

CALCULATION OF LIBRATIONAL FREQUENCIES
IN THE ACENAPHTHENE CRYSTAL

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The force constants of the 12 librational vibrations of molecules in the acenaphthene crystal were calculated from the variation of the intermolecular interaction energy with the rotation angle of the molecules, using the "6—exp" potential function and the harmonic approximation. The librational frequencies evaluated from these constants were compared with spectroscopic (IR and Raman) data. The results were discussed in terms of the validity of the assumed model; conclusions concerning the dominant type of interaction during the librations have been drawn.

In making an analysis of the lattice dynamics of molecular crystals difficulties arise due to the fact they are usually of low symmetry. The use of Cochran's and Pawley's method [1] is not feasible for such crystals, as the number of parameters describing the lattice dynamics rapidly increases with lowering of the symmetry.

The basic problem in the calculation of the lattice vibrations is the determination of the force constant tensors of intermolecular interactions in the crystal; these tensors can be evaluated by assuming a definite force field model. It is generally accepted that in hydrocarbon crystals the packing and mutual orientation of molecules are determined by the van der Waals and repulsion forces [2, 3, 4]. In this approximation the potential energy function of the interactions is given by the so called "6 — exp" function.

$$\Phi = -A \sum_{i,k} r_{ik}^{-6} + B \sum_{i,k} \exp(-\alpha r_{ik}) \quad (1)$$

where r_{ik} is the distance between the non-bonded atoms i and k of a pair of molecules, A , B , α are semiempirical constants; Φ denotes the interaction potential energy. Pawley [5]

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used this function for the evaluation of dispersion curves for anthracene and naphthalene crystals. The intermolecular interaction force constants were determined assuming that the minimum of the potential energy Φ corresponds to the equilibrium structure of the crystal. This assumption does not hold exactly at room temperature because the "6 — exp" function determines the internal energy of the crystal, while its structure is conditioned upon the minimum of free energy.

The aim of this work was a detailed analysis and calculation of librational frequencies in the acenaphthene crystal based on a simplified model and the comparison of this frequencies with experimental data in order to check the validity of some assumptions and to establish the dominant type of interactions (attraction or repulsion; H—H, C—C or C—H) in different librations.

1. The structure of the acenaphthene crystal

The acenaphthene crystal is orthorhombic [6] and belongs to the C_{2v}^2 space group. The unit cell, containing four molecules, has the dimensions:

$$a = 8.290 \text{ \AA} \quad b = 14.000 \text{ \AA} \quad c = 7.225 \text{ \AA}$$

and the following symmetry elements:

- a twofold screw-axis C_2^2 , parallel to the c -axis and intercepting the a -axis at the point $\frac{a}{2}$,
- a glide plane $\sigma^{(cb)}$ normal to the a -axis and intercepting this axis at $\frac{a}{2}$,
- a mirror plane $\sigma^{(ca)}$.

The molecule 1 (Fig. 2a) is situated on the ab plane in such a way that the U - and V -axis (Fig. 1) are parallel to the b - and a -axis, respectively.

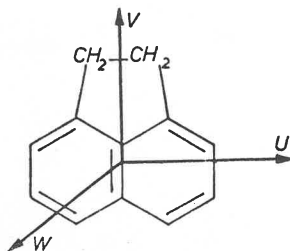


Fig. 1. The principle axis of inertia for the acenaphthene molecule

The coordinates of the molecule 2 can be obtained from those of molecule 1 by using appropriate symmetry relations. Molecules 3 and 4 form a second set so that their coordinates cannot be obtained from the coordinates of either molecule 1 nor 2 by means of symmetry relations. The U -axis of the molecule 3 is parallel to b , and the V -axis forms with a an angle equal to 61.5° [6]. The projection of the structure of the acenaphthene crystal on the (010) plane is given in Fig. 2b.

The analysis of the different types of librations from the viewpoint of group theory may

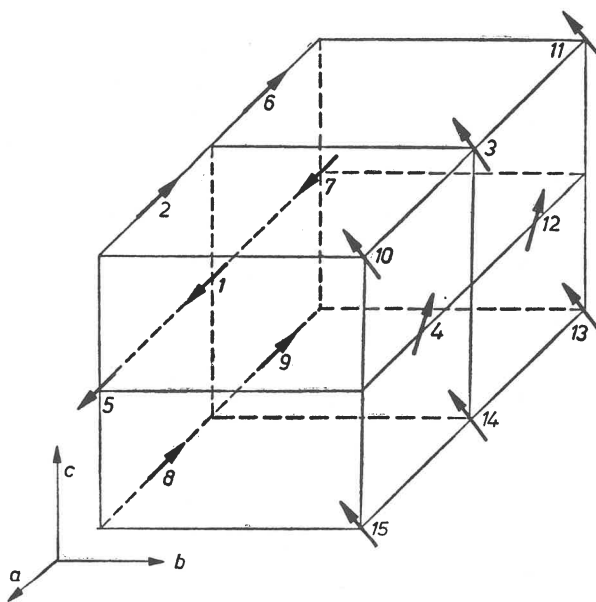


Fig. 2a. The acenaphthene crystal structure (schematic)

