ACTA CHEMICA SCANDINAVICA 16 (1962) 2321–2324

Calculation of Urey-Bradley Potential Constants

II. Planar XY_2Z Molecules

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The Urey-Bradley force constants were calculated for $^{11}BY_2Z$ (Y,Z = F, Cl, Br). The BY stretching constants (K_{XY}) showed a systematic variation with the Pauling electronegativity of the Z-atoms. The calculated vibrational frequencies of $^{10}BY_2Z$ are in good agreement with those reported in the literature.

In the previous article [1] the Urey-Bradley force constants of boron trihalides have been reported. It seems now reasonable to calculate the force constants for mixed boron trihalides.

For small displacements from the equilibrium distances (see Fig. 1) the Urey-Bradley potential function is given by

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

Here K', K, H', H, F', and F denote the force constants. r and α represent the bond lengths and inter-bond angles, respectively, d is used to identify the distances between non-bonded atoms, and $r_{ij} = (r_i r_j)^{\frac{1}{2}}$.

APPLICATION TO THE PLANAR XY_2Z MODEL

In eqns. (1) the Δd's may be eliminated to express the potential function in terms of the valence coordinates (r, α).

Using the redundant condition ($\Delta\alpha_{12} + \Delta\alpha_{13} + \Delta\alpha_{23} = 0$) and following the same procedure as previously outlined [1], the potential function can be transformed to a quadratic form. The appropriate expression is given in Ref. [1] and need not be reported here. Wilson's secular equation [2]

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

has been utilized in the calculations.

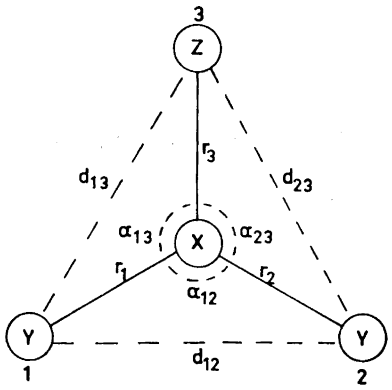

Fig. 1.

The considered planar XY_2Z molecules belong to the C_{2v} symmetry. Hence the following set of symmetry coordinates may be constructed.

Symmetry species A_1: $S_1 = (1/\sqrt{2})\,(\Delta r_1 + \Delta r_2)$
$S_2 = R\Delta\alpha_{12}$
$S_3 = \Delta r_3$
» » B_1: $S_4 = (1/\sqrt{2})\,(\Delta r_1 + \Delta r_2)$
$S^5 = (R/\sqrt{2})\,(\Delta\alpha_{13} + \Delta\alpha_{23})$

The meanings of r and α is the same as in eqns. (1). R designates the X—Y equilibrium distance.

For the presently chosen set of symmetry coordinates the elements of the F and G matrices read:

Species A_1: $F_{11} = K_{XY} + t_{YZ}^2 F'_{YZ} + 2s_{YY}^2 F_{YY} + s_{YZ}^2 F_{YZ}$
$F_{22} = H_\beta - s_{YY}^2 F'_{YY} + t_{YY}^2 F_{YY}$
$F_{33} = K_{XZ} + 2t_{YZ}^2 F_{YZ} + 2s_{YZ}^2 F_{YZ}$
$F_{12} = \sqrt{2}\, t_{YY} s_{YY} (F'_{YY} + F_{YY})$
$F_{23} = 0$
$F_{13} = -\sqrt{2}\, t_{YZ} t_{ZY} F'_{YZ} + \sqrt{2}\, s_{YZ} s_{ZY} F_{YZ}$
Species B_1: $F_{44} = K_{XY} + 2t_{YY}^2 F'_{YY} + t_{YZ}^2 F'_{YZ} + s_{YZ}^2 F_{YZ}$
$F_{55} = H_\alpha - s_{YZ} s_{ZY} F'_{YZ} + t_{YZ} t_{ZY} F_{YZ}$
$F_{45} = -t_{YZ} s_{ZY} F'_{YZ} - t_{ZY} s_{YZ} F_{YZ}$

Here $s_{ij} = (r_i - r_j \cos\alpha_{ij})/d_{ij}$, $s_{ji} = (r_j - r_i \cos\alpha_{ji})/d_{ij}$,
$t_{ij} = r_j \sin\alpha_{ij}/d_{ij}$ and $t_{ii} = r_j \sin\alpha_{ij}/d_{ij}$.

