

## Calculation of Urey-Bradley Potential Constants

### I. Planar $XY_3$ Molecules

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The Urey-Bradley force constants were calculated for  $^{11}BY_3$  ( $Y = F, Cl, Br, I$ ). The forces between non-bonded atoms were assumed to be repulsive, and together with some additional simple assumptions, the relation

$$-0.25 < F'/F < 0$$

was deduced. This condition is in agreement with the usual assumption of  $F' = -0.1 F$ . The calculated force constants reproduced the vibrational frequencies of  $^{10}BY_3$  with great accuracy. The BY stretching constants ( $K$ ) and the YY constants ( $F$ ) were plotted against Pauling's electronegativity showing systematical variations.

The most general form of the potential function in terms of a set of independent internal coordinates, *e.g.*, the valence coordinates, may be expressed as

$$2V = \sum_{i,j} f_{ij} \Delta q_i \Delta q_j$$

where  $f_{ij} = (\partial^2 V / \partial \Delta q_i \partial \Delta q_j)_0$ , and  $\Delta q$  are some displacements from equilibrium. When symmetry coordinates are constructed as linear combinations of valence coordinates ( $S = U \Delta q$ ), the potential function reads

$$2V = \sum_{i,j} F_{ij} S_i S_j$$

where the relation between the  $F$ 's and the  $f$ 's are given in matrix notation by

$$F = U f \tilde{U}$$

If the vibrational normal frequencies are known, the force constants may be computed by means of Wilson's secular equation<sup>1</sup>

$$|GF - \lambda E| = 0 \quad (1)$$

In general, however, the number of force constants is greater than the number of normal frequencies. Hence the secular equation cannot be solved without

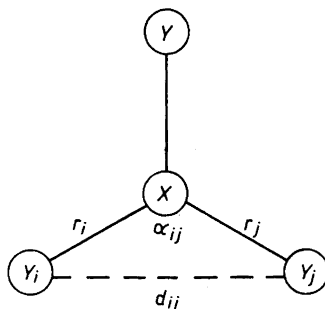


Fig. 1.

ambiguity. Many approximate potential functions have been proposed, one of the most useful ones being suggested by Urey and Bradley<sup>2</sup>. This function is based on the valence force field, but includes central forces between non-bonded atoms.

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

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

Here  $K'$ ,  $K$ ,  $H'$ ,  $H$ ,  $F'$  and  $F$  denote the force constants.  $r$  and  $a$  represent the bond lengths and interbond angles, respectively.  $d$  is the distance between the non-bonded atoms, and  $r_{ij} = (r_i r_j)^{1/2}$ . The first order part of the potential function must be included as there is no reason for assuming no strain in the molecules in its equilibrium position. In other words the XY and YY stretches are not independent. Through the relation

$$d_{ij}^2 = r_i^2 + r_j^2 - 2r_i r_j \cos \alpha_{ij}$$

$\Delta d_{ij}$  may be eliminated, and the following expression for the potential function in terms of the valence coordinates is obtained (Shimanouchi<sup>3</sup>):

$$\begin{aligned}
 V = & \sum [K'_i r_i + \sum_{j(\neq i)} F'_{ij} s_{ij} d_{ij}] (\Delta r_i) \\
 & + \sum_{i < j} [H'_{ij} r_{ij} + F'_{ij} d_{ij} (t_{ij} t_{ji})^{1/2}] (r_{ij} \Delta a_{ij}) \\
 & + 1/2 \sum_{i < j} [K_i + \sum_{j(\neq i)} (t_{ij}^2 F'_{ij} + s_{ij}^2 F_{ij})] (\Delta r_i)^2 \\
 & + 1/2 \sum_{i < j} [H_{ij} - s_{ij} s_{ji} F'_{ij} + t_{ij} t_{ji} F_{ij}] (r_{ij} \Delta a_{ij})^2 \\
 & + \sum_{i < j} [-t_{ij} t_{ji} F'_{ij} + s_{ij} s_{ji} F_{ij}] (\Delta r_i) (\Delta r_j) \\
 & + \sum_{i \neq j} [t_{ij} s_{ji} F'_{ij} + t_{ji} s_{ij} F_{ij}] (r_j / r_i)^{1/2} (\Delta r_i) (r_{ij} \Delta a_{ij})
 \end{aligned}$$

For the explanation of  $s$  and  $t$  the cited work<sup>3</sup> should be consulted.

