

Calculation of Urey-Bradley Potential Constants

III. Pyramidal XY_3 Molecules

E. MEISINGSETH

Institutt for teoretisk kjemi, Norges tekniske høgskole, Trondheim, Norway

The Urey-Bradley force constants were calculated for some pyramidal XY_3 molecules ($X = P, As, Sb$; $Y = F, Cl, Br, I$). The XY stretching constants (K) showed a systematic variation with the Pauling electronegativity for both of the X and Y atoms.

The potential function suggested by Urey and Bradley¹ has been found very useful in calculating force constants^{2,3}. This potential function usually reduces the number of constants, and their physical meaning may often be apparent. In previous papers of this series^{4,5} the Urey-Bradley force constants have been calculated for some planar XY_3 molecules. In those cases the number of force constants exceed the number of normal frequencies. In order to solve the secular equation the assumption of $F' = -0.1F$ was made. For pyramidal XY_3 molecules the number of force constants is equal to the number of frequencies. Hence the force constants can be determined exactly.

In a preliminary report⁶ the Urey-Bradley force constants were found useful for calculating mean amplitudes of vibration and shrinkage effects. It is believed that the presently calculated Urey-Bradley force constants may be of interest in connection with computations of shrinkage effects for PCl_5 and related molecules.

The Urey-Bradley potential function may in general be expressed as (see Fig. 1).

$$\begin{aligned}
 V = & \sum_i [K_i' r_i \Delta r_i + 1/2 K_i (\Delta r_i)^2] \\
 & + \sum_{i < j} [H_{ij}' r_{ij}^2 \Delta \alpha_{ij} + 1/2 H_{ij} (r_{ij} \Delta \alpha_{ij})^2] \\
 & + \sum_{i < j} [F_{ij}' d_{ij} \Delta d_{ij} + 1/2 F_{ij} (\Delta d_{ij})^2]
 \end{aligned} \tag{1}$$

Here K' , K , H' , H , F' and F denote the force constants. r , α and d represent the bond lengths, inter-bond angles and the distances between non-bonded atoms. $r_{ij} = (r_i r_j)^{1/2}$. The linear terms must be included as there may exist redundant sets among the coordinates.

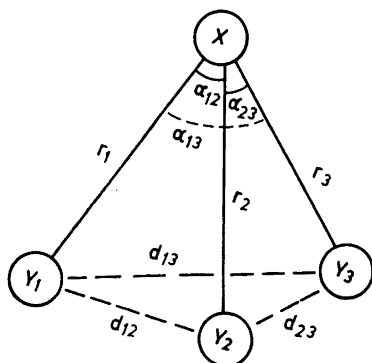


Fig. 1.

APPLICATION TO THE PYRAMIDAL XY_3 MODEL

Following the previously outlined procedure¹, the Δd 's in eqn. (1) may be eliminated to express the potential function in terms of the valence coordinates (Δr , $\Delta\alpha$). For molecules belonging to the pyramidal XY_3 model both the Δr 's and $\Delta\alpha$'s are independent variables. Hence the potential function may be transformed to a quadratic form by removing the linear terms. The appropriate expression turns out to be the same as that for planar XY_3 molecules⁴, for which the redundant condition is of the first order.

The presently studied molecular model belongs to the C_{3v} symmetry. The following set of symmetry coordinates may be constructed

$$\begin{aligned} \text{Symmetry species } A_1: S_1 &= 3^{-\frac{1}{2}}(\Delta r_1 + \Delta r_2 + \Delta r_3) \\ S_2 &= R3^{-\frac{1}{2}}(\Delta\alpha_{23} + \Delta\alpha_{13} + \Delta\alpha_{12}) \\ \text{» » E: } S_{3a} &= 6^{-\frac{1}{2}}(2\Delta r_1 - \Delta r_2 - \Delta r_3) \\ S_{3b} &= R6^{-\frac{1}{2}}(2\Delta\alpha_{23} - \Delta\alpha_{13} - \Delta\alpha_{12}) \\ S_{4a} &= 2^{-\frac{1}{2}}(\Delta r_2 - \Delta r_3) \\ S_{4a} &= R2^{-\frac{1}{2}}(\Delta\alpha_{13} - \Delta\alpha_{12}) \end{aligned}$$

The meanings of r and α are the same as in eqn. (1), and R designate the X–Y equilibrium distance.

