

## A Gas Phase Electron Diffraction Investigation of the Molecular Structures of Trimethylaluminium Monomer and Dimer

A. ALMENNINGEN, S. HALVORSEN and A. HAALAND

*Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway*

The molecular structures of  $(\text{CH}_3)_3\text{Al}$  and  $[(\text{CH}_3)_3\text{Al}]_2$  have been determined by gas phase electron diffraction. The monomer has  $D_{3h}$  symmetry with freely rotating methyl groups. The three independent structure parameters are  $R(\text{C}-\text{H})=1.113(3)$  Å,  $R(\text{Al}-\text{C})=1.957(3)$  Å, and  $\angle \text{Al}-\text{C}-\text{H}=111.7^\circ$  (0.5°). The electron scattering pattern for the dimer is consistent with a model with  $D_{2h}$  symmetry. The main molecular parameters are  $R(\text{C}-\text{H})$  mean = 1.117(2) Å,  $R(\text{Al}-\text{C})$  terminal = 1.957(3) Å,  $R(\text{Al}-\text{C})$  bridge = 2.140(4) Å,  $R(\text{Al}-\text{Al})=2.619(5)$  Å,  $\angle \text{C}_{\text{term}}-\text{Al}-\text{C}_{\text{term}}=117.3^\circ$  (1.5°), and  $\angle \text{C}_{\text{br}}-\text{Al}-\text{C}_{\text{br}}=104.5^\circ$  (0.1°).

Gasous trimethylaluminium consists of monomeric and dimeric species in a pressure- and temperature-dependent equilibrium.<sup>1</sup> The equilibrium constant for the reaction  $[(\text{CH}_3)_3\text{Al}]_2 \rightleftharpoons 2(\text{CH}_3)_3\text{Al}$  is given by  $^2 \log K_D$  (atom) =  $(-4457/T) + 9.44$ . Consequently, trimethylaluminium gas at 60°C and 30 mmHg consists of more than 97 % dimers, while gas at 215°C and the same pressure consists of more than 96 % monomer. It therefore appeared possible to determine the molecular structures of both species by gas phase electron diffraction. It should be pointed out, however, that the composition of the molecular jet leaving the nozzle need not be equal to that calculated for equilibrium conditions. For this reason, it is necessary to check the data obtained with a nozzle temperature of 60°C against the presence of unexpectedly high amounts of monomer, and the data obtained at 215°C against the presence of unexpectedly large amounts of dimer.

The molecular structure of trimethylaluminium dimer was first determined by X-ray diffraction by Lewis and Rundle,<sup>3</sup> and more recently the result of a more accurate X-ray investigation has been published by Vranka and Amma.<sup>4</sup> We nevertheless thought it worth-while to determine the molecular structure of the free molecule unperturbed by crystal packing forces for comparison with the molecular structure of the monomer. The structure of the latter has not been investigated previously.

## EXPERIMENTAL AND CALCULATION PROCEDURE

Trimethylaluminium was purchased from the Ethyl Corporation and re-distilled before use. The electron scattering patterns were recorded on the Oslo electron diffraction unit<sup>5</sup> with the sample reservoir at 40° (v.p. = 30 mmHg). Exposures were first made with a nozzle temperature of 215 ± 5°C, and nozzle-to-photographic plate distances of about 48 cm and 20 cm. The optical densities of 6 plates from the first set were measured at  $\Delta s = 0.125 \text{ \AA}^{-1}$  intervals, the optical densities of three plates from the last set at  $\Delta s = 0.240 \text{ \AA}^{-1}$ . (The scattering parameter  $s = (4\pi/\lambda)\sin(\theta/2)$ , where  $\lambda$  is the electron wavelength (determined by diffraction from CO<sub>2</sub> gas) and  $\theta$  the diffraction angle.) Exposures were then made with a nozzle temperature of 60 ± 5°C, and nozzle-to-photographic plate distances of about 48, 26 and 20 cm. The optical densities of three plates from the first set were measured at  $\Delta s = 0.125 \text{ \AA}^{-1}$  intervals; the optical densities of four plates from the second set and three plates from the last set were read off at  $\Delta s = 0.250 \text{ \AA}^{-1}$  intervals. The optical densities were converted into intensities, and the data processed in the usual way.<sup>6</sup>

The modified molecular intensity curves obtained with a nozzle temperature of 215°C are shown in Fig. 1, and the modified molecular intensity curves obtained with a nozzle temperature of 60° are shown in Fig. 2.