APPLICATION TO THE PLANAR XY<sub>3</sub> MODEL

For the planar symmetrical XY<sub>3</sub> molecule the  $\Delta r$ 's are independent variables, but the following redundant condition exists for the  $\Delta\alpha$ 's

$$\Sigma \Delta\alpha_{ij} = 0$$

Since the redundant condition is exactly of the first order, it is not necessary to introduce the Lagrangian undetermined multiplier to obtain a quadratic form of the potential function. From the conditions  $(\partial V/\partial \Delta r)_0 = (\partial V/\partial \Delta\alpha)_0 = 0$  one obtains

$$K_i r_i + \Sigma F'_{ij} s_{ij} d_{ij} = 0$$

$$H_{ij} r_{ij} + F'_{ij} d_{ij} (t_{ij} t_{ji})^{1/2} = 0$$

Hence the potential function takes the following form:

$$V = 1/2 \Sigma [K_i + \Sigma_{j(\neq i)} (t_{ij}^2 F'_{ij} + s_{ij}^2 F_{ij})] (\Delta r_i)^2$$

$$+ 1/2 \Sigma [H_{ij} - s_{ij} s_{ji} F'_{ij} + t_{ij} t_{ji} F_{ij}] (r_i r_j) (\Delta\alpha_{ij})^2$$

$$+ \Sigma_{i < j} [-t_{ij} t_{ji} F'_{ij} + s_{ij} s_{ji} F_{ij}] (\Delta r_i) (\Delta r_j)$$

$$+ \Sigma_{i \neq j} [t_{ij} s_{ji} F'_{ij} + t_{ji} s_{ij} F_{ij}] (r_j/r_i)^{1/2} (\Delta r_i) (r_{ij} \Delta\alpha_{ij})$$

In the present case  $s_{ij}^2 = s_{ji}^2 = 3/4$ ,  $t_{ij}^2 = t_{ji}^2 = 1/4$  and  $s_{ij} t_{ji} = s_{ji} t_{ij} = \sqrt{3}/4$ .

For the  $F$  and  $G$  matrices the following elements are obtained:

$$F_1 = K + 3F$$

$$F_3 = K + 3/4 F + 3/4 F'$$

$$F_4 = H + 1/4 F - 3/4 F'$$

$$F_{34} = -\sqrt{3}/4 (F + F') \quad (2)$$

$$G_1 = \mu_y$$

$$G_3 = 2/3 (\mu_x + \mu_y)$$

$$G_4 = 3 (3/2 \mu_x + \mu_y) \quad (3)$$

$$G_{34} = 3/2 \sqrt{3} \mu_x$$

Eqns. (2) and (3) are in agreement with the expressions given by Janz and Mikawa<sup>4</sup>.

## DISCUSSION OF FORCE CONSTANTS

For a molecule of the here considered type one has four UB force constants, but only three frequencies. Using Eqn. (1)  $K$  and  $H$  may be eliminated, and  $F$  may be expressed as a function of  $F'$ . A plot of  $F$  vs.  $F'$  is shown in Fig. 2 for <sup>11</sup>BCl<sub>3</sub>.

As the distance between the non-bonded halogen atoms are shorter than two times the van der Waals' radii (see Table 1), one must expect the inter-nuclear forces to be repulsive. Hence  $F'$  is assumed to be negative. Another reasonable assumption is to make  $H$  positive. Furthermore,  $K$  is assumed to

Table 1. Geometrical data and van der Waals' radii.

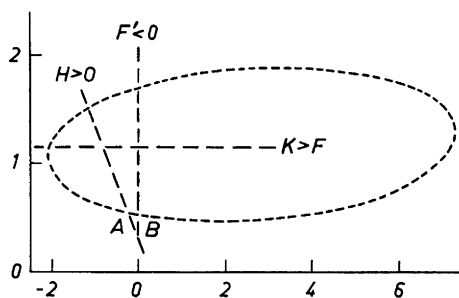
	X—Y (Å) <sup>a</sup>	Y.....Y (Å)	v. d. Waals' radii (Å) <sup>b</sup>
BF <sub>3</sub>	1.29	2.23	1.37
BCl <sub>3</sub>	1.74	3.01	1.81
BBr <sub>3</sub>	1.87	3.24	1.95
BI <sub>3</sub>	2.10	3.64	2.16

<sup>a</sup> Taken from Ref. <sup>6</sup><sup>b</sup> Taken from Ref. <sup>8</sup>

be greater than  $F$ , since  $K$  is the force constant associated with a bonded and  $F$  with a non-bonded atom pair. In consequence, the following relations between the UB force constants are established.

$$\begin{aligned} F' &< 0 \\ H &> 0 \\ K &> F \end{aligned}$$

These conditions are represented graphically in Fig. 2 and lead to the conclusion that only the narrow part of the curve between A and B gives reasonable

Fig. 2.  $F$  plotted against  $F'$  for BCl<sub>3</sub>.Table 2. Calculated force constants mdyne/Å units <sup>a</sup>.

