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The Molecular Structure of Silicon Tetraisocyanate

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Infrared and Raman spectra of silicon tetraisocyanate ($Si(NCO)_4$) have been interpreted both by assuming pseudo T_d symmetry (not necessarily linear SiNCO group)[1] and by assuming "true" T_d symmetry (linear SiNCO group)[2] for the molecular structure. As electron diffraction and other studies on molecules containing isocyanate groups give the bond angle at the nitrogen atoms different from 180° (Table 1), it was of interest to investigate $Si(NCO)_4$ also by electron diffraction.

Experimental. The compound was prepared using the method of Forbes and Anderson.[3] The electron diffraction data were obtained at the University of Oslo. The nozzle-to-plate distances were about 19 and 48 (cm). A modified s^3 sector was used. The data were treated according to the procedure described by Almenningen *et al.*[4] The experimental background was adjusted by considering the observed and the calculated radial distribution (RD) curve for Ångström values less than 1. The experimental molecular intensity function ($s \cdot M(s)$) was obtained for s values from 1.5 to 45.0 ($Å^{-1}$). The RD curves were obtained by Fourier transformations of the modified intensity functions $s \cdot M(s) \cdot \exp(-0.0036s^2)$. The structure was refined by the least-squares methods on the intensity functions assuming the N–O distance of the NCO group to be "independent" and treating separately the distances depending on the angle of rotation of the NCO groups about the Si–N bonds. These distances were calculated for every 30° of angle of rotation. Complex scattering amplitudes were used.

Structure determination. The molecular models considered were based on the assumption of linear NCO groups and tetrahedral arrangement of the nitrogen atoms. Approximate values of the interatomic distances were obtained from the experimental RD curve which gave only the Si–N distance resolved. Various structures were tried and satisfactory agreement was obtained when assuming the N–C bond distance somewhat longer than the C–O bond distance and the bond angle at the nitrogen atom about 150°. In order to obtain agreement for the outer regions of the RD curves various "rigid" models and models based on rotating NCO groups were tried. "Non-bonding" repulsions were considered for the postulations of the "rigid" models and of the various probability functions for assumed internal, hindered rotation of the NCO groups about the Si–N bonds. Best agreement was obtained however, when free rotation was assumed. The u values of the distances which are depending on the angle of rotation, were assumed independent of this angle and were chosen equal to 0.10 Å (N–C and N–O) and 0.15 Å (C–O, C–C, and O–O). The attempts of improving these u values in the least-squares refinement were unsuccessful. This has not yet been studied further. The structural parameters obtained from the least-squares refinement are listed in Table 1. The calculated curves are based on these values (Figs. 1 and 2). For comparison, the RD curve based on one of the "rigid" models, the one of symmetry D_{2d} and the eclipsed configuration, is also drawn in Fig. 2. The RD curve based on the model of the same point group but of the staggered configuration is even more unfavourable.

Discussion. The N–O distance for the NCO group is obtained 0.008 Å shorter than the sum of the N–C and C–O bond distances. This may be assumed due to "shrinkage effects". The values of the bond distances and the bond angle at the

Table 1. Least-squares results. Distances $r_g(1)$[5] and root-mean-squares amplitudes of vibration (u) both with standard deviations (σ) in Å. Uncertainty of wavelength is also included in σ_r. In the parentheses are previously reported values for $(CH_3)_3SiNCO$,[a] $Cl_nSi(NCO)_{4-n}$, $n = 1, 2, 3$,[b] CH_3NCO,[c] and HNCO.[d]

	$r_g(1)$				σ_r	u	σ_u
Si–N	1.688	(1.76[a],	1.65[b])		0.003	0.045	0.001
N–C	1.209	(1.20[a],	1.19[c],	1.207[d])	0.002	0.037	0.001
C–O	1.165	(1.18[a],	1.18[c],	1.171[d])	0.002	0.034	0.001
Si–C	2.777				0.005	0.077	0.007
N–O	2.366				0.004	0.044	0.002
N–N	2.756					0.099	0.011
Si–O	3.894					0.104	0.005

∠ SiNC: 146.4°. (∠ XNC: 150[a], 125[c], 128.1[d] (°).)
[a] Ref. 6, [b] Ref. 6, [c] Ref. 7, [d] Ref. 8.

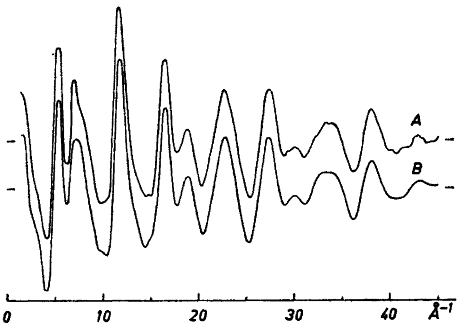

Fig. 1. Experimental (A) and theoretical (B) molecular intensity curves.

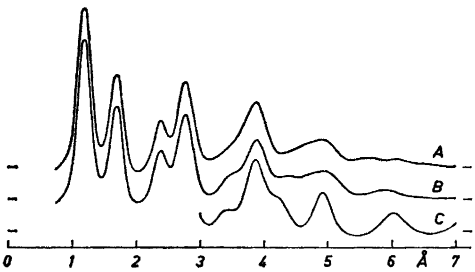

Fig. 2. Radial distribution curves, A, experimental curve and B and C theoretical curves. B, final model and C, the "rigid" model of symmetry D_{2d}, eclipsed configuration. Artificial damping constant: $k = 0.0036$ Å².

nitrogen atom obtained for $Si(NCO)_4$ are reasonable when compared with those reported for related compounds (Table 1).

A full account of this investigation including also diffraction data obtained with 130 cm between nozzle and plate, will be published alter.

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