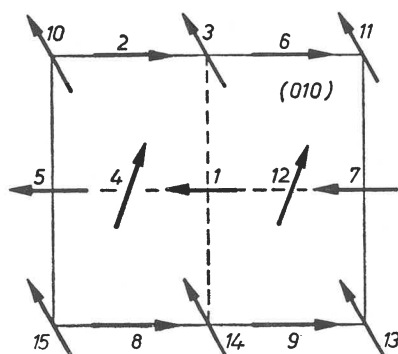


Fig. 2b. The projection of the crystal structure on the (010) plane

be done separately for the set A (molecules 1, 2, 5, 6, 7, 8, 9) and B (molecules 3, 4, 10, 11, 12, 13, 14, 15), because they are crystallographically independent. This is equivalent to the assumption that the motions of the molecules belonging to different sets, *e.g.* 1 and 3, are independent of each other and that there are no couplings between them. The characters of the irreducible representations for the point group C_{2v} are given in Table I. In the last row the characters of the reducible representation of the librations for one set of molecules are quoted. Hence the irreducible representations are

$$A_1 + 2A_2 + B_1 + 2B_2.$$

For the other set the irreducible representations will be identical, hence the types of the twelve librations in the acenaphthene crystal are

$$2A_1 + 4A_2 + 2B_1 + 4B_2.$$

Table of characters for the C_{2v} point group

C_{2v}	E	C_2^c	σ^{cb}	σ^{ca}	
A_1	1	1	1	1	T_c
A_2	1	1	-1	-1	R_c
B_1	1	-1	-1	1	T_a, R_b
B_2	1	-1	1	-1	T_b, R_a
$\chi(R)$	6	0	0	-2	

2. Method of calculation

The calculations of the librational frequencies in the acenaphthene crystal, carried out in this work, were based on following assumptions:

- 1°. the librational motions are independent of the translational ones (*i.e.*, the distances between the centers of gravity of the molecules are constant); this is equivalent to an assumption that the librational and translational components of motion of a molecule are 90° out of phase;
- 2°. the librational motions take place about the principal axes of inertia of the molecules; this assumption has been supported by some additional calculations [7];
- 3°. the librations are harmonic; in this approximation the potential energy of the interactions between the molecules is given by the relation

$$\Phi = \frac{1}{2} k (\theta - \theta_0)^2 + \Phi^0 \quad (2)$$

where k denotes the force constant of a given libration, θ the rotation angle, and θ_0 and Φ_0 the parameters of the minimum of this function. In the above formula the potential energy is equal to the sum of the interaction energy between all pairs of molecules taken into account for a given libration.

The above assumptions simplify considerably the general model and enable a detailed analysis of different types of librations to be made. The interaction energy between the molecules was calculated by means of the "6 — exp" function (1), using in parallel two sets of parameters A, B, α , after Kitaigorodsky [8] and Williams [9]. The parameters used are collected in Table II. The computation was done separately for each type of libration. The A_1 -type libration of the molecules belonging to the set A was realized by turning all molecules of this set by an angle $+\theta$ about their U -axes. The other A_1 -libration for the set B can be similarly represented. The A_2 -libration can be obtained by turning the molecules 1, 5, 7 by $+\theta$ and the molecules 2, 6, 8, 9 by $-\theta$ about the U -axes. If we call a libration in which all molecules of one set are turned about the same axis by the same angle as "symmetric" (and denote it, *e.g.*, U^s) and a libration in which the translationally equivalent molecules are turned by $+\theta$, while the remaining ones by $-\theta$, as "antisymmetric" (and respectively denote it U^a), we can see that U^s corresponds to A_1 , U^a to B_1 , V^s to A_2 , V^a to B_2 , W^s to A_2 and W^a to B_2 .

