Structural Studies of Pentacoordinate Silicon. III. Tetramethylammonium Bis(*o*-phenylenedioxy)phenylsiliconate[1]

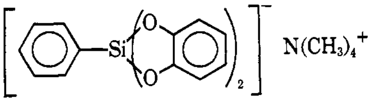
F. P. Boer, J. J. Flynn, and J. W. Turley

Contribution from The Dow Chemical Company, Eastern Research Laboratory, Wayland, Massachusetts 01778, and Chemical Physics Research Laboratory, Midland, Michigan 48640. *Received June 28, 1968*

Abstract: The crystal and molecular structure of the salt $C_6H_5Si(O_2C_6H_4)_2^-N(CH_3)_4^+$ has been determined by a single crystal three-dimensional X-ray diffraction study. This material crystallizes in the noncentric orthorhombic space group Pnn2, and there are two pairs of ions per unit cell of dimensions $a = 9.166 \pm 0.004$, $b = 12.912 \pm 0.006$, and $c = 8.664 \pm 0.003$ Å. Each ion lies on a crystallographic twofold axis. The intensity data were collected on a Picker automatic diffractometer, and the structure was solved by analysis of the Patterson function. Least-squares refinement including anisotropic thermal motion gave a final reliability index $R_1 = 7.0\%$ for 789 reflections. The structure determination confirms the hypothesis that the silicon atom in the anion is pentacoordinate, and shows the geometry of coordination to be a distorted trigonal bipyramid. One oxygen atom of each five-membered ring occupies an equatorial position, while the other is at an axial site. The axial Si–O bonds (1.794 Å) are significantly longer than the equatorial ones (1.700 Å). The O–Si–O angles in the five-membered rings are 87.6°, while the angle formed by the two axial oxygens (167.7°) is bent considerably from the 180° characteristic of an ideal trigonal bipyramid. The carbon–oxygen bonds in the five-membered rings are surprisingly short (1.34 Å), and an unusually short bond distance (1.288 Å) is also found in the arylene rings.

Stable salts of bis(*o*-arylenedioxy)organosiliconic acids were first prepared from alkoxysilanes and catechols by Frye,[2] who proposed that the silicon atoms in the anions were pentacoordinate. The principal evidence for this assertion was the unusually low stretching frequency of the silicon–oxygen bonds observed in the infrared spectrum. Because pentacoordinate silicon intermediates are a fundamental postulate in the theory of organosilicon displacement reactions,[3] the existence of stable pentacoordinate silicon compounds has elicited considerable interest, and the structures of three such compounds have now been directly established.[1,4]

The present three-dimensional X-ray study of tetramethylammonium bis(*o*-phenylenedioxy)phenylsiliconate



was undertaken to confirm Frye's hypothesis,[2] and to determine the geometry of coordination at silicon. The structure is novel in at least two respects: it represents the first study of pentacoordinate silicon in an anion; and it is an example of a pentacoordinate silicon compound without silicon–nitrogen bonds.

A particularly interesting feature of the structure is the substantial distortion of the molecular geometry from an ideal trigonal bipyramid toward a tetragonal pyramid. Just such a distortion is postulated to occur in the pseudorotation mechanism proposed by Westheimer[5,6] to occur in the pentacoordinate intermediates in phosphate ester hydrolysis. These proposed intermediates are crucial to an understanding of how the hydrolysis of strained five-membered cyclic esters can be enormously accelerated (with respect to unstrained compounds) without ring opening. Since this theory is also believed to account for the rapid hydrolysis of certain highly strained silicon compounds,[3] we feel that the present structure tends to support the pseudorotation hypothesis.

