxygen covalent bonds to tetra-,[1] penta-,[1-5] and hexacoordinate[22a] silicon. This bond is also longer, and we presume considerably weaker, than the Si–N bonds (2.116–2.344 Å) found in caged pentacoordinate compounds.[1,2,4,5]

The molecular geometry at the incipiently pentacoordinate silicon atom (Si(2)) can be described in terms of a tetrahedron distorted toward a trigonal bipyramid with O(1) and O(2) approaching axial positions and

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[14] Fourier calculations were performed using Program B-149, (Argonne National Laboratory), a version of Shoemaker, Sly, and Van denHende's ERFR-2, by J. Gvildys.

[15] Least-squares and structure factor calculations were performed using ANL-FLS-14E, J. Gvildys' version of Busing, Martin, and Levy's OR-FLS.

[16] Atomic scattering factors were taken from "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 201.

[17] Hydrogen scattering factors are by R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42,** 3175 (1965).

[18] J. Gvildys' version (ANL Program Library B-115) of Busing, Martin, and Levy's Fortran function and error program, OR-FFE, was used.

[19] ORTEP is a Fortran thermal ellipsoid plot program by C. K. Johnson, Oak Ridge National Laboratory.

[20] Material supplementary to this article has been deposited as Document No. NAPS-00832 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y., 10022. A copy may be secured by citing the document number and remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

[21] The oxygen van der Waals radius is about 1.4 Å: L. Pauling, "The Nature of the Chemical," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260. The Si van der Waals radius can be estimated to be 1.95 Å by extrapolation of the radii of neighboring atoms: P, 1.90; S, 1.85, and Cl, 1.80 (*ibid.*, p 260, or by using the heuristic rule (*ibid.*, p 263) that *r* (van der Waals) = *r*(single bond) + 0.80 Å, where *r*(single bond, Si) = 1.17 Å (*ibid.*, p 246).

[22] (a) J. J. Flynn and F. P. Boer, *J. Amer. Chem. Soc.*, **91,** 5756 (1969). (b) The comparison assumes N(1) would be the apex. (c) NOTE ADDED IN PROOF. A referee has suggested that an alternative explanation for the short Si(2)···O(2) distance and the observed bond angle distortions could be C—H···O hydrogen bonding. (The C(5)···O(2) and C(6)···O(2) distances, between methyl groups and carbonyl oxygen, as found in the present structure are 3.036 ± 0.006 and 3.092 ± 0.006 Å, respectively.) Because some questions have been raised as to the existence of C—H···O hydrogen bonds [J. Donohue in "Structural Chemistry and Molecular Biology," A. Rich and W. Davidson, Ed., W. H. Freeman and Co., San Francisco, Calif., 1968, pp 443–465], the role of the methyl–oxygen interactions is difficult to assess at this time.

Table I. Final Structure Parameters[a] and Standard Errors[b]

