A Neutral Silicon Ether, Linear at Oxygen: *X*-Ray Crystal and Molecular Structure of Oxo-bis[triphenylsilicon(IV)]

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Summary Oxo-bis[triphenylsilicon(IV)], $O(Ph_3Si)_2$, has been found by *X*-ray analysis to contain a linear SiOSi fragment.

Neutral silicon ethers, $O(R_3Si)_2$ ($R = H$[1], F[2], or Cl[3]), exhibit bond angles at oxygen, as determined by gas-phase electron diffraction, of 144·1, 155·7, and 146°, respectively, all much greater than those predicted by the VSEPR model, and for which both electronic[1–3] and steric[4] rationalisations have been suggested. Although linear SiOSi bridges have been observed in coesite, SiO_2,[5] and in some metal disilicates, no such linearity has been observed previously in a neutral molecular ether, but $O(Ph_3Si)_2$ is now found to contain a linear SiOSi fragment.

Crystal data: $C_{36}H_{30}OSi_2$, triclinic, $a = 11{\cdot}301(2)$, $b = 9{\cdot}539(2)$, $c = 8{\cdot}771(2)$ Å; $\alpha = 66{\cdot}343(12)$, $\beta = 114{\cdot}353(8)$, $\gamma = 114{\cdot}243(10)$°; $M = 534{\cdot}77$, $U = 754{\cdot}2$ Å^3, $F(000) = 282$, $D_c = 1{\cdot}177$ kg dm^{-3}, $Z = 1$, $\mu(\text{Mo-}K_\alpha) = 1{\cdot}07$ cm^{-1}.† 2842 reflections were measured using a Phillips PW 1100 diffractometer, of which 2101 having $F_{obs} > 3\sigma(F)$ were used. The E statistics suggested space group $P\bar{1}$, and the structure was solved in this space group by direct methods, and refined with C, O, and Si anisotropic, and H isotropic to a conventional R of 0·0374, and a generalised[7] R_G of 0·0497. A parallel series of refinements in $P1$ converged to R of 0·0338 and R_G of 0·0424, significant[7] at the 0·5% level, whence the space group $P\bar{1}$ should be rejected. However, despite the indications of the R-factor ratio test,[7] we reject the structure in $P1$ on the grounds of the unacceptably wide ranges spanned by chemically equivalent bond distances, thus Si–O, 0·045; Si–C(1), 0·049; C(1)–C(2), 0·072; C(2)–C(3), 0·162; C(3)–C(4), 0·164; and C–H, 0·49 Å; whereas in $P\bar{1}$ these ranges are: Si–C(1), 0·010; C(1)–C(2), 0·022; C(2)–C(3), 0·013; C(3)–C(4), 0·018; and C–H, 0·18 Å. In $P\bar{1}$, the molecule is centrosymmetric and hence the SiOSi fragment is strictly linear, having r(Si–O) 1·616(1) and r(Si · · · Si) 3·232(1) Å, (other parameters are given in the Figure); the refinement in $P1$ led to ∠SiOSi 176·8(7)°, *i.e.* an essentially linear SiOSi group. The possibility that the oxygen position is disordered is eliminated both by the difference map, and by the dimensions of the thermal ellipsoid of the oxygen atom.

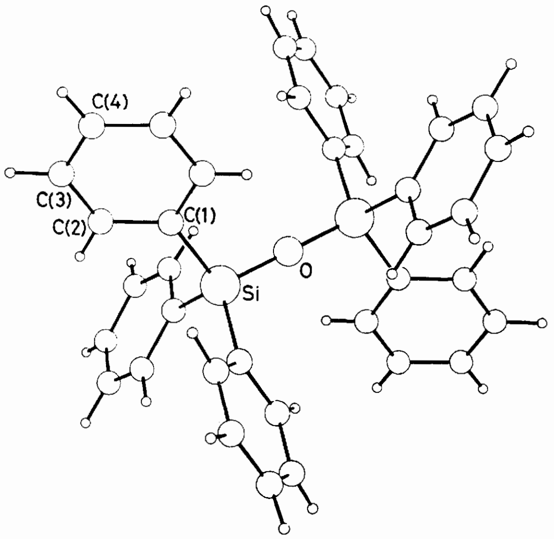

FIGURE. Molecular structure of $O(Ph_3Si)_2$. Mean bond distances are: Si–O, 1·616(1); Si · · · Si, 3·232(1); Si–C(1), 1·864(5); C(1)–C(2), 1·388(8); C(2)–C(3), 1·384(5); C(3)–C(4), 1·359(7); and C-H, 0·94(5) Å.

There is no simple correlation between ∠SiOSi and r(Si–O) in neutral species $O(R_3Si)_2$ (Table), although both wide ∠SiOSi and short r(Si–O) have been supposed[2,3] to be consequent upon $p\pi$–$d\pi$ bonding; however, in ionic disilicates for which accurate data are available there is little significant difference in $r(\text{Si–O}_{br})$ between those with linear SiOSi fragments and those which are markedly non-linear at oxygen.

TABLE

Variation of geometrical parameters with electronegativity of R, x_R, in $O(R_3Si)_2$

R	x_R[a]	∠SiOSi/°	r(Si–O)/Å
H[b]	2·2	144·1(9)	1·634(2)
Cl[c]	3·2	146(4)	1·592(10)
F[d]	4·0	155·7(20)	1·580(25)
Ph	3·0	180·0[e]	1·616(1)

[a] Pauling scale; value for Ph from P. R. Wells, *Progr. Phys. Org. Chem.*, 1968, **6**, 111. [b] Ref. 1. [c] Ref. 3. [d] Ref. 2. [e] By symmetry.

When R = F [2] (although not when R = H[1]) the hypothesis that the molecule has a linear SiOSi fragment in its ground vibrational state could not be rejected; the present result affords a precedent for this hypothesis.

We thank the S.R.C. for support, and Drs. P. G. Owston and M. McPartlin, Polytechnic of North London, for the use of the diffractometer.

(*Received*, 13*th June* 1977; *Com.* 583.)

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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