Experimental Section

A sample of tetramethylammonium bis(*o*-phenylenedioxy)phenylsiliconate recrystallized from acetonitrile was kindly supplied to us by Frye. The crystals were of somewhat irregular shape, but tended to be elongated in the *a* direction. A roughly cylindrical specimen of approximate radius 0.1 mm and length 1.2 mm was selected for further investigation and mounted with its long axis parallel to the spindle of a Weissenberg goniometer to determine the space group and preliminary lattice constants. Accurate lattice constants for the orthorhombic unit cell, $a = 9.166 \pm 0.004$, $b = 12.912 \pm 0.006$, and $c = 8.664 \pm 0.003$ Å, were obtained from least-squares refinement of the setting angles of 12 reflections on a Picker automatic four-circle diffractometer. Cu Kα radiation ($\lambda = 1.5418$ Å) was used. The reflection conditions $0kl{:}k + l = 2n$ and $h0l{:}h + l = 2n$ and the reciprocal lattice symmetry D_{2h} are consistent with the space groups Pnn2 ($C_{2v}{}^{10}$) or Pnnm ($D_{2h}{}^{12}$).

An experimental density of $\rho = 1.281 \pm 0.001$ g cm^{-3} was measured by the density gradient technique using potassium tartrate solutions calibrated with binary solutions of carbon tetrachloride and carbon disulfide. This value is in agreement with the cal-

---

[1] (a) Paper I: J. W. Turley and F. P. Boer, *J. Amer. Chem. Soc.*, **90**, 4026 (1968); (b) paper II: F. P. Boer, J. W. Turley and J. J. Flynn, *ibid.*, **90**, 5102 (1968).

[2] C. L. Frye, *ibid.*, **86**, 3170 (1964).

[3] L. H. Sommer, "Stereochemistry Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965; L. H. Sommer, O. F. Bennett, P. G. Campbell, and D. R. Weyenberg, *J. Amer. Chem. Soc.*, **79**, 3295 (1957); L. H. Sommer and O. F. Bennett, *ibid.*, **79**, 1008 (1957); L. H. Sommer, W. P. Barie, Jr., and D. R. Weyenberg, *ibid.*, **81**, 251 (1959).

[4] R. Rudman, W. C. Hamilton, S. Novick, and T. D. Goldfarb, *ibid.*, **89**, 5157 (1967).

[5] E. A. Dennis and F. H. Westheimer, *ibid.*, **88**, 3432 (1966).

[6] F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).

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

Atom	x/a	y/b	z/c	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Si	0.0	0.0	0.0	81 (3)	44 (1)	113 (4)	−2 (2)		
O(1)	−0.1099 (5)	0.0890 (4)	−0.0862 (7)	123 (6)	62 (3)	143 (8)	−1 (3)	−9 (6)	0 (4)
O(2)	0.1469 (5)	0.0906 (3)	−0.0221 (8)	109 (6)	54 (3)	176 (9)	−7 (3)	7 (10)	16 (5)
N	0.0	0.5	0.2380 (10)	105 (11)	106 (7)	129 (13)	−13 (8)		
C(1)	0.0	0.0	0.2179 (12)	96 (12)	63 (6)	139 (5)	6 (8)		
C(2)	0.0384 (8)	0.0888 (6)	0.2990 (9)	155 (12)	60 (5)	158 (13)	−3 (5)	−36 (10)	−15 (6)
C(3)	0.0350 (10)	0.0886 (9)	0.4614 (11)	157 (13)	113 (8)	166 (15)	20 (8)	−22 (10)	−27 (8)
C(4)	0.0	0.0	0.5390 (12)	155 (18)	135 (12)	103 (16)	22 (14)		
C(5)	−0.0432 (8)	0.1780 (5)	−0.1255 (10)	114 (9)	49 (4)	137 (10)	−1 (5)	0 (8)	7 (6)
C(6)	0.1038 (8)	0.1787 (5)	−0.0903 (9)	136 (10)	49 (4)	130 (11)	4 (5)	19 (9)	6 (6)
C(7)	0.1921 (10)	0.2620 (5)	−0.1232 (12)	190 (13)	48 (4)	205 (14)	−8 (6)	46 (12)	−3 (7)
C(8)	0.1165 (13)	0.3492 (6)	−0.2021 (14)	309 (22)	54 (5)	237 (18)	1 (8)	56 (18)	25 (8)
C(9)	−0.0200 (11)	0.3497 (7)	−0.2374 (14)	184 (16)	75 (6)	231 (16)	11 (7)	−8 (15)	21 (8)
C(10)	−0.1114 (11)	0.2607 (6)	−0.2001 (11)	233 (16)	60 (5)	200 (15)	17 (7)	−24 (13)	13 (7)
C(11)	−0.1346 (15)	0.4760 (14)	0.1498 (18)	238 (23)	345 (22)	253 (23)	−142 (19)	−115 (30)	64 (20)
C(12)	0.0265 (14)	0.4126 (11)	0.3399 (29)	206 (20)	162 (13)	885 (79)	−19 (12)	−130 (31)	229 (29)

