Calculation of Standard Deviations for Interatomic Distances in Benzene Based upon Spectroscopic Data

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A set of force constants in a harmonic potential function for in-plane vibrations of benzene has been computed and used for a normal coordinate determination. The ten types of interatomic distances are studied by group theory methods and the normal coordinate analysis is performed. Finally the standard deviation for all interatomic distances in benzene is given at the temperatures 0, 273, 298 and 323°K.

The subject of this paper is the calculation of standard deviations for interatomic distances in the benzene molecule by making use of a normal coordinate analysis for in-plane vibrations. The vibrations are treated as harmonic oscillations. As for the theory, the treatment given by Wilson, Decius and Cross [1] is followed. The treatment is extended to deal with all types of interatomic distances. Crawford and Miller [2] have previously evaluated a set of force constants for benzene. In this paper another set is used, as obtained by recalculation with a newer set of experimental frequencies [3].

SYMMETRY COORDINATES

The applied symmetry coordinates are of the VFSC type (linear combinations of valence force coordinates) and are specified in Table 1. The notation for valence force coordinates is: σ for C—H stretching (s in Wilson's notation [1]), τ for C—C stretching (t in Wilson's notation), α for C—C—C bending and β for C—H bending (identical with the notations by Wilson). According to Table 1, for instance, $s_{12} = 6^{-\frac{1}{2}} (\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6)$. The symmetry coordinates, as well as the normal coordinates, are numbered in the same way as Wilson's [1] and Langseth's [3] numbering of fundamental frequencies.

Table 1. Symmetry coordinates for in-plane vibrations of benzene.

Species	VFSC	N	1	2	3	4	5	6	
A_{1g}	s_2	$6^{-\frac{1}{2}}$	1	1	1	1	1	1	σ
	s_1	$6^{-\frac{1}{2}}$	1	1	1	1	1	1	τ
	s_r	$6^{-\frac{1}{2}}$	1	1	1	1	1	1	a
A_{2g}	s_3	$6^{-\frac{1}{2}}$	1	1	1	1	1	1	β
B_{1u}	s_{13}	$6^{-\frac{1}{2}}$	1	-1	1	-1	1	-1	σ
	s_{12}	$6^{-\frac{1}{2}}$	1	-1	1	-1	1	-1	a
B_{2u}	s_{14}	$6^{-\frac{1}{2}}$	-1	1	-1	1	-1	1	τ
	s_{15}	$6^{-\frac{1}{2}}$	1	-1	1	-1	1	-1	β
E_{2g}	s_{7a}	$12^{-\frac{1}{2}}$	2	-1	-1	2	-1	-1	σ
	s_{8a}	$12^{-\frac{1}{2}}$	1	-2	1	1	-2	1	τ
	s_{6a}	$12^{-\frac{1}{2}}$	2	-1	-1	2	-1	-1	a
	s_{9a}	$\frac{1}{2}$	0	1	-1	0	1	-1	β
	s_{7b}	$\frac{1}{2}$	0	1	-1	0	1	-1	σ
	s_{8b}	$\frac{1}{2}$	1	0	-1	1	0	-1	τ
	s_{6b}	$\frac{1}{2}$	0	1	-1	0	1	-1	a
	s_{9b}	$12^{-\frac{1}{2}}$	-2	1	1	-2	1	1	β
E_{1u}	s_{20a}	$12^{-\frac{1}{2}}$	2	1	-1	-2	-1	1	σ
	s_{19a}	$\frac{1}{2}$	1	0	-1	-1	0	1	τ
	$s_{r;a}$	$12^{-\frac{1}{2}}$	2	1	-1	-2	-1	1	a
	s_{18a}	$\frac{1}{2}$	0	1	1	0	-1	-1	β
	s_{20b}	$\frac{1}{2}$	0	-1	-1	0	1	1	σ
	s_{19b}	$12^{-\frac{1}{2}}$	-1	-2	-1	1	2	1	τ
	$s_{r;b}$	$\frac{1}{2}$	0	-1	-1	0	1	1	a
	s_{18b}	$12^{-\frac{1}{2}}$	2	1	-1	-2	-1	1	β

Three redundants (see Table 1) are occurring among the symmetry coordinates. These have been removed by the conditions:

$$s_r = 0 \qquad (1)$$

$$s_{r;a} = -s_{19a}/l_2 \qquad (2)$$

$$s_{r;b} = -s_{19b}/l_2 \qquad (3)$$

l_2 is the C—C equilibrium distance.

FORCE CONSTANTS

The adopted force constants of the potential function in terms of symmetry coordinates are given in Table 2. The calculation has been based on fundamental frequencies for benzene and benzene-d_6 from spectroscopic data by Brodersen and Langseth [3].

l_1 and l_2 denote the C—H and C—C equilibrium distances, respectively.