TABLE II

Parameters of the potential function (1)

Parameter	After Kitaigorodsky [8]	After Williams [9]
A_{H-H} (erg $\text{\AA}^{-6} \times 10^{12}$)	3.96	4.93
B_{H-H} (erg $\times 10^{10}$)	29.2	2.78
α_{H-H} (\AA^{-1})	4.86	3.74
A_{C-H} (erg $\text{\AA}^{-6} \times 10^{12}$)	10.7	5.98
B_{C-H} (erg $\times 10^{10}$)	29.2	4.70
α_{C-H} (\AA^{-1})	4.12	3.67
A_{C-C} (erg $\text{\AA}^{-6} \times 10^{12}$)	24.9	41.8
B_{C-C} (erg $\times 10^{10}$)	29.2	62.0
α_{C-C} (\AA^{-1})	3.58	3.60

In the evaluation of the potential energy the interaction between the following pairs of molecules were taken into account:

set A: 1-2, 1-5, 1-6, 1-7, 1-8, 1-9

set B: 3-4, 3-4', 3-10, 3-11, 3-12, 3-12'

The molecules 4' and 12' are the molecules 4 and 12, respectively, shifted along the C-axis by a period. The molecules were turned about each axis successively by the angles: -2° , -1° , -0.5° , 0.5° , 1° , 2° .

During the computations first the coordinates \vec{X}'_{ij} of the C and H atoms of the turned molecules were calculated according to the relation:

$$\vec{X}'_{ij} = \underline{A}_i \cdot \underline{J} \cdot \underline{A}_i \cdot (\vec{X}_{ij} - \vec{X}_i^s) + \vec{X}_i^s \quad (3)$$

where \vec{X}_{ij} denotes the initial coordinates (in \AA) of the j -th C or H atom of the i -th molecule ($\vec{X} = (X_1, X_2, X_3)$), \vec{X}_i^s are the coordinates of the center of gravity of the i -th molecule, \underline{A}_i is the matrix transforming the i -th molecule from the orthogonal to molecular inertia system, and \underline{J} is one of the matrices $\underline{J}_u, \underline{J}_v, \underline{J}_w$, by means which the rotation of the molecules about a definite axis was realized. Afterwards, the interatomic distances between atoms of interacting molecules were obtained. Finally the potential interaction energy for the nonbonded atom pairs were calculated according to Eq. (1) and the values for a considered pair of molecules were summed up. For a pair of acenaphthene molecules there are 100 H-H, 240 C-H, and 144 C-C constants; all the distances were taken into account.

The calculations were carried out on the Elliott-803 B computer in the Wrocław University Computing Center, following Elliott-Algol procedures.

3. Results

From the values of $\Phi = f(\theta)$ the parameters of the parabolas were found by solving the sets equations (2) for different values of Φ and θ . In Table III averaged parameters k and θ_0 are listed, separately for Kitaigorodsky's and Williams' parameters in the „6 — exp” function.

TABLE III

Calculated values of the force constants (k) and equilibrium angles (θ_0)

Set of molecules	Axis of libration	Libration type	Calculated values of k and θ_0			
			after Kitaigorodsky [8]		after Williams [9]	
			$k \times 10^{11}$ (dyne \times cm)	θ_0 (deg.)	$k \times 10^{11}$ (dyne \times cm)	θ_0 (deg.)
A	U	B_1	3.339	-0.21	2.288	-0.31
		A_1	2.025	-1.25	1.962	-2.12
	V	B_2	2.866	-0.57	2.610	-0.33
		A_2	1.638	-0.43	0.680	-1.10
	W	A_2	1.008	+1.07	0.678	+0.87
		B_2	1.0012	+1.16	0.794	-0.19
B	U	B_1	1.554	+0.80	1.500	-0.07
		A_1	0.954	+0.79	0.876	-0.38
	V	B_2	1.066	-0.38	1.188	-1.11
		A_2	1.272	+0.40	1.108	-0.98
	W	A_2	0.728	+0.27	0.734	-1.14
		B_2	0.626	+1.80	0.564	+1.40

Using the force constants given in Table III and the following values of the moments of inertia of the acenaphthene molecule:

$$I_u = 584 \cdot 10^{-40} \text{ g cm}^2$$

$$I_v = 694 \cdot 10^{-40} \text{ g cm}^2$$

$$I_w = 1278 \cdot 10^{-40} \text{ g cm}^2$$

TABLE IV

Comparison of calculated and experimental librational frequencies

Set of molecules	Axis of libration	Libration type	Calculated frequencies		Experimental frequencies	
			after Kitaigorodsky [8]	after Williams [9]	Raman [10]	IR [11]
A	U	B_1	127	105	—	97
A	U	A_1	100	98	—	92
B	U	B_1	87	85	—	84
B	U	A_1	68	66	72	73
A	V	B_2	108	102	104	—
A	V	A_2	82	52	—	—
B	V	B_2	66	69	61	—
B	V	A_2	72	67	—	—
A	W	A_2	47	38	37	—
A	W	B_2	47	41	34	34
B	W	A_2	40	40	28	—
B	W	B_2	37	35	—	30

the 12 librational frequencies were calculated. They are collected in Table IV together with experimental data.