The force constants are calculated by Wilson's secular equation

$$|GF - \lambda E| = 0$$

For the chosen set of symmetry coordinates, the following elements of the F and G matrices are obtained.

$$\begin{aligned} \text{Species } A_1: F_{11} &= K + 4s^2F \\ F_{22} &= H - s^2F' + t^2F \\ F_{12} &= 2st(F + F') \\ \text{Species } E: F_{33} &= K + 3t^2F' + s^2F \\ F_{44} &= H - s^2F' + t^2F \\ F_{34} &= -st(F + F') \end{aligned}$$

Here $s^2 = \frac{1}{2}(1 - \cos A)$, $t^2 = \frac{1}{2}(1 + \cos A)$ and $st = \frac{1}{2}\sin A$

Table 1. Calculated force constants, mdyne/Å units.

	K	H	F	F'
PF ₃	3.910	0.296	0.935	-0.813
PCl ₃	1.680	-0.212	0.743	-0.420
PBr ₃	1.436	-0.142	0.522	-0.313
PI ₃	1.031	-0.080	0.338	-0.214
AsCl ₃	1.126	-0.116	0.792	-0.208
SbCl ₃	0.451	0.045	0.770	-0.416

$$\begin{aligned} \text{Species A}_1: G_{11} &= (1 + 2\cos A) \mu_X + \mu_Y \\ G_{22} &= 2\sin^{-2}A [2(1 - \cos A)^2 (1 + 2\cos A) \mu_X \\ &\quad + (1 + \cos A - 2\cos^2 A) \mu_Y] \\ G_{12} &= -2\sin^{-1}A(1 - \cos A) (1 + 2\cos A) \mu_X \\ \text{Species E: } G_{33} &= (1 - \cos A) \mu_X + \mu_Y \\ G_{44} &= \sin^{-2}A [(1 - \cos A)^3 \mu_X + (2 - \cos A - \cos^2 A) \mu_Y] \\ G_{34} &= \sin^{-1}A(1 - \cos A)^2 \mu_X \end{aligned}$$

Here μ represent the inverse atomic masses, and A is the equilibrium Y-X-Y angle.

NUMERICAL CALCULATIONS

The numerical calculations were based upon frequencies reported by Venkateswarlu and Sunderam⁸. The adopted values for the equilibrium Y-X-Y angles have been taken from Sutton⁹. The resulting force constants are given in Table 1. The negative values of F' indicate that the forces between the non-bonded atoms are repulsive. The same feature was found for the previously studied molecules⁴, and is also consistent with the results obtained by Shimanouchi² for tetrahedral XY₄ molecules. The values of K are found to vary

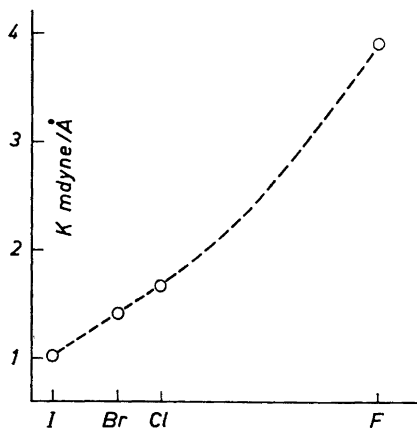


Fig. 2. K plotted against the Pauling electronegativity.

systematically through the halogen series, as also was found in the case of boron trihalides^{4,5}. In Fig. 2 the K 's are plotted against the Pauling electronegativity¹⁰ for the halogens. For SbCl_3 F is found to be greater than K . This is not in agreement with one of the assumptions made in Ref.⁴, viz. $K > F$, i.e. a force constant associated with a bonded atom pair is greater than a force constant for a non-bonded atom pair.

REFERENCES

1. Urey, H. and Bradley, C. A., Jr. *Phys. Rev.* **7** (1939) 1969.
2. Shimanouchi, T. *J. Chem. Phys.* **17** (1949) 245, 734, 818.
3. Janz, G. J. and Mikawa, Y. *J. Mol. Spectr.* **5** (1960) 92.
4. Meisingseth, E. *Acta Chem. Scand.* **16** (1962) 1601.
5. Meisingseth, E. *Acta Chem. Scand.* **16** (1962) 2321.
6. Meisingseth, E. *Acta Chem. Scand.* **16** (1962) 778.
7. Wilson, E. B., Jr., Decius, J. C. and Cross, P. C. *Molecular vibrations*, McGraw-Hill Book Co., New York 1955.
8. Venkateswarlu, K. and Sundaram, S. *Proc. Phys. Soc. (London)* **69A** (1956) 180.
9. Sutton, L. E. *Interatomic Distances*, The Chemical Society, London 1958.
10. Pauling, L. *The Nature of the Chemical Bond*, Cornell Univ. Press, New York 1960.

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