Species A_1: $G_{11} = 2\mu_x \cos^2 A + \mu_y$
$G_{22} = 4\mu_x \sin^2 A + 2\mu_y$
$G_{33} = \mu_x + \mu_y$
$G_{12} = 2\sqrt{2}\, \mu_x \cos A \sin A$
$G_{23} = 2\mu_x \sin A$
$G_{13} = \sqrt{2}\, \mu_x \cos A$
Species B_1: $G_{44} = 2\mu_x \sin^2 A + \mu_y$

$$G_{55} = 2\mu_x\left(\frac{R}{L}-\cos A\right)^2 + \mu_y + 2\left(\frac{R}{L}\right)^2\mu_z$$

$$G_{45} = 2\mu_x\left(\frac{R}{L}-\cos A\right)\sin A$$

Here μ represent the inverse atomic masses. R and L are the X—Y and X—Z equilibrium distances, respectively. A is used to designate the equilibrium YXZ angle.

NUMERICAL RESULTS

For the molecule model here considered one has eight UB force constants, but only five frequencies. To solve the secular equation, the number of independent force constants have to be reduced. Here the usual assumption of $F' = -1/10\ F$ was made. Furthermore, F_{YY}/K_{XY} values were transferred

Table 1. Calculated force constants mdyne/Å units

	BF_3	BF_2Cl	BF_2Br	BCl_3	BBr_2Cl	BBr_3
F_{YY}	(0.9263)	0.8813	0.8734	(0.5370)	0.4982	(0.4459)
K_{XY}	(6.0446)	5.7550	5.7036	(3.0212)	2.5708	(2.2997)
K_{XZ}		2.9374	2.6328		2.7328	
$H\alpha$		0.3737	0.5718		0.0665	
$H\beta$	(0.2125)	0.5916	0.5267	(0.0549)	0.1208	(0.0880)

$H\alpha$ and $H\beta$ represent the force constants for the YXZ and YXY angle bending, respectively. The values in parentheses are taken from Ref. [1]

Table 2. Calculated and observed frequencies for $^{10}BY_2Z$. * (cm^{-1} units.)

		$\nu_{obs.}$	$\nu_{calc.}$	% dev.
$^{10}BF_2Cl$	ν_1	1268	1283	0.2
	ν_2	701	725	3.4
	ν_3		399	
	ν_4	1470	1473	0.2
	ν_5	366	368	0.5
$^{10}BF_2Br$	ν_1	1247	1250	0.2
	ν_2	637	650	2.0
	ν_3		312	
	ν_4	1468	1470	0.2
	ν_5		347	
$^{10}BBr_2Cl$	ν_1	954	957	0.3
	ν_2		351	
	ν_3		153	
	ν_4	864	891	2.9
	ν_5		211	

* The data are taken from Ref[3].

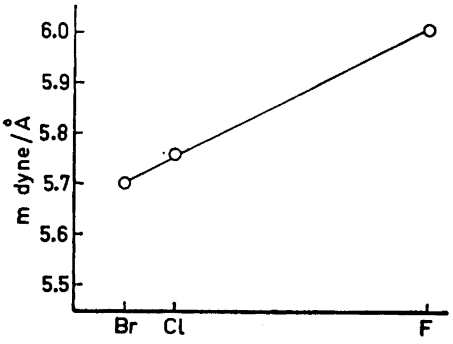

Fig. 2. K_{XY} plotted against the Pauling electronegativity of the Z-atom.

from the calculations on boron trihalides [1]. The numerical calculations were carried out using $a = A = 120°$ and based upon experimental frequencies from Ref. [3] The resulting force constants for the three molecules here considered are given in Table 1, and are compared to those for the boron trihalides.

The vibrational frequencies for $^{10}BY_2Z$ were computed from the presently calculated UB force constants. The results are given in Table 2 and show good agreement with the observed frequencies.

CORRELATION WITH ELECTRONEGATIVITY

Except for K_{XZ} in BF_2Cl, the values of the stretching force constants (K) showed to vary systematically with the electronegativity of the halogens.

In Fig. 2 the values of K_{XY} in BF_3, BF_2Cl and BF_2Br are plotted against the Pauling electronegativity [4] of the Z-atoms. The diagram shows that the stretching force constants for the B—Y bond increase with increasing electronegativity of the Z-atom. As halogens are more electronegative than boron, a substitution of the Z-atom with a more electronegative one will increase the positive charge on the boron atom. The negative charge displacement from the Y-atom to the boron atom is a second-order effect. In consequent, the resulting effect of the substitution will be a stronger B—Y bond.

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Received May 22, 1962.