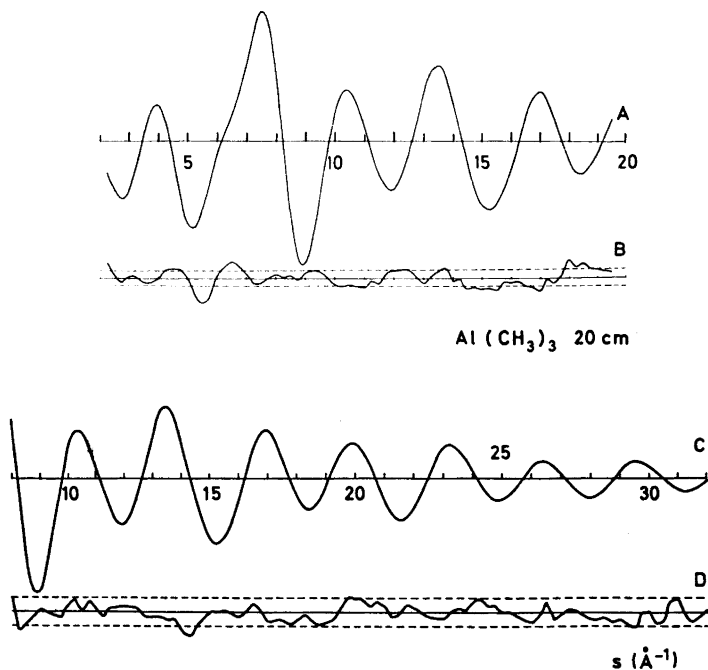


Fig. 1. A and C: experimental modified molecular intensity curves of  $(\text{CH}_3)_3\text{Al}$ . Band D: difference between experimental intensity curves and theoretical curves, calculated for the best model. The stippled lines indicate the estimated uncertainty (two standard deviations) of the experimental curve. Note: the scale of curves B and D is three times the scale of A and C, respectively.

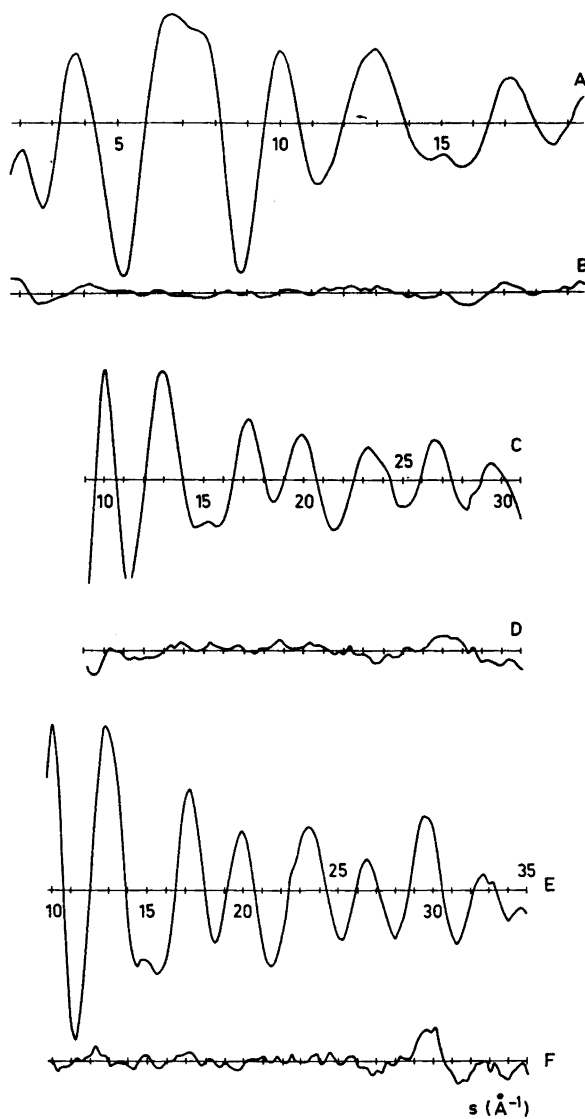


Fig. 2. A, C and E: experimental modified molecular intensity curves of  $(\text{CH}_3)_3\text{Al}$ . B, D and F: difference between experimental intensity curves and theoretical curves, calculated for the best model.