Table 2. Force constants of the potential function in symmetry coordinates (10^5 dyn cm^{-1})

	s_2	s_1	s_3	s_{13}	s_{12}	s_{14}	s_{15}
s_2	5.029	−0.468					
s_1		7.883					
s_3			0.863 l_1^2				
s_{13}				4.994	0.095 l_2		
s_{12}					0.680 l_3^2		
s_{14}						4.363	0.718 l_1
s_{15}							0.837 l_1^2

	s_7	s_8	s_6	s_9	s_{20}	s_{19}	s_{18}
s_7	5.184	0	0	0			
s_8		5.508	0	0			
s_6			0.799 l_2^2	−0.160 l_1^2			
s_9				0.869 l_1^2			
s_{20}					5.098	0	0
s_{19}						11.645	1.586 l_1
s_{18}							0.825 l_1^2

NORMAL COORDINATE ANALYSIS FOR SYMMETRY COORDINATES

A symmetry coordinate is approximated to a linear combination of normal coordinates from the respective symmetry species,

$$s_i = \sum_j B_{ij} Q_j \qquad (4)$$

The transformation coefficients have been determined by Wilson's method [1], and their squares are given in Table 3. M denotes the mass of the carbon atom.

GROUP THEORY TREATMENT OF THE INTERATOMIC DISTANCES

In benzene there are ten types of interatomic distances, each type forming a symmetric equivalent set. The notation used for deviations from the equilibrium distances is as follows.

σ for the distances of type C_1—H_1, σ^* for C_2—H_1, σ^{**} for C_3—H_1 and σ^{***} for C_4—H_1;

τ for the type C_1—C_2 (*ortho*), τ^* for C_1—C_3 (*meta*) and τ^{**} for C_1—C_4 (*para*); ϱ for the type H_1—H_2, ϱ^* for H_1—H_3 and ϱ^{**} for H_1—H_4.

Each of the equivalent sets is taken as basis for a reducible representation of the group D_{6h}. The characters of these representations are given in Table 4. Then it is a simple matter to determine the symmetric structure of the represen-

Table 3. Numerical values of the terms $B_{ij}^2 M$.

	Q_2	Q_1	Q_3	Q_{13}	Q_{12}	Q_{14}	Q_{15}
s_2	12.8664	0.05041					
s_1	0.1141	0.8860					
s_3			$15.0709/l_1^2$				
s_{13}				12.8754	0.04145		
s_{12}				$1.3244/l_2^2$	$10.6756/l_2^2$		
s_{14}						2.1944	0.8056
s_{15}						$0.8717/l_1^2$	$12.0452/l_1^2$

	Q_7	Q_5	Q_6	Q_9	Q_{20}	Q_{19}	Q_{18}
s_7	12.8867	0.02608	0.001646	0.002454			
s_5	0.04313	2.0696	0.1074	0.2798			
s_6	$0.6952/l_2^2$	$2.9623/l_2^2$	$2.9158/l_2^2$	$0.9267/l_2^2$			
s_9	$0.09629/l_2^2$	$10.3134/l_2^2$	$0.2417/l_2^2$	$12.0711/l_2^2$			
s_{20}					12.8798	0.03574	0.001341
s_{19}					0.09085	1.0503	0.3588
s_{18}					$0.03141/l_1^2$	$0.2034/l_1^2$	$14.5233/l_1^2$

tations by usual methods from group theory. The results can be expressed in the following way:

$$\Gamma(\tau \varrho) = A_{1g} + B_{2u} + E_{2g} + E_{1u} \qquad (5)$$

$$\Gamma(\sigma,\sigma^{***},\tau^{*},\varrho^{*}) = A_{1g} + B_{1u} + E_{2g} + E_{1u} \qquad (6)$$

$$\Gamma(\sigma^{*},\sigma^{**}) = A_{1g} + A_{2g} + B_{1u} + B_{2u} + 2E_{2g} + 2E_{1u} \qquad (7)$$

$$\Gamma(\tau^{**},\varrho^{**}) = A_{1g} + E_{2g} \qquad (8)$$

The above results show which of the normal coordinates build up a given interatomic distance coordinate. Thus for instance only normal coordinates from species A_{1g} and E_{2g} will enter into the expression of τ^{**} and ϱ^{**} as linear combinations of normal coordinates.

Table 4. Characters for reducible representations of the group D_{6h}

χ	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	I	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
τ,ϱ	6	0	0	0	0	2	0	0	0	6	2	0
$\sigma,\sigma^{***},\tau^{*},\varrho^{*}$	6	0	0	0	2	0	0	0	0	6	0	2
σ^{*},σ^{**}	12	0	0	0	0	0	0	0	0	12	0	0
τ^{**},ϱ^{**}	3	0	0	3	1	1	3	0	0	3	1	1

NORMAL COORDINATE ANALYSIS FOR INTERATOMIC DISTANCE COORDINATES

A representative set of ten interatomic distance deviations has been expressed by the set of symmetry coordinates,

$$r = Vs \tag{9}$$

V being the transformation matrix. The connection between symmetry coordinates and normal coordinates, eqn. (4), is given in matrix notation by

$$s = BQ \tag{10}$$

Then the transformation matrix in

$$r = CQ \tag{11}$$

can easily be found, since

$$C = VB \tag{12}$$

The squares of the matrix elements rather than the elements themselves have been calculated. The values $l_1 = 1.084$ Å and $l_2 = 1.397$ Å for C—H and C—C equilibrium distances have been adopted. The results are listed in Table 5.