The external vibrations in the acenaphthene crystal were investigated first by Mathieu *et al.* [10] (Raman), who found 16 frequencies, of which only 6 have been assigned. For the others only the symmetry could be given without any precise interpretation. Only the distinctly assigned values are quoted in Table IV.

Hadni *et al.* [11] measured the spectrum of the acenaphthene crystal in the far IR. From the eight IR-active librations ($2A_1$, $2B_1$, $4B_2$) only 6 were assigned ($2A_1$, $2B_1$, $2B_2$). From the spectrum of the acenaphthene crystal (for $E \parallel b$, Fig. 39, ref. [11]), it can be deduced that the frequencies of the two remaining librations of the B_2 type occur between 60 and 80 cm^{-1} .

4. Discussion

The comparison of the calculated and observed frequencies, presented in Table IV, shows a satisfactory agreement. It should be mentioned that the lowest internal frequency of the acenaphthene molecule is equal to 172 cm^{-1} [11]; this frequency can result only from a distortion vibration of the molecule. As pointed out by Pawley, the interactions between the deformed molecules will lower the highest librational frequencies [5]; this may in part explain the differences in Table IV.

TABLE V

Comparison of the energy values for different interaction types (for the A_1 — libration)

Rotation angle	Type of interaction	Energy (erg $\times 10^{15}$)		
		attraction	repulsion	total
-1.0°	H—H	-380.809	113.342	-267.467
	C—H	-1721.683	583.638	-1138.045
	C—C	-1442.108	285.745	-1156.363
-0.5°	H—H	-380.603	113.331	-267.272
	C—H	-1718.077	577.266	-1140.811
	C—C	-1441.610	284.863	-1156.858
0.0°	H—H	-380.659	113.437	-267.222
	C—H	-1716.836	576.092	-1140.744
	C—C	-1441.610	284.752	-1156.858
+0.5°	H—H	-380.983	113.611	-267.372
	C—H	-1717.671	579.614	-1138.057
	C—C	-1442.307	285.401	-1156.906
+1.0°	H—H	-381.522	113.868	-267.654
	C—H	-1720.581	587.439	-1133.142
	C—C	-1443.403	286.837	-1156.566

The interaction energy between the molecules consists of the attraction energy (the R^{-6} term in the "6 — exp" function) and repulsion energy (the exponential term). From our results the following conclusions may be drawn:

- 1°. In the majority of cases the C—H interactions are the most important. The C—C interactions do not change considerably in librations with small amplitudes (up to 1°). This conclusion is illustrated by the energy values of different interaction types for the libration of the A_1 -type given in Table V.
- 2°. The H—H interactions vary considerably only for the pairs of molecules which are translationally equivalent (*e.g.*, 1–5, Fig. 2*a*). In this case the H—H interactions are dominant; this may stem from the characteristic structure of the acenaphthene crystal (Fig. 2*a*, 2*b*).
- 3°. Although the absolute changes in the attraction and repulsion energy are nearly the same, the percentage changes of the repulsion energy are greater; hence, the arrangement of the molecules in the crystal is determined mainly by the exponential term.

It should be emphasized that the accuracy of the coordinates of the H atoms determines to a large extent the final coincidence between the calculated and experimental frequencies. Unfortunately, these coordinates are known as a rule only with poor accuracy. The average error of the H-positions in the acenaphthene crystal is considerable and equal to 0.22 Å. This may also in part explain the discrepancies observed in Table IV.

5. The sublimation heat of acenaphthene

In order to check the interaction model and to decide if a sufficient number of interacting molecule pairs was taken into account, the heat of sublimation was estimated from our interaction energy. The calculated interaction energy of a molecule, *e.g.*, 1 with the remaining ones is equal to

$$E_K = -2564.824 \times 10^{-15} \text{ erg (using Kitaigorodsky's parameters) or}$$

$$E_W = -2674.418 \times 10^{-15} \text{ erg (with Williams' parameters).}$$

Therefore, the molar heat of sublimation equals

$$\Delta U_s^K = -\frac{E_K}{2} = 18.53 \text{ kcal/mol}$$

$$\Delta U_s^W = -\frac{E_W}{2} = 19.32 \text{ kcal/mol}$$

what corresponds to

$$\Delta H_s^K = 19.12 \text{ kcal/mol}$$

$$\Delta H_s^W = 19.91 \text{ kcal/mol.}$$

The coincidence with the experimental value $\Delta H_s = 19.9 \text{ kcal/mol}$ [12] is satisfactory.

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