Atom	x/a	y/b	z/c	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^5\beta_{33}$	$10^4\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
Si(1)	0.5501 (1)	0.6238 (1)	0.14274 (2)	87 (1)	122 (2)	39 (1)	−9 (1)	−14 (2)	13 (3)
Si(2)	0.4313 (1)	0.3621 (1)	0.10074 (2)	94 (1)	103 (2)	42 (1)	−13 (1)	11 (2)	−2 (3)
O(1)	0.4734 (3)	0.5095 (3)	0.07658 (6)	161 (4)	149 (5)	45 (2)	−65 (4)	−12 (7)	21 (8)
O(2)	0.3709 (3)	0.2103 (4)	0.15140 (7)	190 (5)	143 (6)	65 (2)	−50 (4)	92 (8)	−22 (9)
N(1)	0.5838 (3)	0.6930 (4)	0.10669 (7)	91 (3)	138 (6)	42 (2)	−9 (4)	−2 (6)	−13 (9)
N(2)	0.4535 (3)	0.4483 (4)	0.13773 (7)	97 (3)	122 (5)	41 (2)	−11 (4)	23 (7)	9 (8)
C(1)	0.5455 (3)	0.6447 (4)	0.08089 (8)	76 (4)	108 (6)	49 (2)	6 (4)	11 (7)	−2 (10)
C(2)	0.4097 (4)	0.3461 (5)	0.15946 (9)	99 (4)	134 (7)	52 (2)	−0 (5)	20 (8)	18 (11)
C(3)	0.7009 (5)	0.5635 (7)	0.1620 (1)	123 (6)	243 (11)	95 (4)	−14 (7)	−125 (12)	169 (18)
C(4)	0.4685 (5)	0.7882 (6)	0.1644 (1)	148 (6)	161 (8)	59 (3)	−4 (6)	44 (11)	−102 (13)
C(5)	0.2628 (5)	0.3248 (6)	0.0904 (1)	108 (5)	208 (10)	82 (3)	−25 (6)	−47 (11)	−20 (15)
C(6)	0.5405 (5)	0.1892 (6)	0.0935 (1)	149 (6)	164 (8)	65 (3)	36 (6)	49 (11)	−25 (13)
C(7)	0.4043 (4)	0.3894 (5)	0.19262 (8)	96 (4)	120 (6)	46 (2)	−7 (4)	9 (8)	37 (10)
C(8)	0.3087 (4)	0.4907 (5)	0.20322 (9)	107 (5)	156 (8)	55 (3)	15 (5)	5 (9)	−2 (12)
C(9)	0.2950 (5)	0.5166 (6)	0.2347 (1)	134 (6)	171 (9)	64 (3)	11 (6)	40 (11)	36 (14)
C(10)	0.3774 (5)	0.4451 (6)	0.2551 (1)	170 (7)	194 (9)	45 (3)	−31 (7)	−4 (11)	−5 (13)
C(11)	0.4716 (5)	0.3460 (7)	0.2448 (1)	164 (7)	232 (10)	56 (3)	34 (7)	−34 (12)	33 (15)
C(12)	0.4848 (5)	0.3168 (6)	0.2135 (1)	135 (6)	208 (9)	59 (3)	45 (6)	4 (11)	58 (14)
C(13)	0.5736 (3)	0.7258 (4)	0.05129 (8)	81 (4)	104 (6)	43 (2)	9 (4)	19 (7)	−2 (9)
C(14)	0.6627 (4)	0.8481 (5)	0.05013 (9)	94 (4)	138 (7)	50 (2)	−7 (4)	7 (8)	−4 (11)
C(15)	0.6916 (5)	0.9217 (6)	0.0224 (1)	133 (6)	173 (9)	65 (3)	−36 (6)	49 (11)	24 (14)
C(16)	0.6326 (5)	0.8753 (6)	−0.0042 (1)	163 (6)	173 (9)	49 (3)	−23 (7)	40 (11)	43 (13)
C(17)	0.5421 (5)	0.7547 (6)	−0.0032 (1)	169 (7)	174 (8)	44 (3)	−15 (7)	−25 (11)	22 (12)
C(18)	0.5129 (4)	0.6802 (5)	0.02415 (9)	119 (5)	130 (7)	48 (2)	−13 (5)	−20 (9)	9 (11)
				B					
H(8)	0.247 (4)	0.553 (5)	0.1866 (9)	6.0 (1.1)					
H(9)	0.225 (5)	0.598 (6)	0.244 (1)	7.9 (1.4)					
H(10)	0.362 (5)	0.478 (6)	0.279 (1)	7.0 (1.2)					
H(11)	0.535 (4)	0.280 (6)	0.261 (1)	7.1 (1.3)					
H(12)	0.549 (5)	0.222 (6)	0.203 (1)	8.0 (1.4)					
H(14)	0.708 (3)	0.880 (5)	0.0717 (9)	5.0 (1.0)					
H(15)	0.743 (6)	1.012 (7)	0.020 (1)	8.5 (1.7)					
H(16)	0.672 (4)	0.942 (6)	−0.024 (1)	7.0 (1.3)					
H(17)	0.504 (4)	0.719 (6)	−0.021 (1)	5.9 (1.2)					
H(18)	0.449 (5)	0.594 (7)	0.026 (1)	7.6 (1.5)					

[a] The anisotropic thermal parameters are in the form $\exp(-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2hl\beta_{23}))$. [b] Standard errors are given in parentheses.

