

POTENTIAL BARRIER TO INTERNAL ROTATION FOR C_{3v} TOPS FROM VIBRATIONAL SPECTROSCOPIC CALCULATIONS

A. SEBESTYÉN

Department of General and Inorganic Chemistry,
University of Chemical Engineering, H-8201 Veszprém

Summary

Potential barriers to internal rotation for $X_3P \cdot BY_3$, CX_3SO_2Y and $XF_2P \cdot BY_3$ ($X=H, D, F, Cl$; $Y=H, D, F, Cl, Br, I$) molecules have been calculated from torsional frequencies and from calculated mean-square amplitudes of vibration. Results obtained using Pitzer's and Karle's methods of barrier heights calculations are compared.

Introduction

Interdependence and collaboration between electron diffractometry and vibrational spectroscopy are well known. As a recent example determination of potential barrier to internal rotation from data of electron diffraction and vibrational spectra is shown. This kind of works has been made for twelve phosphine-boranes, $X_3P \cdot BY_3$ ($X=H, D$; $Y=H, D, F, Cl, Br, I$) [1] five methane sulphonyl halides, CX_3SO_2Y ($X=H, F, Cl$; $Y=F, Cl, Br$) [2], and five isotopic substituted difluoro phosphine-boranes, $XF_2P \cdot BY_3$ ($X, Y=H, D$; $B=^{10}B, ^{11}B$), respectively. Having made previously the complete vibrational analysis for all the molecules above, calculation of both parallel and perpendicular vibrational mean amplitudes was our main purpose for applying in electron diffraction experiments. During reliability investigations of the mean amplitudes for interatomic distances depending on internal rotation the need to make potential barrier calculations by the Karle's methods [3] has arisen. We wanted to estimate reliability of the mentioned mean amplitudes by comparing the barrier heights calculated from them with those known or calculated from other sources. These works have led then to the more rigorous examination of conditions of the Karle's methods and to the comparison between the Karle's and Pitzer's procedures.

Method and results

The common basic assumptions in either of the methods applied are as follows: i) the selected potential function of the threefold rotating symmetry, namely

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

was the same also for all the three molecular sets; ii) the frame and torsional motions in the molecules were assumed equally separable and iii) the same molecular geometries were used [1, 2, 5].

The Pitzer's procedure [4] gives the potential parameter, V_0 , by use of the internal rotation constant, F , and the torsional frequency, ν_e , as well as the s- and b-parameters of the Mathieu's functions. The Karle's method suggests two graphic solutions starting from the mean-square amplitudes of two or three internal rotation dependent distances as it can be seen in Fig. 1.

Producing the torsional contributions to the mean-square amplitudes in term of V_0 as variable and using the separability expression

$$\langle l^2 \rangle = \langle l^2 \rangle_{\text{tors}} + \langle l^2 \rangle_{\text{frame}} \quad (2)$$

V_0 versus $\langle l^2 \rangle_{\text{frame}}$ curves can be drawn for all distances mentioned. Possessing three distances at least in the version b) dependence of the frame amplitudes on the torsional angle, Φ_e , could be taken into account in the assumed form of

$$\langle l^2 \rangle_{\text{frame}} = \alpha \{ 1 + \beta \exp [-(\pi - |\Phi_e|)^2 / a] \}. \quad (3)$$

Having only two appropriate distances, however, in the version a) an additional constraint, namely independence of the frame amplitudes on the Φ_e , was forced to be introduced. Therefore, in the method a) the common mean-square frame amplitude—as an intersect of the two curves—gives the V_0 -value, while in the method b) the three V_0 versus β_{ij} curves—determined for three pairs of distances—lead to the solution. Here β_{ij} is given as

$$\beta_{ij} = \frac{\langle l_i^2 \rangle_{\text{fr}} - \langle l_j^2 \rangle_{\text{fr}}}{\langle l_j^2 \rangle_{\text{fr}} \exp [-(\pi - |\Phi_{ei}|)^2 / a] - \langle l_i^2 \rangle_{\text{fr}} [\exp -(\pi - |\Phi_{ej}|)^2 / a]}. \quad (4)$$

In certain cases ($X_3P \cdot BY_3$, X_3CSO_2Y) the required frame amplitudes could also be calculated from the vibrational analysis. Then introduction of these

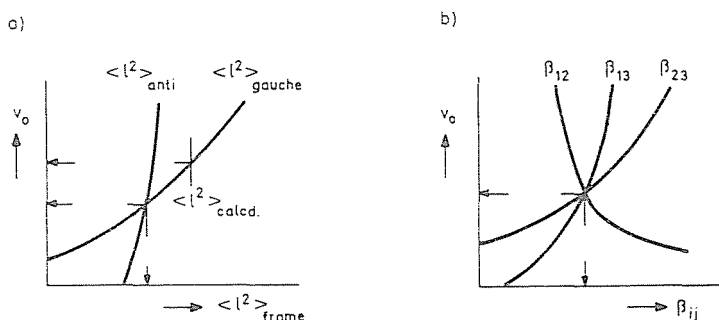


Fig. 1

Table 1

Potential barrier to internal rotation, V_0 , for $X_3P \cdot BY_3$, CX_3SO_2Y and $XF_2P \cdot BY_3$ molecules

