sentially identical with that observed for I (Figure 1). It appears therefore that the C_2 distortion, evident in the 20 K structure of I, is an intrinsic structural characteristic of the $[Fe_6S_6Cl_6]^{2-}$ anion, and lattice effects are not the cause of the observed distortions in the $[Fe_6S_6]^{4+}$ core. This work represents another case in which caution must be exercised in the association of spectroscopic data obtained at cryogenic temperatures with structure and function characteristics obtained at ambient temperatures.

Acknowledgment. We acknowledge the generous support of this research by a grant from the National Institutes of Health, D.C. (GM-26671) and C.E.S. (GM-35329-02)

Supplementary Material Available: Tables of crystal and refinement data, positional and thermal parameters, and intramolecular distances from the 20 K structure (9 pages); listing of observed and calculated structure factors for $Fe_6S_6Cl_6^{2-}$ (24 pages). Ordering information is given on any current masthead page.

Disilaoxiranes: Synthesis and Crystal Structure

Howard B. Yokelson, Anthony J. Millevolte,
Gregory R. Gillette, and Robert West*

Department of Chemistry
University of Wisconsin—Madison
Madison, Wisconsin 53706

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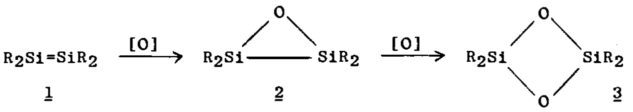
Since the discovery of the first stable disilenes in 1981,[1] studies on the reactivity of the silicon–silicon double bond have revealed a rich and diverse chemistry.[2] It is now well established that the disilenes **1** react readily with triplet oxygen either in solution or



(a) R = Mes = 2,4,6-trimethylphenyl

(b) R = Xyl = 2,6-dimethylphenyl

(c) R = Dmt = 2,6-dimethyl-4-tert-butylphenyl

the solid state to give the 1,3-cyclodisiloxanes **3**.[3] A monooxygenated adduct, the disilaoxirane **2**, was identified as a minor product in the low-temperature oxidation of (*E*)-1,2-dimesityl-1,2-di-*tert*-butyldisilene.[4] We now report the synthesis of several tetraaryldisilaoxiranes, prepared by the reaction of tetraaryldisilenes **1a–c** with dinitrogen oxide as well as the molecular structure of tetramesityldisilaoxirane, **2a**.

When a stream of dinitrogen oxide was bubbled through a bright yellow solution of disilene **1a** in benzene at room temperature, the solution decolorized slowly. Only a single new resonance (δ −27.2) was observed in the silicon-29 spectrum of the reaction mixture. Crystals of the benzene solvate of **2a** ($C_{36}H_{44}Si_2O{\cdot}C_6D_6$, m = 633.0) suitable for X-ray crystallographic analysis were obtained from this reaction mixture on standing.[5] Disilaoxirane **2a** is inert to further oxidation by dinitrogen oxide, even when heated in benzene solution at 80 °C for several days. However, on exposure to air **2a** undergoes further oxidation to the cyclodisiloxane **3a** with a half-life in solution of several hours at 20 °C. As was noted for their disilene precursors, the air stability of the disilaoxiranes is greatly enhanced in the solid state.

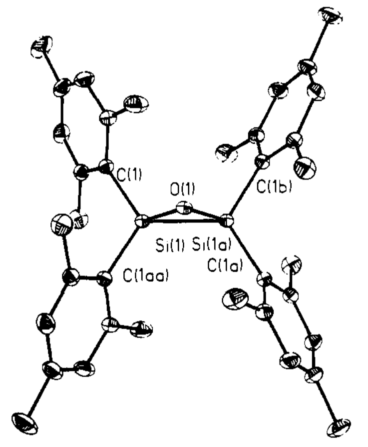


Figure 1. Molecular structure of **2a**. (Hydrogens omitted for clarity.) Bond lengths (pm) are as follows: Si(1)–Si(1a), 222.7 (2); Si(1)–C(1), 187.8 (2); Si(1)–O(1), 173.3(3). Bond angles (deg) are as follows: Si(1)–Si(1a)–O(1), 50.0 (1); Si(1)–O(1)–Si(1a); 80.0 (2).

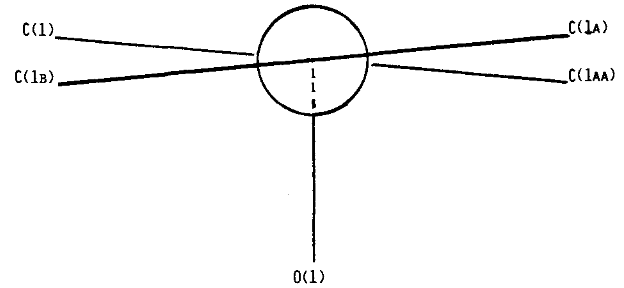


Figure 2. Newman projection of **2a** along the Si–Si axis showing the twist angle. The numbering scheme is shown in Figure 1; Si(1) is in the back of Si(1a).