Theoretical intensity curves were calculated from

$$I^{\text{AIC}}(s) = \sum_{i \neq j} \frac{|f_i(s)||f_j(s)|}{|f_{\text{Al}}(s)||f_{\text{C}}(s)|} \cos(\eta_i(s) - \eta_j(s)) \frac{\sin(R_{ij}s)}{R_{ij}} \exp(-\frac{1}{2}u_{ij}^2s^2)$$

The sum extends over all atom pairs  $i, j$  in the molecule.  $R_{ij}$  is the inter-nuclear distance,  $u_{ij}$  the root mean square amplitude of vibration.  $f_j(s) = |f_j(s)| \exp(i\eta_j(s))$  is the complex atomic scattering factor of atom  $j$ . It has been calculated for Al, C and H by the partial wave approximation with a program written by Peacher.<sup>7</sup> The scattering potentials of Al and C have been found by non-relativistic Hartree-Fock calculations.<sup>8,9</sup>

Radial distribution (RD) functions were calculated by Fourier inversion of experimental or theoretical intensity curves after multiplication with the artificial damping function  $\exp(-ks^2)$ . The experimental intensity functions obtained for different nozzle-to-photographic plate distances were then first spliced to each other and to the theoretical curve obtained for the best model below  $s = 2 \text{ \AA}^{-1}$ .

The molecular structures were refined by least-squares calculations on the intensity data with a non-diagonal weight matrix and a separately refined scale factor for the intensity values obtained for each nozzle-to-plate distance.<sup>10</sup> The standard deviations obtained were expanded to take into account an estimated uncertainty of 1.4 ppt in the electron wavelength.

### STRUCTURE ANALYSIS

*Trimethylaluminium monomer.* An experimental RD function obtained from the intensity data, recorded with a nozzle temperature of  $215^\circ$ , is shown in Fig. 3. The absence of any appreciable peaks in the region above  $3.8 \text{ \AA}$

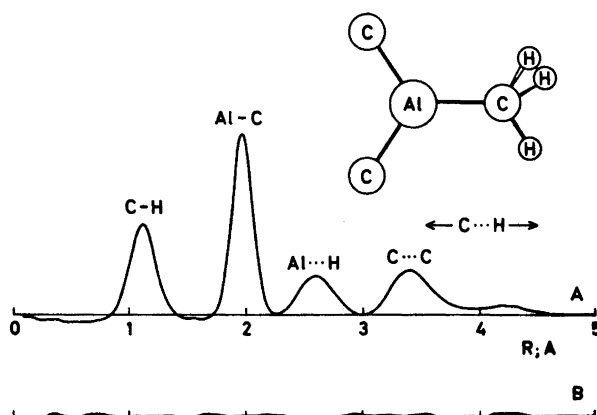


Fig. 3. A: experimental radial distribution curve for  $(\text{CH}_3)_3\text{Al}$ . The artificial damping constant  $k = 0.002 \text{ \AA}^2$ . B: difference between the experimental curve and a theoretical curve calculated for best model.

shows that the amount of dimer in the molecular jet is negligible. The curve can be readily interpreted: The peak at  $1.1 \text{ \AA}$  corresponds to the C-H bond distance, the peak at  $2.0 \text{ \AA}$  to the Al-C bond distance, the peak at  $2.6 \text{ \AA}$

corresponds to the nonbonded distance Al...H, and the peak at 3.4 Å to the nonbonded distance C...C. Finally, the very broad peak extending from 3.2 Å (under the C...C peak) to 4.6 Å corresponds to nonbonded distances of type C...H. The lack of structure of this peak shows that the barrier to internal rotation of the methyl groups must be quite low, less than 2 kcal/mol. The structure determination was therefore based on a model with freely rotating ( $V_0=0$ ) methyl groups. If the AlC<sub>3</sub> trunk of the molecule has  $D_{3h}$  symmetry, the molecular structure is determined by three parameters, *e.g.* by the Al-C and Al-H bond distances, and the  $\angle$ Al-C-H valence angle. It was, however, anticipated that out-of-plane molecular vibrations would lead to a significant shrinkage of the C...C distance; this distance was therefore refined as an additional independent parameter.

The main molecular parameters, obtained by least-squares calculations, and their estimated standard deviations are listed in Table 1.