| Molecule | T (K) | ν_2 (cm^{-1}) | V_0 ($\text{kJ} \cdot \text{mol}^{-1}$) | | | | Reference ^(d) |
|-------------------------|------------|---------------------------------|---|----------------------|----------------------|--------------------------|--------------------------|
| | | | Pitzer | Karle ^(a) | Karle ^(b) | Mod Karle ^(c) | |
| $H_3P \cdot BH_3$ | 213 | 225 | 10.4 | 2.4 | — | 9.5 | 10.3 (MW) |
| $D_3P \cdot BD_3$ | 213 | 159 | 9.9 | 3.3 | — | 10.1 | |
| $F_3P \cdot BH_3$ | 213 | 199 | 13.5 | 6.1 | — | 10.6 | 13.6 (MW) |
| $F_3P \cdot BD_3$ | 213 | 143 | 13.4 | 9.4 | — | 13.5 | |
| $H_3P \cdot BBr_3$ | 77 | 174 | 12.0 | 3.1 | — | 7.5 | 12.2 (SP) |
| $D_3P \cdot BBr_3$ | 77 | 133 | 13.4 | 4.1 | — | 9.4 | 13.7 (SP) |
| CH_3SO_2F | 378 | 201 | 10.3 | 5.5 | 9.0 | 11.9 | 10.6 (MW) |
| CH_3SO_2Cl | 378 | (200) | 10.4 | 8.1 | 8.1 | 12.4 | > 8.4 (MW) |
| CH_3SO_2Br | 345 | (200) | 11.4 | 9.0 | 8.8 | 13.2 | |
| CF_3SO_2Cl | 283 | 55 | 14.5 | 14.4 | 13.8 | 16.4 | 9.2–20.9 (ED) |
| CCl_3SO_2Cl | 343 | 50 | 22.7 | — | — | — | 16.3–23.5 (ED) |
| $HF_2P \cdot ^{10}BH_3$ | 195 | 250 | 19.6 | — | 16.1 | — | |
| $HF_2P \cdot ^{11}BH_3$ | 195 | 247 | 19.0 | 3.5–8.0 | 16.7 | — | 15.0–18.8 (MW) |
| $DF_2P \cdot ^{11}BH_3$ | 195 | 243 | 18.5 | — | 20.9 | — | |
| $HF_2P \cdot ^{11}BD_3$ | 195 | 176 | 18.3 | — | 14.5 | — | |
| $DF_2P \cdot ^{11}BD_3$ | 195 | 174 | 17.8 | — | 15.5 | — | |

(a) Graphic solutions from pairs of *anti* and *gauche* $\langle I^2(X \dots Y) \rangle$ amplitudes(b) Graphic solutions from three $\langle I^2(X \dots O) \rangle$, as well as three $\langle I^2(F \dots Y) \rangle$ amplitudes(c) Solutions obtained by use of calculated $\langle I^2 \rangle_{\text{frame}}$

(d) References in reports [1, 2, 5]

calculated frame amplitudes resulted in the so-called modified Karle's V_0 -values.

Results of potential barrier calculations obtained by different procedures at temperatures of electron diffraction or spectroscopic experiments are collected and compared in Table 1.

Discussion

In the comparison of results obtained by different methods the various assumptions introduced into the calculations should not be disregarded. Level of approximation, however, was the same for both—Pitzer's and Karle's—procedures, consequently differences found among the potential barriers, V_0 , could be assigned mainly to methodological deviations. Barrier heights measured by independent experiments or the Pitzer's values for lack of the formers were accepted as reference basis.

Considering the assumptions above potential function of the threefold rotating symmetry only for the $\text{XF}_2\text{P} \cdot \text{BY}_3$ molecules is a crude approximation but a necessity due to deficiency of measured data. Separability of the frame and torsional motions, however, is a generally accepted condition in the conformational analysis, although it is valid—in a strict sense—only for the $\text{X}_3\text{P} \cdot \text{BY}_3$ molecules. It was found that in the case of $\text{CX}_3\text{SO}_2\text{Y}$ molecules interaction between the two kinds of motion was also negligible. Making use of this fact and choosing the torsional force constant infinitely high, it was possible to calculate the mean-square frame amplitudes, too. Hence an opportunity was opened to investigate torsional angle dependence of the mean-square frame amplitudes and to obtain the modified Karle's V_0 values, as well. We could observe that the constraint made in version a) of the Karle's method was a rather crude approximation.

Since calculated mean square amplitudes were used in the Karle's methods their errors should also be taken into account. Deviations, however, between the Pitzer's and Karle's V_0 -values are much greater than they would be due to the errors in the amplitudes. The modified V_0 -values, after elimination of constraint in version a), well approximate those of Pitzer.

The Karle's β -method—version b)—assumes equation (3) for the torsional angle dependence of the mean-square frame amplitudes. Cyvin et al. [6] suggested a trigonometric function with three parameters but they thought that a better approximation could be obtained with $a=4$ in the original exponential function. In the course of our calculations we retained the exponential function with $a=1$ and $a=2$ in $\text{CX}_3\text{SO}_2\text{Y}$ and $\text{XF}_2\text{P} \cdot \text{BY}_3$ sets, respectively. The results calculated by this way led to the conclusion that the form of this function has also an important role.

References

1. SEBESTYÉN, A.—MEGYERI, L.—VIZI, B.: *J. Mol. Struct., THEOCHEM*, 89, 259 (1982)
2. SEBESTYÉN, A.—VIZI, B.: *Acta Chim. Hung.*, 118, 111 (1985)
3. KARLE, J.: in *Diffraction Studies on Non-Crystalline Substances*, (Ed. I. Hargittai and W. J. Orville-Thomas), Elsevier, Amsterdam 1981
4. CUNLIFFE, A. V.: *Internal Rotation in Molecules* (Ed. W. J. Orville-Thomas), J. Wiley, London 1974
5. TAYLOR, R. C.—DUNNING, V. D.: *J. Mol. Struct.*, 95, 23 (1982)
6. CYVIN, S. J.—ELVEBREDD, I.—CYVIN, B. N.—BRUNVOLL, J.—HAGEN, G.: *Acta Chem. Scand.*, 21, 2405 (1967)

Attila SEBESTYÉN, H-8201 Veszprém POB 158