The X-ray crystal structure of **2a** was solved by direct methods and refined by blocked-cascade least-squares refinement[6] based on F with use of 1801 data with $F_o > 3\sigma(F_o)$. Final discrepancy indices are R1 = 0.060, R2 = 0.069, GOOF = 1.71.[7] Figure 1 shows an ORTEP diagram of **2a**. The molecule possesses a twofold rotation axis which passes through the oxygen and bisects the silicon–silicon bond. It is remarkable that the silicon and the carbon atoms directly attached to each silicon are coplanar. That is, the sum of the bond angles C–Si–Si′, C′–Si–Si′, C–Si–C′ about each silicon atom is 360°. The torsional distortion along the silicon–silicon axis results in a twist angle of 10°, as illustrated

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(1) (a) West, R.; Fink, M. J.; Michl, J. *Science* (Washington, D.C.) **1981**, *214*, 1343. (b) Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J. *J. Am. Chem. Soc.* **1982**, *104*, 1150.

(2) For reviews of disilenes, see: (a) West, R. *Angew. Chem.* **1987**, in press. (b) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419–509. (c) West, R. *Pure Appl. Chem.* **1984**, *56*, 163–173.

(3) (a) Fink, M. J.; De Young, D. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 1070–1071. (b) Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1984**, *106*, 822–823. (c) Michalczyk, M. J.; Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1986**, *5*, 531–538.

(4) (a) Michalczyk, M. J.; West, R.; Michl, J. *J. Chem. Soc. Chem. Commun.* **1984**, 1525–1526. (b) The formation of a tetraalkyldisilaoxirane has been proposed as a reactive intermediate in the photolysis of hexaneopentyltrisilaoxetane, see: Watanabe, H.; Tabei, E.; Goto, M.; Nagai, Y. *Ibid.* **1987**, 522–523.

(5) For compund **2a**: mp 187–190 °C; ^{1}H (270 MHz, C_6D_6) δ 2.02 (s, 12 H), 2.56 (s, 24 H), 6.61 (s, 8 H); ($CDCl_3$) δ 2.21 (s, 12 H), 2.31 (s, 24 H), 6.68 (s, 8 H); ^{29}Si NMR (71.5 MHz, C_6D_6) δ −26.92; IR (KBr, cm^{-1}) 3000, 1610, 1460, 1275, 1070, 1020; UV (THF) λ_{max} 235, 293, 341 (sh); mass spectrum (30 eV) calcd for $C_{36}H_{44}Si_2O$ m/e 548.2931, found m/e 548.2930.

(6) SHELXTL, Nicolet X-ray Instruments, Madison WI, 1985.

(7) (a) Four molecules of **2a** and four molecules of benzene-d_6 crystallize in the orthorhombic space group (*Ccca*) with cell dimensions as follows: a = 12.181 (2) Å, b = 19.736 (4) Å, c = 14.671 (3) Å, (T = 150 ± 2 K), λ(Mo Kα) = 0.71073 Å; V = 3046.2 Å^3, D(calcd) = 1.21 g/cm^3, and Z = 4. Each molecule is required to possess crystallographic symmetry, and **2a** is located on a 222 site at (0 $^1/_4$ $^3/_4$) with the Si–Si bond along one twofold axis, and the bridging oxygen atom on one of the twofold axes perpendicular to the Si–Si bond axis. Thus there are two positions for the oxygen atom, and refinement of the occupancy factor for the oxygen atom showed the unique portion to be $^1/_4$ occupied, confirming the oxygen to silicon ratio in the unit cell is 1:2; subsequently this occupancy factor was fixed at 0.25. Each of the (ordered) benzene molecules is located on a 222 site. (b) Tables of the final atomic coordinates, anisotropic thermal parameters, and selected distances and angles are given as Supplementary Material.

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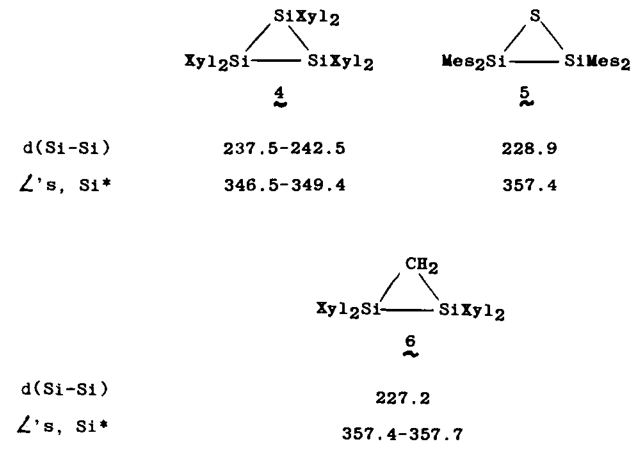
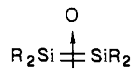
Chart I



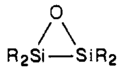
*Sum of ∠'s C-Si-Si', C'-Si-Si', C-Si-C'

in Figure 2. Another surprising feature of the disilaoxirane structure **2a** is the short Si–Si distance, only 222.7 pm, which is more similar to that of a Si–Si double bond (216 pm) than a normal Si–Si single bond (235 pm).