N(2), C(5), and C(6) displaced toward the equatorial sites. Thus, the O(1)–Si(2)–N(2), O(1)–Si(2)–C(5), and O(1)–Si(2)–C(6) angles, which have values of 103.9 ± 0.1, 103.0 ± 0.2, and 106.9 ± 0.2°, respectively, have closed down from the tetrahedral value of 109.5° toward the 90° angles of an ideal trigonal bipyramid with O(1) at the apex. While the average of these three angles, 104.6°, is definitely lower than the average of the corresponding angles[22b] around Si(1), 107.8°, this figure is still considerably higher than angles of 97–100° found in the more strongly coordinated triptych compounds.[1,2,4,5] The angles between the equatorial atoms have increased to 114.9 ± 0.2, 114.3 ± 0.2, and 112.4 ± 0.2° for C(5)–Si(2)–C(6), C(5)–Si(2)–N(2), and C(6)–Si(2)–N(2), respectively, and thus tend toward the 120° between equatorial ligands in a trigonal bipyramid: their average value of 113.9° may be compared to the analogous[22b] 111.0° found around Si(1) or alternatively to the 109.5° tetrahedral angle. In brief, of the six angles of an imaginary tetrahedron, three have opened while three have closed in such a way as to facilitate the approach of the fifth (carbonyl) ligand.[22c]

The interaction between Si(2) and the exocyclic oxygen is also favored by the pronounced closing of the Si(2)–N(2)–C(2) angle from its expected value of about 120 to 109.7 ± 0.3°, a result which provides additional evidence for the presence of some pentacoordination. The adjacent Si(1)–N(2)–C(2) angle is correspondingly opened to 128.3 ± 0.3°. This distortion about N(2) serves both to shorten the Si(2)···O(2) distance and to allow O(2) to approach in a direction more nearly opposite the Si(2)–O(1) bond, resulting in an O(1)–Si(2)–O(2) angle of 161.0 ± 0.1°. This arrangement is not inconsistent with the general rule that the most electronegative ligands tend to occupy axial positions in trigonal bipyramidal structures.[23]

The observed geometry may be considered with respect to some alternative conformations. For example, the carbonyl could in principle interact with Si(1), which is directly bonded to two nitrogens, yielding a pentacoordinate conformation similar to that above, but with N(1) and O(2) at the "apices." It is, however, the silicon atom with the more electronegative ligands, namely Si(2), that appears to have the greater capacity for extracoordination. An alternative type of pentacoordination, involving a tetragonal pyramidal geometry *via* a transannular Si(2)···N(1) interaction, has also been proposed for the 2,4-disila-1,3,5-oxadiazines.[11] This ground state conformation was suggested as a possible precursor to hexacoordinate transition states postulated for the observed tautomerizations.[11] However, the Si(2)···N(1) distance of 3.187 Å and the nearly planar heterocyclic ring (*vide infra*) found in this structure indicate that no unusual transannular interactions occur. The above results have led the present authors to communicate[24] an alternative mechanism for the disilaoxadiazine tautomerisms based on attack at silicon by car-

(23) R. F. Hudson, *Angew. Chem. Intern. Ed. Engl.*, **6**, 749 (1967).