[a] The anisotropic thermal parameters are in the form exp $(-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}))$. [b] Standard errors, given in parentheses, are multiplied by 10^4.

culated density of 1.281 g cm^{-3} assuming a molecular weight of 395.531 and $Z = 2$. We therefore conclude that the ions must use the crystallographic C_2 axes of the noncentric space group Pnn2. Pnnm is excluded because it requires the ions to exhibit C_{2h} symmetry.

The intensity data were collected using the 2θ scan mode of the diffractometer with Ni-filtered Cu Kα radiation. The X-ray tube was placed at a 3° take-off angle, and a detector aperture 4.0 mm square was positioned 30 cm from the sample. Scan angles from 2.0 to 2.6° were employed over the range (0–130°) of 2θ examined. The scan speed was 2°/min. Background counts of 15 sec were taken at each end of the scan by the stationary crystal–stationary counter technique. A data set comprising 918 of the 1256 independent reflections in the Cu Kα sphere was observed. An error

$$\sigma(I) = [(0.05I)^2 + N_0 + k^2N_b]^{1/2}$$

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. Here N_0 is the gross count, N_b is the background count, and k is the ratio of scan time to background time. The intensities of the 128 measured reflections for which $\sigma(I)/I > 0.3$ were judged to be too weak to be statistically significant, and were omitted from the analysis. Absorption corrections were neglected, but the low linear absorption coefficient of 12.2 cm^{-1} suggests that transmission factors range between 0.75–0.85. Finally, the data were corrected for Lorentz and polarization effects, and an absolute scale factor and an over-all temperature parameter were computed by Wilson's method.

Structure Determination and Refinement

A three-dimensional normal-sharpened Patterson function was computed.[7] The structure was apparent from examination of this map, except for a twofold ambiguity in the relative orientation of the phenyl group to the arylene rings, and a fourfold ambiguity in the relative position of the tetramethylammonium ion. This ambiguity was readily resolved in an electron density map based on phases calculated[8] from the positions of Si, O(1), O(2), C(1), C(4), and C(5) through C(10). The positional parameters of the 16 heavy atoms in the resulting structure were then varied in two cycles of full-matrix least-squares refinement.[8] The reliability index $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$ decreased from an initial value of 0.22 to 0.18, while the value R_2

$$R_2 = \{\sum w[F_0 - F_c]^2/\sum wF_0^2\}^{1/2}$$

decreased from 0.32 to 0.25. Two more cycles of least squares in which isotropic temperature factors were also permitted to vary reduced R_1 to 0.10 and R_2 to 0.15.

At this point we calculated an electron density map[7] from which the 16 heavy atoms were subtracted. The highest peaks in this map were of the order of 0.65 e/Å^3. Considerable residual density appeared in the vicinity of the tetramethylammonium ion. The absence of any high peaks of spherical shape suggested, however, that a disordered model for the cation was inappropriate, and the marked reduction of these higher density regions after subsequent anisotropic refinement indicated that they originated largely from thermal motion. Seven peaks, ranging in height from 0.16 to 0.37 e/Å^3 were observed in positions chemically reasonable for hydrogen atoms of the anion. Not all of these peaks were well defined. An attempt was nevertheless made to refine their positions and temperature factors, but some of these atoms moved to chemically unreasonable positions and/or refined to strange temperature factors (while others behaved reasonably well). Therefore, we omitted the hydrogens from subsequent structure factor calculations.