Table 1. Structure parameters with estimated standard deviations of (CH<sub>3</sub>)<sub>3</sub>Al (column A) and (CH<sub>3</sub>)<sub>6</sub>Al<sub>2</sub> (columns B and C). The distances are given as  $r_a^{20}$ . The angles have not been corrected for shrinkage.

| A. (CH <sub>3</sub> ) <sub>3</sub> Al <sup>a</sup><br>R (Å)    u (Å) | B. (CH <sub>3</sub> ) <sub>6</sub> Al <sub>2</sub> <sup>a</sup><br>R (Å)    u (Å) | C. (CH <sub>3</sub> ) <sub>6</sub> Al <sub>2</sub> <sup>b</sup><br>R (Å) |
|--|---|--|
| C-H 1.113(3) 0.078(2)  | (C-H) mean 1.117(2) 0.082(2)  | 1.958(11), 1.983(10)<br>2.134(10), 2.153(12)<br>2.600(4)                 |
| Al-C 1.957(3) 0.061(1)   | Al1-C1 1.957(3) 0.061(2)<br>Al1-C3 2.140(4) 0.091(2)<br>Al1-Al2 2.619(5) 0.079(3) |  |
| $\angle$ Al-C-H = 111.7°<br>(0.5)°                                   | ( $\angle$ Al1-C1-H) mean 112.1° (0.8°)   | 132.1°(0.4°)<br>105.3°(0.4°)   |
| $\angle$ C-Al-C = 120°<br>(assumed)                                  | $\angle$ C1-Al1-C2 117.3° (1.5°)<br>$\angle$ C3-Al1-C3 104.5° (0.1°)              |  |
| Al...H 2.585(7) 0.137(4)   | Al1...C5 4.003(15) 0.216(9)   |  |
| C...C 3.390(5) 0.133(5)  | Al1...H <sub>i</sub> 2.593(12) 0.149(9)   |  |
|  | C1...C2 3.344(28) } 0.139(21)   |  |
|  | C3...C4 3.385(7) } 0.139(21)  |  |
|  | C1...C3 3.228(10) 0.144(2)  |  |
|  | C1...C5 4.770(78) 0.278(52)   |  |
|  | C1...C6 5.610(19) 0.148(10)   |  |
| Shrinkage (C...C)<br>0.012(7)  | Shrinkage(C <sub>1</sub> ...C <sub>2</sub> ) -0.115(80)                           |  |
|  | Shrinkage(C <sub>1</sub> ...C <sub>6</sub> ) +0.122(26)                           |  |

<sup>a</sup> This work.    <sup>b</sup> Ref. 4.

The differences between the experimental intensity curves and theoretical intensity curves calculated for the best model are shown in Fig. 1. The difference between the experimental RD function and a theoretical RD function calculated for the best model is shown in Fig. 3. The agreement is seen to be satisfactory.

*Trimethylaluminium dimer.* The experimental RD function obtained with a nozzle temperature of 60° is shown in Fig. 4. The curve may be readily inter-

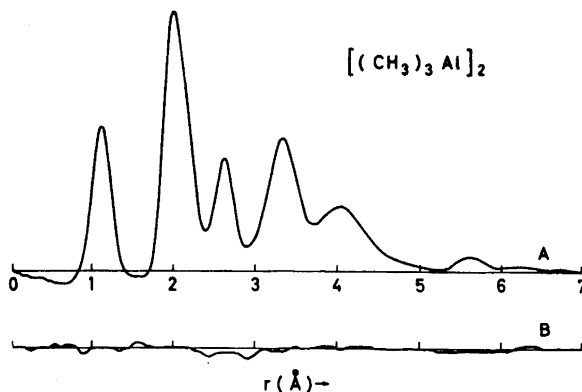


Fig. 4. A: experimental radial distribution curve for  $(\text{CH}_3)_6\text{Al}_2$ . The artificial damping constant  $k=0.002 \text{ \AA}^2$ . B: difference between the experimental curve and a theoretical curve, calculated for the best model.

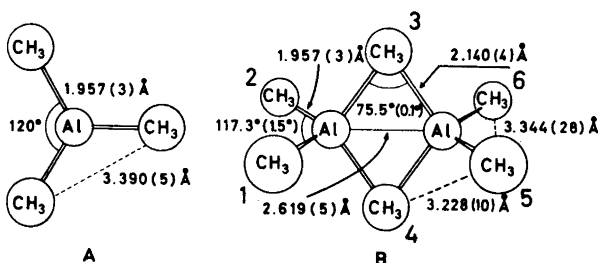


Fig. 5. Molecular models of  $(\text{CH}_3)_3\text{Al}$  (A) and  $(\text{CH}_3)_6\text{Al}_2$  (B).

preted in terms of the molecular structure of trimethylaluminium dimer (see Fig. 5): The peak at 1.1 Å again corresponds to the C-H bond distances, the peak at 2.0 Å to distances of the type Al1-C1 and Al1-C3. The peak at 2.7 Å is also composite; it consists of peaks representing the Al1-Al2 distance and the 12 distances of type Al1...H1. The peak at 3.4 Å corresponds to the eight distances of type C1...C3, the two distances of type C1...C2, and the C3...C4 distance. The peak at 4.0 Å corresponds to the four distances of type Al1...C5, the shoulder at 4.5 Å to the two distances of type C1...C5, and the small peak at 5.6 Å to the two distances of type C1...C6.