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Table II. Distances and Angles[a]

A. Bond Distances (Å)

Bonds in central ring		Bonds in phenyl rings	
Si(1)–N(1)	1.706 (3)	C(7)–C(8)	1.390 (5)
Si(1)–N(2)	1.788 (3)	C(7)–C(12)	1.381 (6)
Si(2)–O(1)	1.670 (3)	C(8)–C(9)	1.391 (6)
Si(2)–N(2)	1.774 (3)	C(9)–C(10)	1.376 (6)
O(1)–C(1)	1.366 (4)	C(10)–C(11)	1.365 (7)
N(1)–C(1)	1.256 (5)	C(11)–C(12)	1.385 (6)
Carbon–nitrogen bonds		C(13)–C(14)	1.383 (5)
		C(13)–C(18)	1.393 (5)
C(1)–N(1)	1.256 (5)	C(14)–C(15)	1.385 (6)
C(2)–N(2)	1.349 (5)	C(15)–C(16)	1.367 (6)
		C(16)–C(17)	1.382 (7)
Carbon–oxygen bonds		C(17)–C(18)	1.373 (6)
C(1)–O(1)	1.366 (4)		
C(2)–O(2)	1.247 (5)	Carbon–hydrogen bonds	
		C(8)–H(8)	1.10 (4)
Exocyclic carbon–carbon bonds		C(9)–H(9)	1.08 (5)
		C(10)–H(10)	1.10 (4)
C(1)–C(13)	1.481 (5)	C(11)–H(11)	1.12 (5)
C(2)–C(7)	1.485 (5)	C(12)–H(12)	1.14 (5)
		C(14)–H(14)	1.08 (4)
Silicon–methyl bonds		C(15)–H(15)	0.93 (6)
Si(1)–C(3)	1.864 (5)	C(16)–H(16)	1.09 (5)
Si(1)–C(4)	1.865 (5)	C(17)–H(17)	0.94 (4)
Si(2)–C(5)	1.858 (5)	C(18)–H(18)	0.98 (5)
Si(2)–C(6)	1.864 (5)		
Exocyclic oxygen–silicon bond			
Si(2)–O(2)	2.613 (3)		

B. Bond Angles (Degrees)

Vertex	Atom 1	Atom 2		Vertex	Atom 1	Atom 2	
Si(1)	N(1)	N(2)	106.3 (0.1)	C(7)	C(2)	C(8)	119.6 (0.4)
	N(1)	C(4)	108.3 (0.2)		C(2)	C(12)	120.7 (0.4)
	N(1)	C(3)	108.9 (0.2)		C(8)	C(12)	119.3 (0.4)
	N(2)	C(3)	108.8 (0.2)	C(8)	C(7)	C(9)	119.6 (0.4)
	N(2)	C(4)	113.1 (0.2)		C(7)	H(8)	120 (2)
	C(3)	C(4)	111.3 (0.2)		C(9)	H(8)	121 (2)
Si(2)	O(1)	O(2)	161.0 (0.1)	C(9)	C(8)	C(10)	120.2 (0.4)
	O(1)	N(2)	103.9 (0.1)		C(8)	H(9)	122 (3)
	O(1)	C(5)	103.0 (0.2)		C(10)	H(9)	118 (3)
	O(1)	C(6)	106.9 (0.2)	C(10)	C(9)	C(11)	120.4 (0.4)
	O(2)	N(2)	57.5 (0.1)		C(9)	H(10)	114 (2)
	O(2)	C(5)	83.7 (0.2)		C(11)	H(10)	125 (2)
	O(2)	C(6)	85.6 (0.2)	C(11)	C(10)	C(12)	120.1 (0.5)
	N(2)	C(5)	114.3 (0.2)		C(10)	H(11)	121 (2)
	N(2)	C(6)	112.4 (0.2)		C(12)	H(11)	119 (2)
	C(5)	C(6)	114.9 (0.2)	C(12)	C(7)	C(11)	120.5 (0.5)
O(1)	Si(2)	C(1)	131.4 (0.2)		C(7)	H(12)	113 (3)
O(2)	Si(2)	C(2)	73.9 (0.2)		C(11)	H(12)	126 (3)
N(1)	Si(1)	C(1)	130.2 (0.3)	C(13)	C(1)	C(14)	120.0 (0.3)
N(2)	Si(1)	Si(2)	120.8 (0.2)		C(1)	C(18)	121.3 (0.3)
	Si(2)	C(2)	109.7 (0.3)		C(14)	C(18)	118.7 (0.3)
	Si(1)	C(2)	128.3 (0.3)	C(14)	C(13)	C(15)	120.2 (0.4)
C(1)	O(1)	N(1)	124.2 (0.3)		C(13)	H(14)	116 (2)
	O(1)	C(13)	111.3 (0.3)		C(15)	H(14)	123 (2)
	N(1)	C(13)	124.5 (0.3)	C(15)	C(14)	C(16)	120.8 (0.4)
C(2)	O(2)	N(2)	118.8 (0.4)		C(14)	H(15)	125 (3)
	O(2)	C(7)	118.5 (0.4)		C(16)	H(15)	114 (3)
	N(2)	C(7)	122.7 (0.3)	C(16)	C(15)	C(17)	119.3 (0.4)
					C(15)	H(16)	110 (2)
					C(17)	H(16)	130 (2)
				C(17)	C(16)	C(18)	120.5 (0.4)
					C(16)	H(17)	120 (3)
					C(18)	H(17)	119 (3)
				C(18)	C(13)	C(17)	120.5 (0.4)
					C(13)	H(18)	116 (3)
					C(17)	H(18)	123 (3)

