Electron-diffraction Study of Gaseous Tris(dimethylamino)chlorosilane

By L. V. VILKOV* and N. A. TARASENKO

(*Chemistry Department, Moscow State University, Moscow* B–234 *U.S.S.R.*)

Summary The electron diffraction radial distribution curve for $ClSi(NMe_2)_3$ is consistent with a C_3 model and planarity at nitrogen.

AN electron-diffraction study by Hedberg[1] demonstrated that the Si_3N group in trisilylamine, $(SiH_3)_3N$, was planar within experimental error. In the recent investigation[2] of $(SiH_3)_2NH$ and $(Me_3Si)_2NH$ it was found that the NH bond lay in the Si_2N plane. But in general the configuration of the nitrogen atom has not been reliably determined. It seemed to us of interest to find out whether the configuration is the same in the case where only one silicon atom is bonded to the nitrogen atom. Here we present gas-phase electron-diffraction results for tris(dimethylamino)chlorosilane.

Electron diffraction photographs were taken using ЭГ–100А apparatus. The nozzle temperature was 83°. Data processing was carried out using our usual techniques.[3] The molecular structure of tris(dimethylamino)-chlorosilane is shown in Figure 2. (We have assumed a C_3 model). The experimental radial distribution curve is shown in Figure 1. The interatomic distances r(C–N), r(Si–N), r(Si–Cl), and r(Si · · · C-1′) and their mean-square amplitudes were determined from the $f(r)_{exp}$ curve.

Difficulties arose while determining the angle CNC because of the very small scattering by the pair of atoms

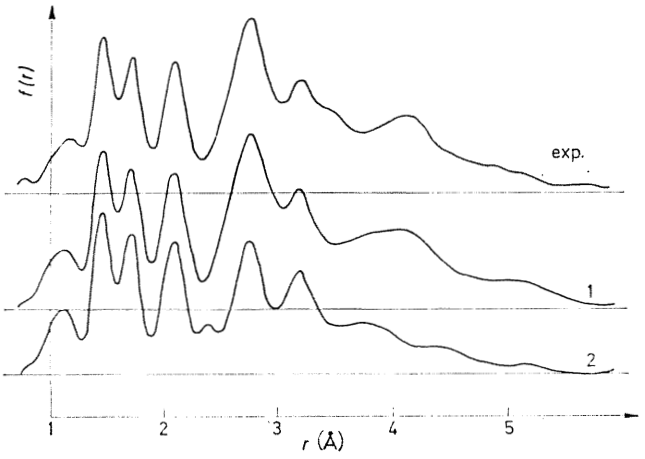

FIGURE 1. *The experimental and theoretical radial distribution curves for tris(dimethylamino)chlorosilane.*

C-1′ · · · C-2′. The $sM(s)$ and $f(r)$ curves were calculated for CNC angles from 109·5° to 118·5° at 3° intervals to estimate the reliability of r(C-1′ · · · C-2′). The best curve is one for the molecular model with CNC angle 118·5° (curve 1, Figure 1). The $sM(s)$ and $f(r)$ curves for the model with this angle less than 118·5° do not agree well with the experimental results [see curve 2 (Figure 1) for the model with angle 109·5°].

The orientation of the dimethylamino-group was determined by variation of the dihedral angle about the Si–N bond. The best curve is one for the model in which the group is twisted by 22·5° from the conformation in which the Si–Cl bond is in the plane perpendicular to the plane of amino-group.

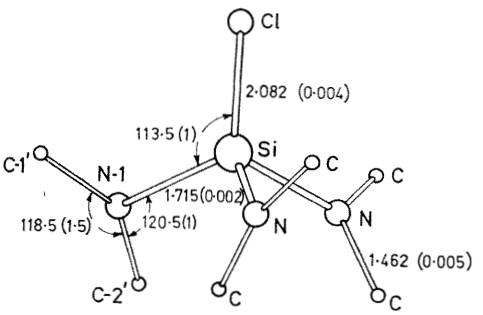

FIGURE 2. *Bond lengths* (Å), *angles* (*degrees*), *and conformation of the tris(dimethylamino)chlorosilane skeleton.*

The estimated standard deviations given in parentheses are values obtained using the equation of Bonham and Bartell[6] *and Kuchitsu.*[7]

r (C–H) *was assumed to be* 1·10 Å *and* ∠ HCN = 109·5°.

The mean-square amplitudes were: 1 (C–H) = 0·13 Å (in agreement; 1 (N–C) = 0·045 ± 0·006 Å; 1 (Si–N) = 0·060 ± 0·002 Å; 1 (Si–Cl) = 0·06 ± 0·004 Å.

Thus the nitrogen atom in the molecule tris(dimethylamino)chlorosilane has a planar configuration with

$$\angle \text{SiNC} = 120{\cdot}5° \pm 1°$$
$$\angle \text{CNC} = 118{\cdot}5° \pm 1{\cdot}5°$$

The bond length r(Si–N) 1·715 Å is considerably smaller than 1·80 Å calculated using the equation of Schomaker and Stevenson.[4] The elongation of the Si–Cl bond (2·082 Å) as compared with the Si–Cl bond in SiH_3Cl (2·048 Å)[5] is noteworthy.

(*Received, July* 25*th*, 1969; *Com.* 1137.)

[1] K. Hedberg, *J. Amer. Chem. Soc.*, 1955, **77**, 649.
[2] A. G. Robiette, G. M. Sheldrick, W. S. Sheldrick, B. Beagley, D. W. J. Cruickshank, J. J. Monaghan, B. J. Aylett, and I. A. Ellis, *Chem. Comm.*, 1968, 909.
[3] L. V. Vilkov and N. A. Tarasenko, *Zhur. strut. Khim.*, in the press.
[4] D. P. Stevenson and V. Schomaker, *J. Amer. Chem. Soc.*, 1940, **62**, 1913.
[5] B. Bak and J. Bruhn, *Acta Chem. Scand.*, 1954, **8**, 367.
[6] R. A. Bonham and L. S. Bartell, *J. Chem. Phys.*, 1959, **31**, 702.
[7] K. Kuchitsu, *Bull. Chem. Soc. Japan*, 1959, **32**, 748.