Refinement was continued assuming anisotropic thermal parameters for the 16 heavy atoms; after one cycle R_1 dropped to 0.081 and R_2 to 0.111. At this point the (320) reflection, for which $\Delta F/\sigma$ was greater than 30, was omitted from the analysis. Some high-intensity low-order reflections, such as (002), (200), and (110) appeared to be affected by extinction, but the apparent errors were sufficiently small that we chose not to apply a correction. After three more cycles of least squares, the disagreement factors converged to the final values of $R_1 = 0.070$ and $R_2 = 0.088$ for 789 reflections. The mean parameter shift in the final cycle was 0.05 σ. Final atomic parameters and their standard deviations as calculated in the last least-squares cycle are listed in Table I. A table of observed and calculated structure factors is available on request.[9]

(7) Fourier calculations were performed using program B-149 (Argonne National Laboratory), a version of Shoemaker, Sly, and Van den Hende's ERFR-2 by J. Gvildys.

(8) (a) Least-squares and structure factor calculations were performed using ANL-FLS-14E, J. Gvildys's version of Busing, Martin, and Levy's OR-FLS. (b) Atomic scattering factors were taken from "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 201.

(9) Material supplementary to this article has been deposited as Document No. NAPS-00085 with the ASIS National Auxiliary Publication Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. 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.

Table II. Hydrogen Atom Positions as Determined from Final Electron Density Map

Atom	x/a	y/b	z/c	Height, e/Å^3	Bond length, Å
H(2)	0.092	0.142	0.240	0.28	0.98
H(3)	0.058	0.158	0.517	0.62	1.04
H(4)	0.0	0.0	0.620	0.37	0.70
H(7)	0.290	0.273	−0.080	0.25	0.98
H(8)	0.197	0.403	−0.233	0.25	1.05
H(9)	Not well resolved			<0.12	. . .
H(10)	−0.220	0.253	−0.240	0.28	1.06

Table III. Distances and Angles[a]

A. Bond Distances, Å			
Si-O(1)	1.700 (9)	C(5)-C(6)	1.381 (11)
Si-O(2)	1.794 (5)	C(6)-C(7)	1.375 (10)
Si-C(1)	1.888 (11)	C(7)-C(8)	1.489 (14)
O(1)-C(5)	1.347 (8)	C(8)-C(9)	1.288 (15)
O(2)-C(6)	1.342 (8)	C(9)-C(10)	1.459 (12)
C(1)-C(2)	1.390 (10)	C(10)-C(5)	1.396 (11)
C(2)-C(3)	1.408 (11)	N-C(11)	1.484 (15)
C(3)-C(4)	1.365 (13)	N-C(12)	1.453 (17)
B. Bond Angles,[b] deg			
O(1)-Si-O(1)	127.9 (0.4)	O(1)-C(5)-C(6)	113.1 (0.6)
O(1)-Si-C(1)	116.0 (0.5)	O(2)-C(6)-C(5)	112.3 (0.6)
O(1)-Si-O(2)	87.6 (0.4)	C(5)-C(6)-C(7)	122.2 (0.7)
O(1)-Si-O(2)′	87.1 (0.4)	C(6)-C(7)-C(8)	114.4 (0.8)
O(2)-Si-O(2)′	167.7 (0.4)	C(7)-C(8)-C(9)	124.4 (0.9)
O(2)-Si-C(1)	96.1 (0.7)	C(8)-C(9)-C(10)	120.1 (0.9)
Si-C(1)-C(2)	120.4 (0.6)	C(9)-C(10)-C(5)	116.6 (0.8)
C(2)-C(1)-C(2)′	119.3 (1.0)	C(10)-C(5)-C(6)	122.3 (0.7)
C(1)-C(2)-C(3)	119.9 (1.0)	C(11)-N-C(12)	106.8 (0.9)
C(2)-C(3)-C(4)	119.9 (1.0)	C(11)-N-C(12)′	109.6 (1.1)
C(3)-C(4)-C(4)′	121.0 (1.0)	C(11)-N-C(11)	118.1 (1.3)
Si-O(1)-C(5)	114.8 (0.5)	C(12)-N-C(12)′	105.2 (2.1)
Si-O(2)-C(6)	112.2 (0.5)		

[a] Standard errors, in parentheses were computed from the variance-covariance matrix obtained in the final cycle of least squares. [b] Primes indicate atoms related by the crystallographic twofold axes.