	BF <sub>3</sub>	BCl <sub>3</sub>	BBr <sub>3</sub>	BI <sub>3</sub>
$F$	0.9263	0.5370	0.4459	0.2860
$F'$	-0.0926	-0.0537	-0.0446	-0.0286
$K$	6.0446	3.0212	2.2997	1.8400
$H$	0.2125	0.0549	0.0880	0.0407
$F_1$	8.8235	4.6324	3.6373	2.6983
	(8.8236)	(4.6324)	(3.6374)	(2.6984)
$F_3$	6.6698	3.3837	2.6007	2.0331
	(7.4068)	(3.3424)	(3.3021)	(1.7292)
$F_4$	0.5135	0.2295	0.2329	0.1337
	(0.5001)	(0.2308)	(0.1807)	(0.1508)
$F_{34}$	-0.3609	-0.2092	-0.1737	-0.1114
	(-0.6398)	(-0.1958)	(-0.3455)	(-0.0349)

<sup>a</sup> The values in parentheses are calculated by Cyvin <sup>7</sup>.

Table 3. Calculated and observed frequencies (cm<sup>-1</sup>).<sup>a</sup>

		obs.	calc.	% dev.
<sup>10</sup> BF <sub>3</sub>	$\nu_1$	888.0	888.0	0
	$\nu_3$	1504.7	1507.0	0.2
	$\nu_4$	480.4	482.3	0.4
<sup>10</sup> BCl <sub>3</sub>	$\nu_1$	471.0	471.0	0
	$\nu_3$	993.7	993.4	<0.1
	$\nu_4$	243.0	243.6	0.3
<sup>10</sup> BBr <sub>3</sub>	$\nu_1$	278.0	278.0	0
	$\nu_3$	856.0	854.1	0.2
	$\nu_4$	148.0	163.2	10
<sup>10</sup> BI <sub>3</sub>	$\nu_1$	190.0	190.0	0
	$\nu_3$	737.0	737.2	<0.1
	$\nu_4$	100.0	100.0	0

<sup>a</sup> The data for BF<sub>3</sub> and BCl<sub>3</sub> are from Ref. <sup>5</sup>, and for BBr<sub>3</sub> and BI<sub>3</sub> from Ref. <sup>6</sup>.

force-constant values. The variations between A and B are found to be within the order of magnitude of 0.02 mdyne/Å and 0.06 mdyne/Å for  $F$  and  $K$  respectively. The same conclusion was obtained for the other boron trihalides considered. For all these molecules the following restriction was deduced

$$-0.25 < F'/F < 0$$

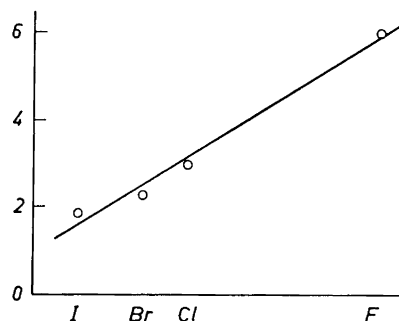


Fig. 3.  $K$  plotted against the Pauling electronegativity.

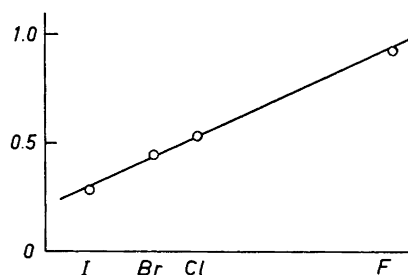


Fig. 4.  $F$  plotted against the Pauling electronegativity.

It seems reasonable to choose  $F' = -0.1 F$  for all the boron trihalides. This choice is identical with the frequently applied approximation first proposed by Shimanouchi<sup>3</sup>.

#### NUMERICAL RESULTS

The numerical calculations were carried out using  $F' = -0.1 F$ , and based on experimental frequencies from Ref.<sup>5</sup> for  $\text{BF}_3$  and  $\text{BCl}_3$ , and from Ref.<sup>6</sup> for  $\text{BBr}_3$  and  $\text{BI}_3$ . The resulting force constants are given in Table 2. Those for the fluoride, chloride and bromide are in good agreement with recently published UB force constants of Janz and Mikawa<sup>4</sup>. The symmetrized F-matrix elements were calculated according to Eqns. (2) and are included in Table 2. The results are compared to those calculated by Cyvin<sup>7</sup>.

The vibrational frequencies for  $^{10}\text{BY}_3$  (Y = F, Cl, Br, I) were computed from the presently calculated UB force constants. The results are presented in Table 3 and show good agreement with the observed frequencies.

#### CORRELATION WITH ELECTRONEGATIVITY

The values of  $K$  and  $F$  change systematically through the series of the boron trihalides. In Figs. 3 and 4 these constants are plotted against the Pauling electronegativity for the halogenes<sup>8</sup>.

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Received January 26, 1962.