The Role of Molecular Structure in the Disilaoxadiazine Tautomerism

Sir:

The disilaoxadiazine tautomerization was recently discovered by Klebe:[1] derivatives of 2,4-disila-1,3,5-oxadiazine were shown to undergo reversible temperature-dependent isomerizations among the four tautomers A–D at two different exchange rates, r_1 and r_2 (see Figure 1). The mechanism originally proposed[1] for these rearrangements assumed a hexacoordinate configuration for silicon in the transition state; a ground-state geometry for the disilaoxadiazine system where Si(2) of structure A had a tetragonal-pyramidal geometry with a transannular Si(2)–N(1) interaction was also postulated.

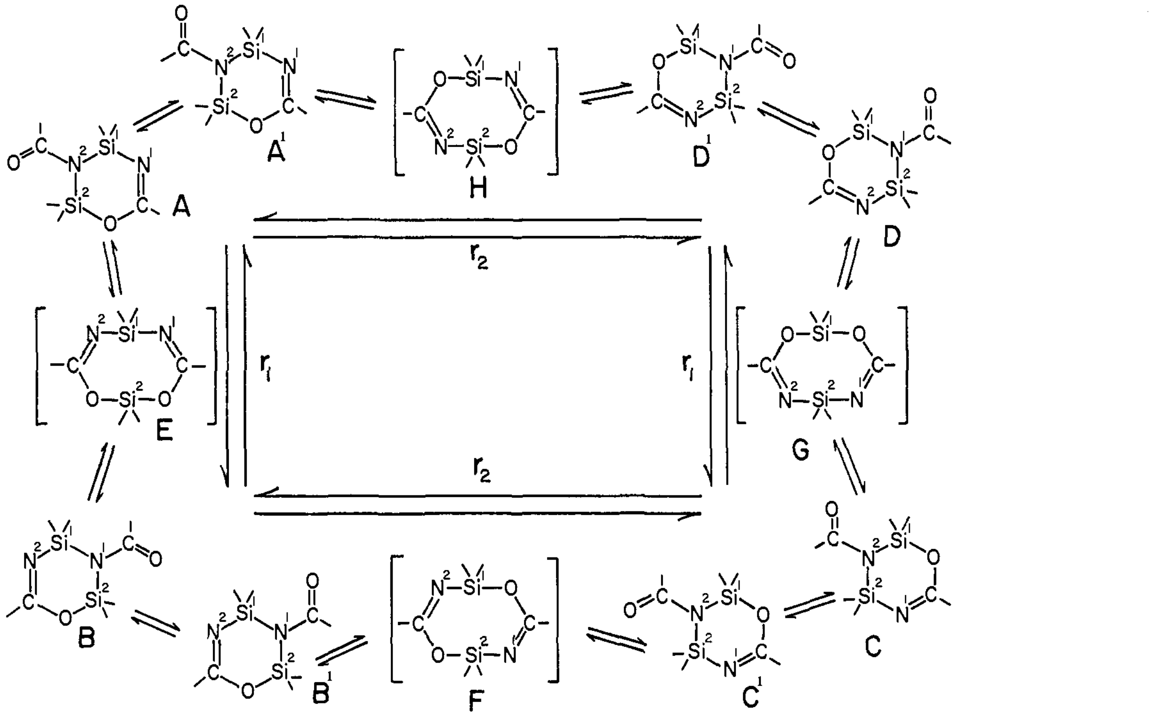
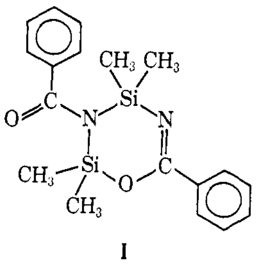


Figure 1. Rearrangements between tautomeric disilaoxadiazine structures. The faster rates, r_1, govern the exchange of chemical environments for the amide functions, while r_2 exchanges the substituents of the silicon atoms.