Table IV. Root-Mean-Square Thermal Displacements along Principal Axes[a,b]

Atom	Axis 1, Å	Axis 2, Å	Axis 3, Å
Si	0.184 (3)	0.195 (3)	0.207 (3)
O(1)	0.222 (7)	0.230 (6)	0.239 (7)
O(2)	0.202 (6)	0.216 (7)	0.267 (7)
N	0.209 (11)	0.221 (11)	0.301 (11)
C(1)	0.200 (13)	0.230 (12)	0.233 (12)
C(2)	0.203 (10)	0.240 (9)	0.280 (10)
C(3)	0.235 (11)	0.252 (10)	0.327 (11)
C(4)	0.198 (15)	0.250 (15)	0.343 (16)
C(5)	0.201 (8)	0.220 (9)	0.231 (9)
C(6)	0.200 (10)	0.213 (10)	0.252 (10)
C(7)	0.199 (9)	0.247 (11)	0.314 (11)
C(8)	0.203 (11)	0.290 (12)	0.376 (14)
C(9)	0.236 (11)	0.284 (12)	0.305 (11)
C(10)	0.214 (10)	0.276 (11)	0.322 (11)
C(11)	0.215 (15)	0.328 (16)	0.579 (18)
C(12)	0.250 (15)	0.298 (14)	0.639 (27)

[a] Ordered on increasing magnitude. [b] Standard errors, multiplied by 10^3, are given in parentheses as computed from the variance–covariance matrix obtained in the final least-squares cycle.

A final difference map again revealed the positions of most of the seven unique hydrogen atoms of the anion. The largest peak in the map, of height 0.37 e/Å^3, was quite close to the expected position for a hydrogen atom bonded to C(4), although at too short a bond distance. No peak could be seen for H(9). The positions, estimated bond lengths, and map heights for the hydrogen atoms are listed in Table II. Not unexpectedly, hydrogen atoms of the cation could not be resolved.

Bond distances and angles with standard deviations calculated[10] from the variance–covariance matrix obtained in the final cycle of least squares are shown in Table III, and Table IV lists the root-mean-square components of thermal displacement along the principal axes, as defined by the anisotropic thermal parameters. The directions of these axes may be inferred from Figure 1, in which the three-dimensional structure[11] is shown using 50% probability ellipsoids to represent the thermal motion.

Discussion of the Structure

The geometry at the silicon atom is probably best described as a distorted trigonal bipyramid, although the distortion is of an interesting type not previously encountered in pentacoordinate silicon structures. The equatorial phenyl substituent is collinear with the crystallographic twofold axis, while one oxygen of each five-membered ring occupies an axial, and the other an equatorial, site (Figure 1). The phenylenedioxy moieties are, of course, crystallographically equivalent by the twofold axis. This conformation is in accord with the general rule[12] that the most electronegative ligands (here the oxygen atoms) will occupy the axial positions of trigonal bipyramidal structures.

The distortion in the structure is indicated by the reduction of the angle, O(2)–Si–O(2)′, between the axial oxygens from an ideal 180 to 167.7°. The direction of this distortion produces an increase in the angles

---

(10) J. Gvildy's version (ANL Program Library B-115) of Busing, Martin, and Levy's FORTRAN function and error program, OR-FFE, was used.

(11) ORTEP is a FORTRAN thermal ellipsoid plot program by C. K. Johnson, Oak Ridge National Laboratory, Oak Ridge, Tenn.