Comparison of Fig. 3 and Fig. 4 shows that it is impossible to establish at the outset whether the gas jet contained significant amounts of monomeric trimethylaluminium. It was nevertheless decided to analyze the data under the assumption that the gas jet contained dimeric species only. The presence of significant amounts of monomeric species should then lead to theoretical RD functions that were higher than the experimental in the region above 2.3 Å.

It was assumed that the  $\text{Al}_2\text{C}_6$  trunk has  $D_{2h}$  symmetry. Since it was impossible to determine the positions of all the hydrogen atoms, only a mean C-H bond distance was refined. It was assumed that the terminal methyl

groups have  $C_{3v}$  symmetry, and that the threefold axes coincide with the Al–C bonds; the (mean)  $\angle$ Al1–C1–H angle was refined as an independent parameter. Likewise it was assumed that the bridging methyl groups have  $C_{3v}$  symmetry, and that the threefold axes bisect the Al1–Al2 bond. The angles between the C–H bonds and the threefold axes were set equal to the corresponding angle in the terminal methyl groups, and were not refined. The terminal methyl groups were assumed to be staggered with respect to the Al–C bonds radiating from the aluminium atoms (this corresponds to the equilibrium conformation of the methyl groups found in tetramethyldiborane<sup>11</sup>). The bridging methyl groups were assumed to undergo non-hindered rotation. The symmetry of the entire molecule is thus  $D_{2h}$ .

The molecular structure is then determined by six parameters, *e.g.* the mean C–H, the Al1–C1, the Al1–C2, and the Al1–Al2 bond distances, and the mean  $\angle$ Al1–C1–H valence angle, and the  $\angle$ C1–Al1–C2 valence angle. Since it was anticipated that the C1···C5 and C1···C6 distances might exhibit considerable shrinkage, these distances were refined as independent parameters.

The main molecular parameters obtained by least-squares calculations on the intensity data and their estimated standard deviations are shown in Table 1.

The difference between the experimental intensity curves and the theoretical curve calculated for the best model is shown in Fig. 2. The difference between the experimental RD function and a theoretical function calculated for the best model is shown in Fig. 4. The good agreement obtained in the area above  $r=2.3$  Å shows that the initial assumption, that the monomer concentration in the gas was negligible, was warranted.

## DISCUSSION

The structure of trimethylaluminium monomer is entirely analogous to that of trimethylboron.<sup>12</sup> The  $AlC_3$  trunk has  $D_{3h}$  symmetry, but out-of-plane vibration leads to an apparent shortening (shrinkage) of the C···C distance of 0.012(7) Å. The barrier to internal rotation of the methyl groups is too low to be detected, it must be between 0 and 1 kcal/mol, most probably it is closer to the first figure.

The Al–C bond distance would correspond to a (trigonal) single bond radius<sup>13</sup> for Al of 1.265 Å, a value equal to the tetrahedral covalent radius of 1.26 Å, listed by Pauling.<sup>14</sup> It is further seen that the bond distance is equal to the terminal Al–C bond distance in the dimer. There is therefore at this point no evidence that the Al–C bond in the monomer is shortened through hyperconjugation. Similar negative conclusions have been reached in recent electron diffraction investigations of  $(CH_3)_3B$ <sup>12</sup> and  $(CH_3)_2Be$ .<sup>15</sup>

The good agreement obtained for trimethylaluminium dimer shows that the structure of the molecule must be very close to that of the  $D_{2h}$  model. The apparent elongation of the C1···C5 distance, 0.115(80) Å, and the apparent shortening of the C1···C6 distance, 0.122(26) Å, can best be explained as the effect of large amplitude wagging vibrations of the  $AlC$  (terminal)<sub>2</sub> fragments about the Al–Al axis. A similar wagging of the terminal  $BH_2$  fragments occurs in aluminium borohydride,  $Al(BH_4)_3$ .<sup>16</sup>

