The Conformation of Three Disilazanes

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AN electron diffraction study by Hedberg[1] demonstrated that the Si_3N group in trisilylamine $(SiH_3)_3N$, is planar within experimental error; the SiNSi angle was found to be 119·6 ± 1·0° and the Si–N bond length 1·738 ± 0·02 Å. In the crystal structure[2] of the four-membered-ring compound $(Me_3SiNSiMe_2)_2$ the nitrogen and silicon atoms in the molecule are virtually coplanar, with a mean Si–N bond length of 1·719 Å. The stereochemical inactivity of the lone pair on the nitrogen atom and the relatively short Si–N bond lengths in these molecules are usually attributed to $(p \rightarrow d)$ π-bonding from nitrogen to silicon. Here we present preliminary gas-phase electron diffraction results for disilazane, $(SiH_3)_2NH$; hexamethyldisilazane $(Me_3Si)_2NH$; and *N*-difluoroboryldisilazane $(SiH_3)_2N{\cdot}BF_2$.

Disilazane[3] and *N*-difluoroboryl-disilazane[4] were prepared by the published procedures and purified by fractional condensation in a vacuum line; their purity was checked by i.r. spectroscopy and (for the latter) gas-phase molecular weight determination. The hexamethyldisilazane was a commercial product. Electron diffraction photographs were taken in the Balzer's apparatus[5] at Glasgow and subsequently at the University of Manchester Institute of Science and Technology. Data processing and least-squares refinement has been carried out at Manchester and Cambridge using our usual techniques.[6,7] At present, data from the 50 cm. and 25 cm. camera distances have been used for each compound in the refinements.

The molecular structures are depicted in the Figure; the estimated standard deviations given in parentheses are twice the values obtained in the least-squares refinements. Both the Si–N–Si angle and examination of the radial distribution curve suggest that in disilazane the N–H bond lies in the Si_2N plane; thus we have assumed C_2 models for both disilazane and hexamethyldisilazane. There is some evidence from our least squares refinements that in disilazane the Si–H bonds are approximately staggered with respect to the N–H bond, whereas the Si–C and N–H bonds are probably nearly eclipsed in hexamethyldisilazane. The Si · · · F peaks in the radial distribution curve indicate that the silicon and fluorine atoms in *N*-difluoroboryldisilazane are probably coplanar; we have assumed a C_{2v} model with the nitrogen and boron atoms also in this plane, staggered Si–H and N–B bonds, tetrahedral angles at silicon and Si–H bond lengths of 1·485 Å. For each molecule reasonable values were obtained for the bonded and non-bonded amplitudes included in the refinement.

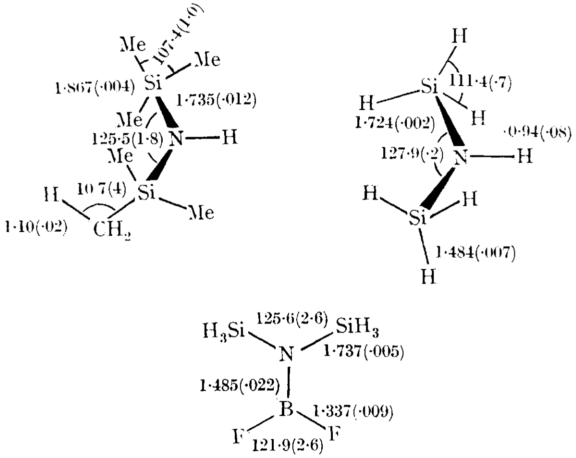

FIGURE. *Bond lengths* (Å), *angles* (degrees), *and conformations of the disilazanes.*

The bond lengths and angles obtained are consistent with the hypothesis of $(p \rightarrow d)$ π-bonding from nitrogen to silicon. The B–N bond lengths which have been measured previously fall into two classes: (i) borazoles[8] (B–N = 1·41 to 1·44 Å) and boron nitride[9] (1·446 Å) where both boron and nitrogen are 3-co-ordinate with a possibility of delocalised π-bonding, and (ii) compounds in which boron and nitrogen are both 4-co-ordinate, where B–N ranges from 1·50 Å $(H_2NB_2H_5)$[10] to 1·59 Å $(Me_2NBH_2)_3$.[11] In view of the analogy with C–C bonds (benzene 1·40 Å, single bonds between 3-co-ordinate carbon atoms 1·46 to 1·48 Å and between 4-co-ordinate carbon atoms 1·53 to 1·55 Å),[12] the B–N bond length of $1{\cdot}48_5 \pm 0{\cdot}02_2$ Å in *N*-difluoroboryldisilazane is unexceptional.

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