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

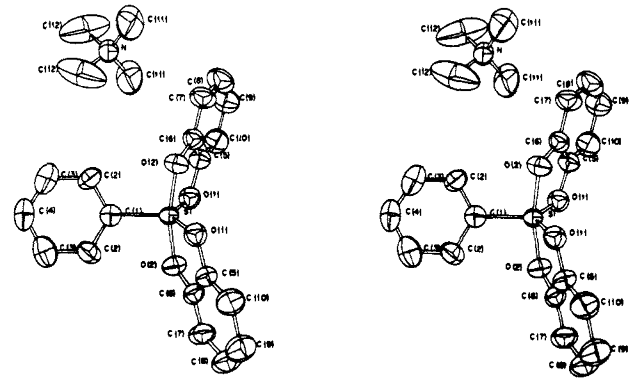
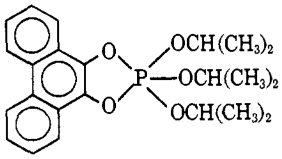


Figure 1. Three-dimensional view of the configuration of tetramethylammonium bis(*o*-phenylenedioxy)phenylsiliconate, indicating the ellipsoids of thermal motion. The crystallographic twofold axes are horizontal.

between the axial oxygens and the equatorial phenyl group (to 96.7°). On the other hand, the angle between the equatorial oxygens O(1)–Si–O(1)′ increases from an ideal 120 to 127.9°. As mentioned above, these distortions from ideality are particularly interesting because of the proposed role[5,6] of pseudorotation[13] processes in the hydrolysis of certain phosphorus and silicon[3] derivatives. In such mechanisms, pairs of substituents on a trigonal bipyramidal intermediate interchange axial and equatorial sites by passing through a transition state that is assumed to be a tetragonal pyramid. The distortions in the present structure are in the correct direction for a trigonal bipyramid undergoing pseudorotation with the phenyl group as pivot: a tetragonal pyramid would be achieved when the angles O(1)–Si–O(1)′ and O(2)–Si–O(2)′ become equal.

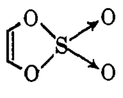
On this basis, the angular distortions have brought the structure about a third of the way from an ideal trigonal bipyramid to the assumed transition state. Another measure is the deviation (0.27 Å) of the individual atoms from a least-squares plane through the four oxygens. This number is of the same order as the rms amplitudes of thermal vibration for these atoms (Table IV). We note also that the angles in the five-membered rings, 87.6°, are unusually low; presumably such an angle can be achieved with substantially less strain in pentacoordinate, *vs.* tetracoordinate, compounds. By contrast to this structure, recent X-ray studies[14] of a pentaoxyphosphorane (I), an analog of the pentacoordinate intermediate in phosphate ester hydrolysis, indicate the phosphorus to be coordinated as a nearly ideal trigonal bipyramid.



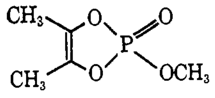
I

The Si–O bond distances obey a second general rule[13] for trigonal bipyramidal coordination: that axial bonds (here 1.794 ± 0.005 Å) are significantly longer than equatorial (1.700 ± 0.009). Both of the unique Si–O bonds are, moreover, substantially longer than values[15–20] previously reported for tetrahedral silicon (1.61 to 1.67 Å) or for pentacoordinate silicon[1] (1.635–1.665 Å). The Si–C bond length (1.888 ± 0.011 Å) also appears to be on the long side (compare 1.843 Å in phenylsilane[21]). These increased bond distances may in part be associated with the distribution of silicon bonding orbitals to five centers instead of four (we recall[1] that in pentacoordinate nitrilotriethoxysilanes and nitrilotriphenoxysilanes the fifth (N → Si) bond was relatively weak compared to a normal single bond). Excess negative charge accommodated on silicon in this anionic species may also contribute to increased bond lengths by causing an expansion in the silicon covalent bonding radius.

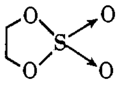
The nine atoms, Si, O(1), O(2), and C(5) through C(10), are coplanar within experimental error: the average distance from the least-squares plane,[22] $-1.9651x + 5.1352y + 7.7293z = 0.00100$, through these points is only 0.008 Å, with a maximum deviation of 0.020 Å. Some unusual bond distances occur in this system. The C–O bond lengths in the five-membered rings are very short, 1.342 ± 0.008 and 1.347 ± 0.008 Å. A similar bond distance, 1.341 Å, has been reported for another five-membered cyclic diester, vinylene sulfate[23] (II). Some apparent shortening from the normal C–O single bond[24] distance of 1.43 Å also occurs[25] in an unsaturated phosphorus analog (III), to an average value of 1.37 Å. By contrast, no diminution of C–O bond lengths *vs.* the single bond value has as yet been reported[23,26,27] for saturated diesters, such as IV[23] (1.459 Å) or V[26] (1.43 Å average). In the pentaoxyphosphorane I, one of the two C–O bonds in the five-membered ring is quite short[14b] (1.347 Å), the other longer (1.433 Å). These variations are too large