We report below an X-ray diffraction study of cyclobis(benzamidodimethylsilane) (I) which indeed shows



I

that the ground state of this disilaoxadiazine derivative has an incipiently pentacoordinate silicon atom (in the solid). However, pentacoordination at Si(2) occurs *via* the exocyclic carbonyl oxygen rather than any transannular Si–N interaction. This structure suggests an alternate mechanism for the reported tautomerizations (Figure 1).

Single crystals of I were grown in heptane from a sample prepared by Klebe's method.[1] The crystals belong to the space group Pbca, and the lattice parameters, $a = 10.543 \pm 0.005$, $b = 8.281 \pm 0.003$, and $c = 43.443 \pm 0.020$ Å, give a calculated density of 1.243 g cm^{-3} for $Si_2O_2N_2C_{18}H_{22}$ assuming eight molecules per unit cell. The intensities of 3255 independent reflections were examined using Cu Kα radiation and the 2θ scan mode of a Picker automatic diffractometer. The structure was solved by reiterative application of Sayre's equation[2] on a set of 388 E's greater than 1.5. The correct solution, which assumed the signs of seven reflections, gave a consistency index of $C = \langle|E_h\Sigma_k E_k E_{h-k}|\rangle / \langle|E_h|\Sigma_k |E_{h-k}|\rangle = 0.78$ after six cycles. The heavier atoms were found unambiguously from an E map calculated with the 388 signs. The atoms O(1) and N(1) were originally distinguished by integration of the appropriate regions of an electron density map; their identity is consistent with the final bond distances. Atomic positions and thermal parameters (assuming anisotropic motion for the heavier atoms and isotropic for hydrogens) were refined by full-matrix least squares to a discrepancy index of $R = 0.061$ for the 2376 observed reflections.

The molecular geometry, with calculated bond distances and angles, is shown in Figure 2. Of particular interest is the close interaction (2.613 Å) between the carbonyl oxygen O(2) and Si(2). This distance is substantially less than the sum of Si and O van der Waals radii, 3.3 Å, but is somewhat longer than Si–N

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[1] J. F. Klebe, *J. Am. Chem. Soc.*, **90**, 5246 (1968).

[2] D. Sayre, *Acta Cryst.*, **5**, 60 (1952); R. E. Long, "A Program for Phase Determination by Reiterative Application of Sayre's Equation," Ph.D. Thesis, University of California at Los Angeles, 1965.

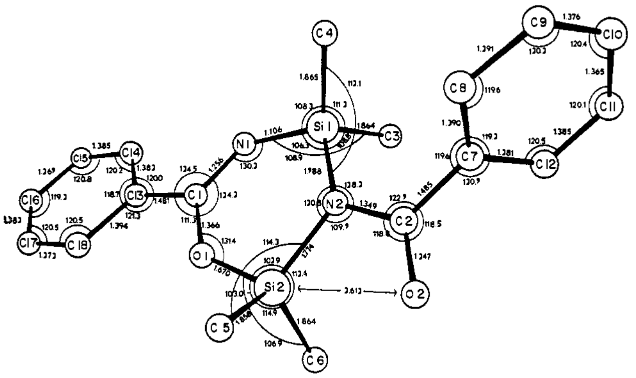

Figure 2. The molecular structure of cyclobis(benzamidodimethylsilane) with bond distances and angles indicated. Typical standard errors, as computed from the variance–covariance matrix, are ±0.003 Å for Si–N, Si–C, and Si–O distances; ±0.006 Å for C–C, C–N, and C–O distances; and ±0.3° for the angles.

distances ranging between 2.116 and 2.344 Å found in caged pentacoordinate silicon compounds.[3] The C(5)–Si(2)–C(6), C(5)–Si(2)–N(2), and C(6)–Si(2)–N(2) angles are seen to have opened considerably from the tetrahedral values, presumably to provide room for the Si···O interaction. The bond angles at N(2) have also distorted in a manner that permits O(2) to approach C(2): the Si(2)–N(2)–C(2) angle has closed down to 109.7°, while Si(1)–N(2)–C(2) has opened up to 128.3°. On the other hand no evidence can be found for a transannular Si(2)···N(1) interaction; this distance is 3.187 Å. The disilaoxadiazine heterocycle is nearly planar with a maximum deviation of 0.13 Å from the least-squares plane.