[a] Standard errors calculated from the variance-covariance matrix obtained in the final least-squares cycle are given in parentheses.

bonyl and requiring only pentacoordinate transition states.

The central ring shows small, but statistically significant deviations from planarity. The least-squares plane[25] through these six atoms is described by the equa-

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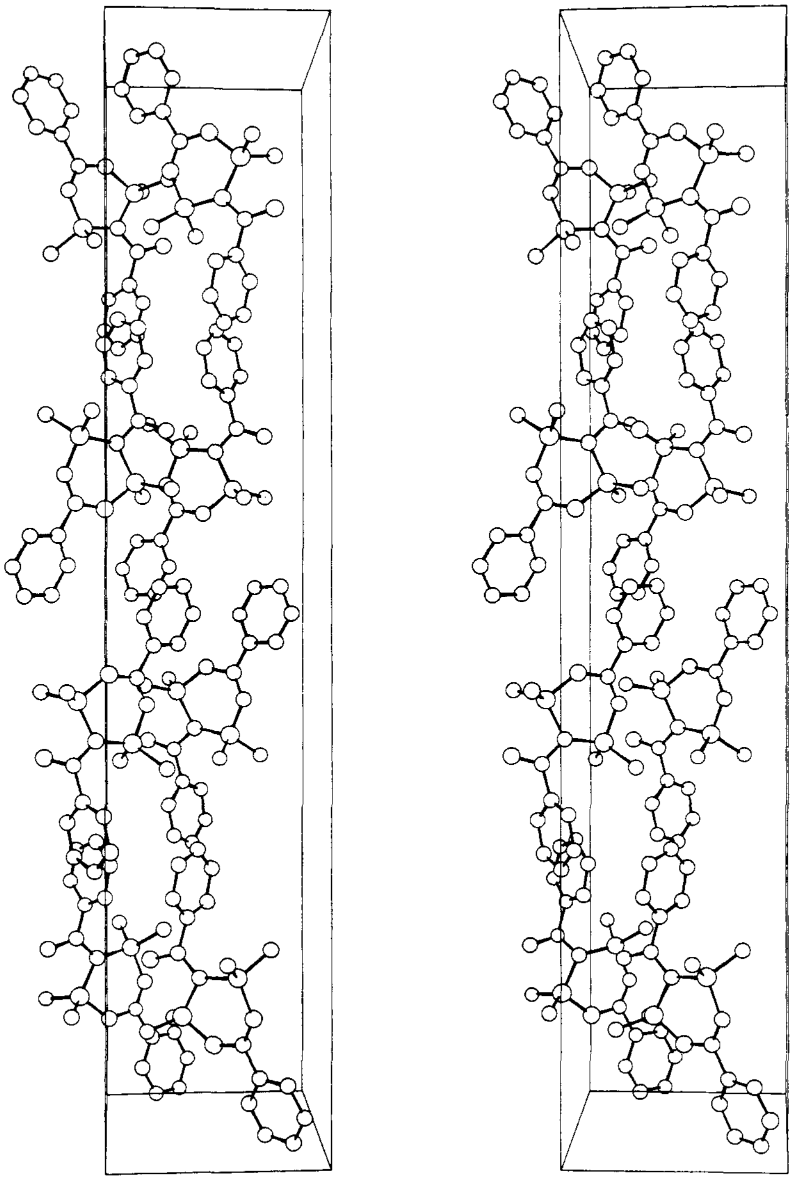