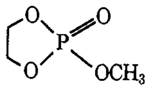
II



III



IV



V

---

(13) R. J. Gillespie, *J. Chem. Soc.*, 4672 (1963).

(14) (a) W. C. Hamilton, S. J. Laplaca, F. Ramirez, and C. P. Smith, *J. Amer. Chem. Soc.*, **89**, 2268 (1967); (b) R. D. Spratley, W. C. Hamilton, and J. Ladell, *ibid.*, **89**, 2272 (1967); one of the ring oxygens is equatorial, the other axial.

(15) W. L. Roth and D. Harker, *Acta Cryst.*, **1**, 34 (1948).

(16) E. H. Aggarwal and S. H. Bauer, *J. Chem. Phys.*, **18**, 42 (1950).

(17) K. Yamasaki, A. Kotera, M. Yokoi, and Y. Ueda, *ibid.*, **18**, 1414 (1950).

(18) G. Pyronel, *Atti Accad. Naz. Lincei, Rend., Cl. Sci. Fis. Mat. Nat.*, **16**, 231 (1954).

(19) H. Steinfink, B. Post, and I. Fankuchen, *Acta Cryst.*, **8**, 420 (1955).

(20) M. Yokio, *Bull. Chem. Soc. Jap.*, **30**, 100 (1957).

(21) F. A. Keidel and S. H. Bauer, *J. Chem. Phys.*, **25**, 1218 (1956).

(22) J. Gvildy's ANL Program Library B-125 (1965). See V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Cryst.*, **12**, 600 (1959).

(23) F. P. Boer, J. J. Flynn, E. T. Kaiser, O. R. Zaborsky, D. A. Tomalia, A. E. Young, and Y. C. Tong, *J. Amer. Chem. Soc.*, **90**, 2970 (1968).

(24) "Table of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958, pp S13, S17.

(25) D. Swank, C. N. Caughlan, F. Ramirez, O. P. Madan, and C. P. Smith, *J. Amer. Chem. Soc.*, **89**, 6503 (1967).

(26) T. A. Steitz and W. N. Lipscomb, *ibid.*, **87**, 2488 (1965).

(27) M. G. Newton, J. R. Cox, Jr., and J. A. Bertrand, *ibid.*, **88**, 1503 (1966).

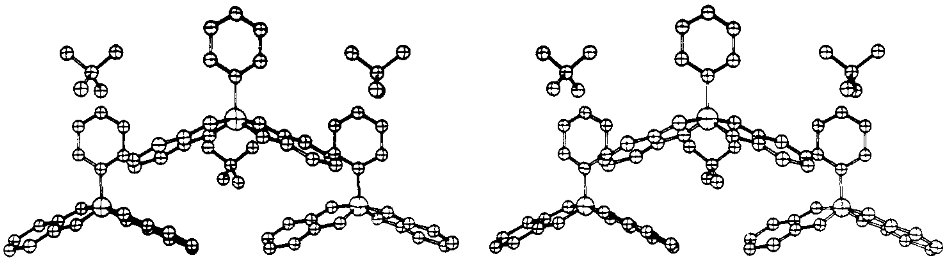


Figure 2. x axis view of molecular packing in tetramethylammonium bis(*o*-phenylenedioxy)phenylsiliconate. The y axis is horizontal and the z axis is vertical. The Si atom at the lower left of the figure is at (0, 1, 0), and that at the center is at ($^1/_2$, $^1/_2$, $^1/_2$).

