Inorganica Chimica Acta, 31 (1978) L379–L380
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

On the Barrier to Internal Rotation in the Trimethylamine Complexes of Boron Trifluoride and Boron Trichloride

MAGDOLNA HARGITTAI and JON BRUNVOLL*

Central Research Institute of Chemistry, Hungarian Academy of Sciences, H1525 Budapest, Pf. 17, Hungary

Received August 7, 1978

The molecular structure of the two trimethylamine–boron halide adducts has recently been determined by electron diffraction in our laboratory [1]. A staggered conformation was unambiguously established for both molecules. This is illustrated by the experimental and calculated radial distributions for the chlorine derivative in Fig. 1.

In the present report we communicate the results of our estimates for the barrier to internal rotation around the boron–nitrogen bond. The method proposed by Karle [2] was used which is based on the experimentally determined mean amplitudes of vibration for the rotation–dependent distances. This method has proved to yield valuable information on the barrier height for several molecules [2–4]. The following two basic assumptions are utilized in Karle's method. (1) The shape of the potential function of internal rotation is assumed to be known. In case of the present ethane-like molecules it is

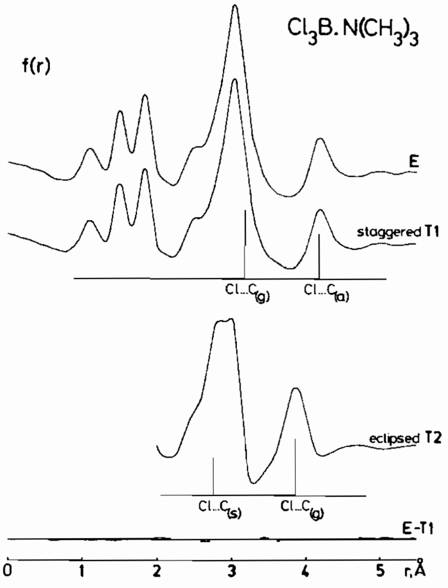

Figure 1. Electron diffraction radial distributions (E–experimental, T1–theoretical staggered model, T2–theoretical eclipsed model) The positions of the Cl...C distances are indicated.

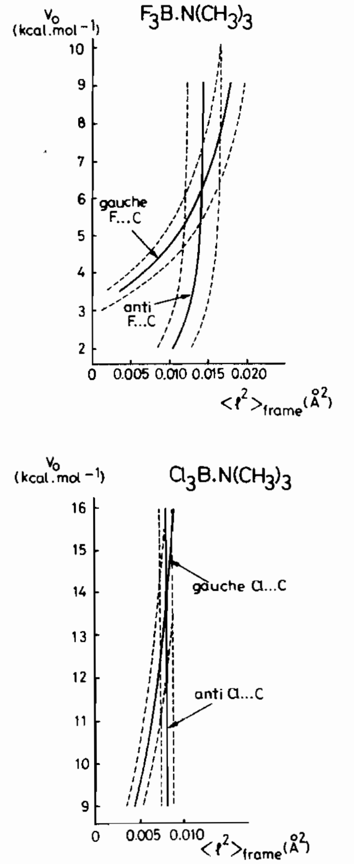

Figure 2. Graphical determination of the barrier to internal rotation according to Ref. 2.

$$V(\phi) = V_0/2\,(1 - \cos 3\phi)$$

where V_o is the barrier height and ϕ is the angle of rotation. (2) The framework vibrational amplitudes of the rotation–dependent distances are assumed to be the same.

Figure 2 shows the graphical solution of the equations determining the potential barrier according to Karle's method. This indicates a barrier of V_o = 6.2 and 13.7 kcal mol^{-1} for $F_3B{\cdot}N(CH_3)_3$ and $Cl_3B{\cdot}N(CH_3)_3$, respectively. Considering the error limits of the mean amplitudes of vibration V_o falls between 4.6 and 9.9 kcal mol^{-1} in case of the fluorine derivative. For $Cl_3B{\cdot}N(CH_3)_3$ the lower limit is 11.0 kcal mol^{-1} while the steepness of the curves does not make it possible to get a reasonable upper limit.

The relatively high potential barrier in the trimethylamine complexes of boron halides is consistent with the electron diffraction results. The considerably higher torsional barrier in the chlorine deriva-

---

*On leave from the University of Trondheim.

tive corresponds to the stronger van der Waals interaction in this molecule.

In $Cl_3Al \cdot N(CH_3)_3$ the same method yields a barrier of ~2.8 kcal mol^{-1} as estimated by us from the electron diffraction data of Haaland *et al.* [5]. This is considerably lower than that in $Cl_3B \cdot N(CH_3)_3$. However, this is not unexpected, considering the longer Al–N coordination bond and, consequently, the much longer chlorine–carbon distances in the aluminium derivative ($Cl \ldots C_{(gauche)}$ = 3.180 and 3.569 Å for $Cl_3B \cdot N(CH_3)_3$ and $Cl_3Al \cdot N(CH_3)_3$, resp.). The same trend is observed in analogous carbon and silicon compounds, *e.g.* for $Cl_3C \cdot CCl_3$ V_o is 11.0–14.6 kcal mol^{-1} (using different geometrical data) and for $Cl_3C \cdot SiCl_3$ V_o = 3.9 kcal mol^{-1} (*cf.* [3]).

References

1 M. Hargittai and I. Hargittai, *J. Mol. Struct.*, *39*, 79 (1977).
2 J. Karle, *J. Chem. Phys.*, *45*, 4149 (1966).
3 I. Hargittai and J. Brunvoll, *J. Mol. Struct.*, *44*, 107 (1978).
4 J. Brunvoll, I. Hargittai and R. Seip, *Z. Naturforsch.*, *33a*, 222 (1978).
5 A. Almenningen, A. Haaland, T. Haugen and D. P. Novak, *Acta Chem. Scand.*, *27*, 1821 (1973).