Figure 2. Three-dimensional diagram of the molecular packing in a unit cell of cyclobis(benzamidodimethylsilane) viewed along the negative x axis. The y axis is horizontal and the z axis is vertical. The origin of the box is at 0,0,0.

tion $9.003x - 4.300y - 1.515z = 2.043$. Atoms Si(1), Si(2), and N(1) are 0.011, 0.130, and 0.071 Å below; and O(1), N(2), and C(2) are 0.088, 0.097, and 0.027 Å below this plane, respectively. The internal angles of 103.9 and 106.3° at the Si atoms have already been noted to be somewhat below the tetrahedral value, while the bond angles at the imino nitrogen N(1) and the ether oxygen O(1), 130.2 and 131.4°, respectively, are quite large. Similar trends have been reported for a 3-azacyclotrisiloxane[26] and for other Si, O and Si, N heterocycles.[27] The internal Si–N–Si angle, 120.8 ± 0.3°, is not as large as the 126.3 ± 0.9° reported in the azacyclotrisiloxane structure.

The bond distances in the heterocycle show that the π electrons are, as expected, principally localized between C(1) and N(1), although some delocalization into the adjacent C–O and Si–N bonds may also occur. Surprisingly few localized C=N distances have been measured, but the value of 1.256 ± 0.005 Å obtained here appears to be slightly longer than a C=N bond of 1.23 ± 0.01 Å in a cyclic imino ether.[28] The adjacent C–O bond of 1.366 ± 0.004 Å is substantially shorter than the standard[29] value of 1.43 Å for saturated organic ethers. Other short C–O bonds have been reported for oxygen linkages between unsaturated organic functions and second row elements.[3,30] The scarcity of accurate measurements on suitable reference compounds makes comparison of our Si–N bond lengths with a "standard" Si–N single bond difficult. Indeed, the literature contains a variety of Si–N "single" bonds ranging from 1.69 to 1.78 Å.[31-35] A fairly consistent

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Table III. Root-Mean-Square Thermal Displacements (Å) along Principal Axes[a]

Atom	Axis 1	Axis 2	Axis 3
Si(1)	0.190	0.201	0.228
Si(2)	0.184	0.200	0.235
O(1)	0.189	0.209	0.326
O(2)	0.204	0.235	0.349
N(1)	0.198	0.215	0.232
N(2)	0.190	0.207	0.240
C(1)	0.190	0.206	0.218
C(2)	0.210	0.224	0.242
C(3)	0.209	0.266	0.360
C(4)	0.192	0.264	0.299
C(5)	0.222	0.279	0.289
C(6)	0.212	0.254	0.306
C(7)	0.187	0.222	0.235
C(8)	0.223	0.231	0.254
C(9)	0.223	0.257	0.283
C(10)	0.208	0.248	0.319
C(11)	0.222	0.273	0.321
C(12)	0.217	0.248	0.309
C(13)	0.185	0.200	0.221
C(14)	0.216	0.218	0.234
C(15)	0.210	0.256	0.296
C(16)	0.200	0.251	0.310
C(17)	0.202	0.244	0.312
C(18)	0.209	0.212	0.263
H(8)	0.276		
H(9)	0.316		
H(10)	0.297		
H(11)	0.300		
H(12)	0.319		
H(14)	0.251		
H(15)	0.329		
H(16)	0.298		
H(17)	0.274		
H(18)	0.310		