Some other features of the structure are worth noting. The C(1)–N(1) distance of 1.256 Å shows that these two atoms are in fact doubly bonded.[1] The exocyclic C(2)–N(2) bond length of 1.349 Å and the C(2)-O(2) distance of 1.247 Å are close to the corresponding values in benzamide[4] (1.31 and 1.24 Å). The geometry at Si(1) is more nearly tetrahedral, and the other bond distances and angles in the system are in excellent agreement with literature values.

The incipiently pentacoordinate structure found for I suggests that the lower energy tautomerization governed by r_1 may proceed through the eight-membered cyclic intermediates E and G (Figure 1) *via* carbonyl attack at Si(2)[5] and cleavage of the Si(2)–N(2) bond. The higher temperature r_2 process could then result from an alternative attack by oxygen at Si(1) yielding a different pair of eight-membered cyclic intermediates, F and H. We note that this mechanism differs formally from that postulated by Klebe[1] in that the r_2 process exchanges tautomers A ↔ D and B ↔ C instead of A ↔ C and B ↔ D. The r_1 process may occur at lower energy because the greater inductive ability of oxygen (*vs.* nitrogen) predisposes Si(2) to accept an electron pair However, the rotation barrier[6] about the amidic C(2)–N(2) bond may play a role in limiting the rate of the r_2 process since the carbonyl group must be rotated from a position near Si(2) (structures A–D) to one near Si(1) (structures A′–D′). The mechanism proposed here has the advantage of not requiring hexacoordinate transition states and is consistent with the known ability of eight-membered rings, such as cyclooctatetraenes[7] and diazocines,[8] to undergo transannular rearrangements.

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[3] J. W. Turley and F. P. Boer, *J. Am. Chem. Soc.*, **90**, 4026 (1968); F. P. Boer, J. W. Turley, and J. J. Flynn, *ibid.*, **90**, 5102 (1968). Distances of 2.116 and 2.344 Å were found in *m*-nitrophenyl(2,2′,2″-nitrilotriethoxy)silane and in methyl(2,2′,3-nitrilodiethoxypropyl)silane, respectively (F. P. Boer and J. W. Turley, *ibid.*, in press).

[4] B. R. Penfold and J. C. B. White, *Acta Cryst.*, **12**, 130 (1959).

[5] In this discussion Si(2) is defined as the silicon bonded directly to a nitrogen and an oxygen, and Si(1) is the atom bonded to two nitrogens.

[6] Rotation barriers in amides typically have free energies of 15–25 kcal: M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962).

[7] W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Ann.*, **560**, 11 (1948).

[8] W. Metlesics and L. H. Sternbach, *J. Am. Chem. Soc.*, **88**, 1077 (1966).

F. Peter Boer, François P. van Remoortere
The Dow Chemical Company, Eastern Research Laboratory
Wayland, Massachusetts 01778

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The Norbiphenylene Anion

Sir:

We wish to report evidence for the synthesis of the norbiphenylene anion (I) and the conversion of the latter to an unusual dimeric hydrocarbon on protonation. Anion I is particularly interesting in that it is isoelectronic with biphenylene, from which it differs structurally only by replacement of a benzene ring by a cyclopentadienide ring. Molecular orbital calculations predict a total π energy of 15.025β for this anion.[1]

The previously reported dicarboxylic acid II[2] was converted *via* the liquid diethyl ester III[3] to the crystalline dihydrazide IV, mp 251–252°. Reaction of IV with nitrous acid gave the diazide V, pyrolysis of which in benzyl alcohol yielded the benzylurethan VI, mp 145–146°. Hydrogenolysis of urethan VI gave the diamine VII, which was converted by formaldehyde and formic acid to the tertiary amine VIII, which in turn afforded the dimethiodide IX, mp 311–312°, on

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[1] A. Streitwieser, Jr., and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Pergamon Press, New York, N. Y., 1965.

[2] H. E. Simmons, *J. Am. Chem. Soc.*, **83**, 1657 (1961).

[3] All new compounds gave elemental analyses and spectral data in accord with the assigned structures.