Table 5. Numerical values of the terms $C^2_{ki}M$.

	σ	σ^*	σ^{**}	σ^{***}	τ	τ^*	τ^{**}	ϱ	ϱ^*	ϱ^{**}
Q_2	2.1444	1.1828	1.2835	1.4129	0.01901	0.05703	0.07603	1.7596	5.2789	7.0385
Q_1	0.008402	0.1778	0.5517	0.7399	0.1477	0.4430	0.5906	0.2265	0.6795	0.9060
Q_3		0.7922	0.3177							
Q_{13}	2.1459	1.2314	1.2933	2.1459		0.05518			5.3008	
Q_{12}	0.006908	0.1292	0.5419	0.006908		0.4448			0.6576	
Q_{14}		0.5751	0.001537		0.3657			1.6000		
Q_{15}		0.2171	0.3161		0.1343			4.3583		
Q_7	4.2956	2.4215	3.4386	2.9434	0.01438	0.01873	0.1274	0.9277	2.6603	14.3505
Q_8	0.008694	0.4713	0.07046	0.2900	0.6899	0.04949	0.1983	0.8968	0.8308	0.3991
Q_6	0.000549	0.09576	0.4498	0.9444	0.03581	0.4314	0.8995	0.03121	0.4578	0.9905
Q_9	0.000818	1.3166	0.3463	0.1276	0.09328	0.000179	0.1080	8.0724	2.0096	0.1489
Q_{20}	4.2933	2.3747	3.3563	4.2933	0.03028	0.03028		2.5849	2.5849	
Q_{19}	0.01191	0.6332	0.7062	0.01191	0.3501	0.3501		1.5777	1.5777	
Q_{18}	0.000447	1.2978	0.2431	0.000447	0.1196	0.1196		1.7957	1.7957	

STANDARD DEVIATIONS OF INTERATOMIC DISTANCES

At this point the standard deviations of interatomic distances,

$$u = \overline{(r^2)}^{1/2} \tag{13}$$

can be calculated by means of the formula

$$u^2 = \overline{r_k^2} = \sum_i C^2_{ki} \frac{|h}{8\pi^2 \nu_i} \coth \frac{h\nu_i}{2kT} \tag{14}$$

Table 6. Standard deviations for interaromic distances in benzene

Distance	Calculated standard deviations in Å units			
	$T = 0$	273.16	298.16	323.16
C_1-H_1	0.0771	0.0771	0.0771	0.0771
C_2-H_1	0.1000	0.1003	0.1004	0.1006
C_3-H_1	0.0952	0.0958	0.0960	0.0963
C_4-H_1	0.0928	0.0939	0.0942	0.0946
C_1-C_2	0.0457	0.0459	0.0459	0.0460
C_1-C_3	0.0534	0.0544	0.0547	0.0551
C_1-C_4	0.0576	0.0592	0.0597	0.0603
H_1-H_2	0.1556	0.1559	0.1561	0.1563
H_1-H_3	0.1313	0.1318	0.1321	0.1323
H_1-H_4	0.1179	0.1188	0.1191	0.1195

(see, *e.g.*, Morino *et al.*[4]) C_{ki} denotes the coefficients of eqn. (11), the squares of which have been enumerated in the previous section. v_i is a fundamental frequency, h Planck's constant, k Boltzmann's constant and T is the absolute temperature.

Table 6 shows the calculated values for u at the temperatures $T = 0$, 273.16, 298.16 and 323.16°K. The values have been compared with results from electron diffraction data as obtained by Karle [5] and later by Bastiansen *et al.*[6] A report about this has been submitted for publication elsewhere [7].

It is planned to work out the same calculations also for benzene-d_6.

REFERENCES

1. Wilson, E. B. Jr., Decius, J. C. and Cross, P. C. *Molecular Vibrations*, N.Y., Toronto, London 1955.
2. Crawford, B. L. Jr. and Miller, F. A. *J. Chem. Phys.* **17** (1949) 249.
3. Brodersen, S. and Langseth, A. *Mat. Fys. Skr. Dan. Vid. Selsk.* **1** (1956) 1.
4. Morino, Y., Kuchitsu, K. and Shimanouchi, T. *J. Chem. Phys.* **20** (1952) 726.
5. Karle, I. *J. Chem. Phys.* **20** (1952) 65.
6. Almenningen, A., Bastiansen, O. and Fernholt, L. *Kgl. Norske Videnskabs Selskabs Skrifter* (1957). *In press.*
7. Bastiansen, O. and Cyvin, S. J. *Nature* (1957). *In press.*