[a] Ordered on increasing magnitude.

set of values (1.724–1.738 Å) has been reported[31,32] for some planar di- and trisilylamines, but partial Si–N π bonding is thought to be reflected in these distances. In the present structure, the geometry at N(2) is distorted moderately from planarity: the line between C(2) and N(2) forms an angle of 10.9° with the Si(1)–N(2)–Si(2) plane. The Si(1)–N(2) and Si(2)–N(2) distances observed here, 1.788 ± 0.003 and 1.774 ± 0.003 Å, are significantly longer than in the planar silylamines. Our distances, measured with more precision than has been previously reported, suggest that a pure Si–N single bond (without π character) might have a bond distance at or above the upper end of the reported values ($\geq$1.78 Å), and that shorter distances, when found, may indicate π bonding. Such shortening is observed in the Si(1)–N(1) distance of 1.706 ± 0.003 Å. The Si(2)–O(1) distance of 1.670 ± 0.003 Å is slightly longer than a tabulated average[28] of 1.633 ± 0.005 Å for Si–O single bonds. The four Si–CH_3 distances are normal and show very good internal consistency.

The exocyclic N(2)–C(2) and C(2)–O(2) distances of 1.349 ± 0.005 and 1.247 ± 0.005 Å, respectively, are well within the range of values reported for amides[36] (1.288–1.356 Å for C–N and 1.220–1.276 Å for C–O). Carbon–oxygen bonds in amides are appreciably longer than in aldehydes and ketones[29] (1.21 Å), presumably through partial delocalization of electron density into the C–N bonds, which are shortened and which show substantial rotational barriers.[37] Because the high-temperature disilaoxadiazine tautomerization[11] is believed[24] to proceed by attack of carbonyl at Si(1), the barrier about the C(2)–N(2) bond could possibly determine the rate for this process.

The equations of the least-squares planes[25] through the phenyl groups bonded to C(1) and C(2) are $-7.532x + 5.631y + 7.161z = 0.1393$ and $6.510x + 6.489y - 2.967z = 4.585$. The maximum deviations (-0.005 for C(16) and -0.008 for C(9)) indicate that these rings are planar within experimental error. The twelve (n) C–C bond distances (d_i) in these groups have an average value $\bar{d} = 1.381$ Å with a standard error

$$\sigma = \left[\sum_{i=1}^{n}(\bar{d} - d_i)^2/(n - 1)\right]^{1/2}$$

of 0.009 Å, slightly larger than errors of 0.005 to 0.007 Å calculated[18] from the variance–covariance matrix. The hydrogen atoms are reasonably well behaved, with bond distances ranging from 0.93 to 1.14 Å, and isotropic temperature factors between 5.0 and 8.5 Å^2.

The plane of the phenyl bonded to C(1) is twisted by 14.3° with respect to the plane of the heterocycle, while that of the phenyl bonded to C(2) forms an angle of 82.9° with the heterocycle, and of 74.3° with the plane of the amide moiety defined by N(2), C(2), and O(2). The latter value differs widely from the corresponding 26° angle found in benzamide,[38] and might be related to the close C(4)···C(8) intramolecular contact of 3.429 Å.

The crystal packing (Figure 2)[19] shows few unusual features except for the very long c axis of 43.443 Å. The closest intermolecular contact between C atoms is 3.496 Å for C(16)···C(16), between C and N 3.879 Å for C(5)···N(1), and between C and O 3.459 Å for C(8)···O(2).

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