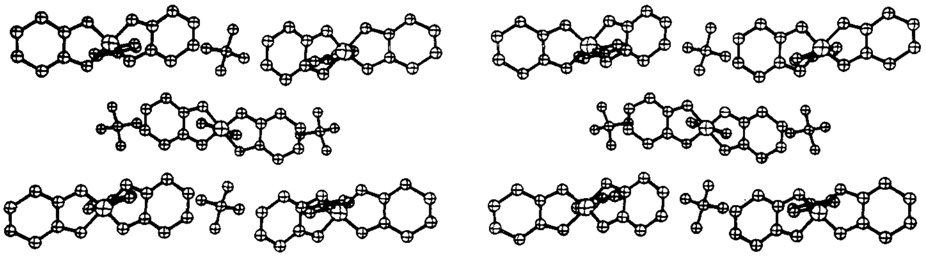


Figure 3. Three dimensional view of molecular packing in tetramethylammonium bis(*o*-phenylenedioxy)phenylsiliconate as viewed down the z axis, with the y axis horizontal.

to be accounted for by changes in carbon hybridization alone, and may arise from interactions of the oxygen 2p orbitals perpendicular to the ring with the π orbitals of carbon and any available 3p or 3d orbitals on the heteroatom (see below).

The C–C bond lengths in the arylene rings show some remarkable deviations from the normal value[24] of 1.397 Å for aromatic bonds, as in benzene. In particular, the C(8)–C(9) bond is exceptionally short (1.288 ± 0.015 Å), about three standard deviations below the standard double bond value[24] of 1.335 Å, while the two bonds adjacent to it, C(7)–C(8) and C(9)–C(10), are unusually long (1.489 ± 0.014 and 1.459 ± 0.012 Å, respectively). These latter distances are near the value of 1.48 Å expected for a single bond between sp^2-hybridized carbon atoms. These apparent changes in bond distance may result from the role of the π system of the arylene rings in delocalizing the excess negative charge associated with a pentavalent silicon atom.[2] Because such delocalization presumes contributions from resonance structures where an electron pair is promoted from silicon σ-bonding orbitals to 3d or 3p orbitals of π symmetry with respect to the rings, the observed alterations from normal phenyl distances are unexpectedly large. For this reason, the possibility that part of the differences in the phenyl bond lengths arise from vibrational motion in the crystal, or from systematic errors in the data, cannot be entirely discounted. It is hoped that some theoretical evidence on this point will be obtained when wave functions calculated by a nonempirical method[28] based on an exact LCAO–SCF wave function for silane[29] are computed.

The unique bond lengths in the phenyl ligand (1.390, 1.408, and 1.365 Å) are essentially normal, in contrast to the arylene rings, and this ring is also planar within experimental error. The least-squares plane[22] through C(1), C(2), C(3), and C(4) is $8.7942x - 3.6399y + 0.0383z = 0.0144$, and forms a dihedral angle of 108°-18′ with the nine-atom plane defined above.

Bond angles and distances in the tetramethylammonium cation are unremarkable. The anisotropic temperature parameters of the carbon atoms indicate that the methyl groups have large amplitudes of thermal motion (Figure 1 and Table IV), particularly in directions tangential to the nitrogen–carbon bonds.

Two three-dimensional diagrams[11] of the crystal packing in tetramethylammonium bis(*o*-phenylenedioxy)phenylsiliconate are given in Figures 2 and 3. The former gives a view perpendicular to the twofold axes, while the latter shows the crystal looking down these symmetry elements. No unusually short intermolecular contracts occur. The *para* carbon of the phenyl ligand, C(4), is 3.99 Å from the silicon atom directly above it, and is 3.59 Å from O(1) and 3.73 Å from C(5). The closest contacts of the methyl carbons of the tetramethylammonium ion are C(11)···C(4), 3.50; C(11)···C(3), 3.54; C(11)···O(2), 3.58; C(11)···O(1), 3.58; C(12)···O(1), 3.39; C(12)···O(2), 3.68.

Acknowledgment. We are indebted to Cecil Frye for providing the sample and for helpful discussions.

(28) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **88**, 2353 (1966).

(29) F. P. Boer and W. N. Lipscomb, to be published.