In consideration of the both the short Si–Si bond length and the planar conformation of atoms at silicon, we propose a bonding model in which a significant amount of the double bond character of the disilene is retained in the oxirane. This view is further supported by the silicon-29 NMR coupling constant, ^1J(Si–Si), for an unsymmetrical oxirane, $Xyl_2Si(O)SiR_2$, where R = 2,6-dimethyl-4-*tert*-butylphenyl. The measured value of 99 Hz is again intermediate between that for tetraaryldisilenes (155 Hz)[8] and organodisilanes (85 Hz).[9] All these facts suggest that the disilaoxiranes have some of the character of disilene–oxygen π-complexes A as well as oxiranes B.



A



B

This interpretation of the data is consistent with a theoretical treatment that Cremer[10] has developed to describe the continuum between three-membered rings (3MR) and π-complexes in the ethylene system, C–C–X. This model predicts increased π-complex character, and thus a shortening of the olefinic bond, as the electron acceptor ability of X toward the π-bond increases. The Cremer model may also apply to 3MR containing two silicon atoms, $\overline{\mathrm{Si{-}Si{-}X}}$. In **2a**, the Si–Si π-bond should be a powerful electron donor and the oxygen atom an excellent electron acceptor, leading to a large amount of charge transfer and hence significant π-complex character.[11]

Related compounds with known structures include cyclotrisilane **4**,[1b] disilathiirane **5**[12] and disilacyclopropane **6**.[13] (Chart I). Compounds **5** (X = S) and **6** (X = CH_2) may represent intermediate cases, with shortening of the Si–Si bond and flattening of the configuration about silicon but less extreme than in **2a**.

Acknowledgment. We thank Drs. L. F. Dahl and K. J. Haller for their assistance with the X-ray crystallography. This work was supported by the Air Force Office of Scientific Research, Air Force Systems Command, USAF under Contract no. F49620-86-C-0010 and the National Science Foundation, Grant no. CHE-8318810-02.

Supplementary Material Available: Tables of crystallographic data, atomic coordinates and anisotropic thermal parameters, and bond distances and angles (4 pages); listing of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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[11] However, recent MO calculations on unsubstituted disilaoxiranes are consistent with an oxirane-like structure, with strong bending of the Si–Si σ-bond. Boatz, J. A.; Gordon, M. S., submitted for publication.

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Molecular Recognition: Watson–Crick, Hoogsteen, and Bifurcated Hydrogen Bonding in a Model for Adenine Recognition

Julius Rebek, Jr.,* Ben Askew, Pablo Ballester, Chris Buhr, Ana Costero, Sharon Jones, and Kevin Williams

Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

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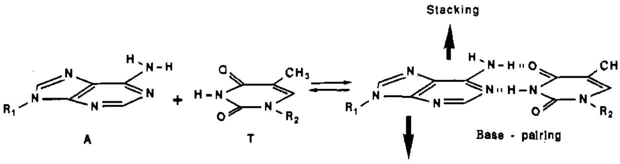
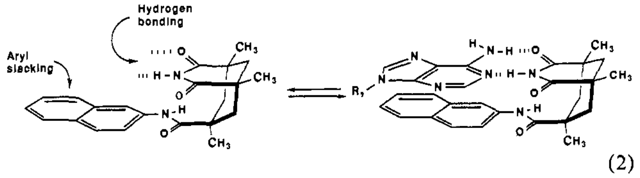
The principal intermolecular forces that stabilize double-stranded nucleic acids involve Watson–Crick hydrogen bond base-pairing sense and aryl stacking interactions between adjacent base pairs[1] (eq 1). In an effort to dissect the relative contributions of these forces to the overall stability, we recently introduced a model system in which stacking and hydrogen bonding converge from perpendicular directions to recognize and complex adenine derivatives[2] (eq 2). Previously we explored the effects of surface area and molecular chelation on the binding event, and in this communication we are concerned with the geometric details involved in the hydrogen bonds to adenine.



(1)



(2)

Spectroscopic methods involving NOE techniques[3] were used to map out the geometries in the intermolecular complex. Resonance assignments were made for both anthraquinone **1** and 9-ethyladenine (**2**), and, following the determination of relaxation times, pulse sequences were designed for experiments involving intermolecular NOE (heteronuclear and homonuclear) in the complex. In $CDCl_3$ at ambient temperature the association constant is known[2] to be $K_a = 220\ M^{-1}$, and at typical NMR concentrations roughly 50% of the components are bound as a 1:1 complex. The K_a's are determined by Hildebrand–Benesi or Eadie[4] treatment of the binding data in the range of 0.2–15 equiv

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[1] Saenger, W. *Principles of Nucleic Acid Structure*; Springer-Verlag: New York, 1984; Chapter 6.

[2] Rebek, J., Jr.; Askew, B.; Buhr, C.; Jones, S.; Nemeth, D.; Williams, K.; Ballester, P. *J. Am. Chem. Soc.* **1987**, *109*, 5033–5035. The K_a for eq 2 is erroneously reported as 120 M^{-1} in the previous paper.

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