In the crystal, the molecule is found to exhibit a significant deviation from  $D_{2h}$  symmetry, the aluminium atoms and the four terminal carbon atoms are not coplanar, the parallel planes C1C2Al1 and Al2C5C6 being separated by 0.12 Å.<sup>4</sup> We cannot rule out such a distortion in the free molecule, but we are inclined to believe that it has been introduced by crystal packing forces. One of the two crystallographically independent molecules in crystalline dimethylphenylaluminium is similarly distorted.<sup>17</sup> The  $\angle$  C1–Al2–C1 angle is also significantly different in the gas and in the crystal; again crystal packing forces would seem to offer a convenient explanation. The bond distances and the  $\angle$  C3–Al1–C4 valence angle are in good agreement.

Recently, Nyberg and coworkers<sup>18</sup> have suggested that the trigonal axes of the bridging methyl groups are approximately aligned, one with the Al1–C3 bond, the other with the Al2–C4 bond, and that the monomeric units are joined through two electron hydrogen bonds Al–H–C. Since we have not been able to locate the bridging methyl hydrogen atoms, we can neither prove nor disprove the suggestion. It should be pointed out, however, that the small vibrational amplitude for the Al1–C3 distance, found by refinement on a  $D_{2h}$  model,  $u = 0.091(2)$  Å, shows that the Al1–C3 and Al1–C4 distances cannot differ by more than 0.1 Å. The hydrogen bridge model has been challenged on the basis of the <sup>27</sup>Al nuclear quadrupole resonance spectrum.<sup>19</sup>

It has already been pointed out that the terminal Al–C distances are identical in monomer and dimer. So, in fact, are the mean C–H distance, the mean  $\angle$  Al–C–H angle, and the C–H, Al–C and Al···H vibrational amplitudes. Apart from a possible change of the  $\angle$  C–Al–C angle, there is surprisingly little change in the (CH<sub>3</sub>)<sub>2</sub>Al fragment, in going from the monomeric to the dimeric unit.

*Acknowledgement.* We are grateful to the Norwegian Research Council for Science and the Humanities for financial support.

#### REFERENCES

1. Laubengayer, A. W. and Gilliam, W. F. *J. Am. Chem. Soc.* **63** (1941) 477.
2. Henrickson, C. H. and Eyman, D. P. *Inorg. Chem.* **6** (1967) 1461.
3. Lewis, P. H. and Rundle, R. E. *J. Chem. Phys.* **21** (1953) 986.
4. Vranka, R. G. and Amma, E. L. *J. Am. Chem. Soc.* **89** (1967) 3121.
5. Bastiansen, O., Hassel, O. and Risberg, E. *Acta Chem. Scand.* **9** (1955) 232.
6. Andersen, B., Seip, H. M., Strand, T. G. and Stølevik, R. *Acta Chem. Scand.* **23** (1969) 3224.
7. Peacher, J. L. and Wills, J. C. *J. Chem. Phys.* **46** (1967) 4807.
8. Watson, R. E. and Freeman, A. J. *Phys. Rev.* **123** (1961) 521.
9. Clementi, E., Roothaan, C. C. J. and Yoshimine, M. *Phys. Rev.* **127** (1962) 1618.
10. Seip, H. M., Strand, T. G. and Stølevik, R. *Chem. Phys. Letters* **3** (1969) 617.
11. Carroll, B. L. and Bartell, L. S. *Inorg. Chem.* **7** (1968) 219.
12. Bartell, L. S. and Carroll, B. L. *J. Chem. Phys.* **42** (1965) 3076.
13. Pauling, L. *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York 1960, pp. 228–229.
14. Pauling, L. *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York 1960, p. 246.
15. Almenningen, A., Haaland, A. and Morgan, G. L. *Acta Chem. Scand.* **23** (1969) 2921.
16. Almenningen, A., Gundersen, G. and Haaland, A. *Acta Chem. Scand.* **22** (1968) 328.
17. Malone, J. F. and McDonald, W. S. *Chem. Commun.* **1970** 280.



18. Byram, S. K., Fawcett, J. K., Nyberg, S. C. and O'Brian, R. J. *Chem. Commun.* **1970** 16.
19. Dewar, M. J. S. and Patterson, D. B. *Chem. Commun.* **1970** 544.
20. Kuchitsu, K., Fukuyama, T. and Morino, Y. *J. Mol. Structure* **1** (1967-1968) 463.

Received October 14, 1970.