Gas-phase Electron Diffraction Structure of Tetrameric Prosiloxane, $(H_2SiO)_4$

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Summary The molecular structure of $(H_2SiO)_4$ in the vapour phase has been established by electron diffraction.

THE volatile material of composition $(H_2SiO)_n$ first obtained by Stock *et al.*[1,2] was further investigated by Campbell-Ferguson,[3] who concluded from the molecular weight and mass spectrum that the predominant oligomer has $n=4$. Examination of the vapour by electron diffraction confirms this conclusion and provides the molecular structure of this tetramer.

Samples of the compound were prepared by the reaction of SiH_2I_2 vapour with copper(I) oxide or hydrated lead(II) oxide, and purified by fractional condensation *in vacuo*: their i.r. and mass spectra agreed with those reported.[3] Electron diffraction data were collected photographically at U.M.I.S.T. and processed using our usual techniques.[4]

The radial distribution curve $P(r)/r$ (Figure 1) shows strong peaks at 1·63, 2·70, and 3·13 Å (1 Å = 10^{-10}m). These can be identified with Si–O (bonded), O · · · O and Si · · · Si (each across one angle), giving values of 149° for the Si–O–Si angle and 112° for the O–Si–O angle (*cf.* Si–O 1·634 Å and angle Si–O–Si 144·1° in disiloxane).[5] The features in $P(r)/r$ above 3·4 Å can be accounted for by a

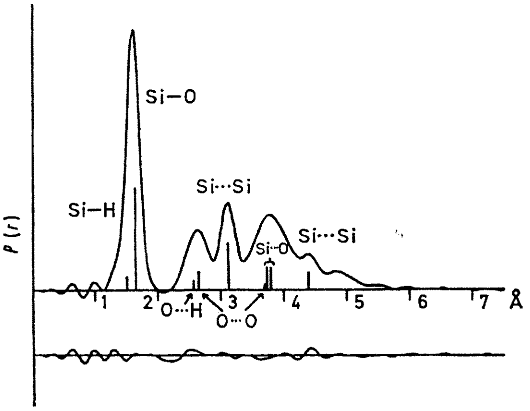

FIGURE 1

puckered cyclic tetramer of S_4 ($\bar{4}$) molecular symmetry, although other cyclic tetramer structures of lower symmetry cannot definitely be excluded. Preliminary least-squares refinements with the S_4 model (assuming further all Si–O bonds equal, all Si–H bonds equal and all H–Si–O angles equal) gave the molecular parameters shown with estimated standard deviations in parentheses in Figure 2.

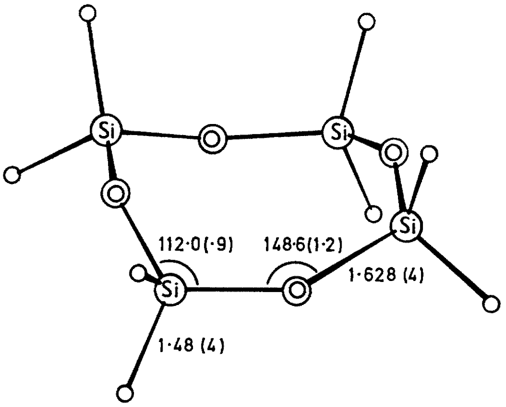

FIGURE 2

The structure can be generated by the symmetry operations of S_4 on the co-ordinates (in Å): O (1·86, 0, 0·31), Si (1·59, 1·51, −0·25), H (2·15, 1·61, −1·61), and H (2·25, 2·47, 0·65). The contributions of the more important non-bonded interatomic distances are indicated in Figure 1: in additions to those given above, these are O · · · O 3·71, Si · · · Si 4·38, Si · · · O 3·72 and 3·80 Å. All features above 4·5 Å are due to Si · · · H, O · · · H and H · · · H atom pairs.

The difference radial distribution curve in Figure 1 provides no evidence for the presence of trimer, pentamer, or other oligomers. For a cyclic trimer, the mean of the Si–O–Si and O–Si–O angles cannot exceed 120°; with reasonable molecular parameters a prominent Si · · · O peak is expected at about 3·2—3·3 Å, with no strong non-bonded peaks at longer distances. Any pentameric structure with the expected large Si–O–Si angles would possess longer Si · · · O and Si · · · Si distances than those of Figure 1: a C_{5v} pentamer with the Si–O distance and angles of Fig. 2 would have O · · · O 4·37, Si · · · Si 5·06, Si · · · O 4·04 and 4·98 Å. The parameters found for $(H_2SiO)_4$ are similar to those reported[6] for crystalline $(Me_2SiO)_4$ (mean SiO 1·65 Å, mean Si–O–Si 142·5°, and mean O–Si–O 109°).

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[1] A. Stock, C. Somieski, and R. Wintgen, *Ber.*, 1917, **50**, 1764.
[2] A. Stock and C. Somieski, *Ber.*, 1919, **52**, 1851.
[3] H. J. Campbell-Ferguson, *J. Inorg. Nuclear Chem.*, 1965, **27**, 2121.
[4] D. W. H. Rankin, A. G. Robiette, G. M. Sheldrick, W. S. Sheldrick, B. J. Aylett, I. A. Ellis, and J. J. Monaghan, *J. Chem. Soc.* (*A*), 1969, 1224.
[5] A. Almenningen, O. Bastiansen, V. Ewing, K. Hedberg, and M. Traetteberg, *Acta Chem. Scand.*, 1963, **17**, 2455.
[6] H. Steinfink, B. Post, and I. Fankuchen, *Acta Cryst.*, 1955, **8**, 420.