(Rabinovich & Shakked, 1984). Initially, only very low-order reflections (less than 40 Å resolution) will be used for the searches.

We would like to thank Drs K. Nierhaus and H. J. Rheinberger for very stimulating discussions, J. Piefke and T. Arad for their outstanding contribution to this work in conducting the electron microscopy experiments, Professor D. Rabinovich for his constant interest and help, Professor J. L. Sussman for his enthusiasm and willingness to adapt the computer display programs, Dr K. R. Leonard for his active interest and critical comments, Drs B. Shaanan, H. Bosshard, M. A. Saper and Mr A. Levy for assistance with computer problems, as well as H. S. Gewitz, J. Müssig, C. Glotz, B. Romberg and J. Halfon for skillful technical assistance.

This work was supported by research grants from BMFT(MPBO 180), NIH (GM 34360), Heineman (4694 81) and the Kimmelman Center for Biomolecular Structure and Assembly. ZBY is a Minerva fellow and AY holds the Martin Kimmel professorial chair.

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Thermal Motion Analysis in [5]-, [6]- and [7]-Circulene Crystals: a Harmonic Lattice-Dynamical Calculation

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(*Received* 6 *December* 1989; *accepted* 28 *March* 1990)

Abstract

A harmonic lattice-dynamical model has been used to calculate crystallographic atomic displacement parameters (a.d.p.'s) for crystals of [5]-circulene (corannulene) at 293 and 203 K, [6]-circulene (coronene) and [7]-circulene at 293 and 163 K. Empirical internal and external force fields, which were derived for a series of other aromatic hydrocarbons, have been employed. The agreement between calculated and experimental a.d.p.'s is very good: this is particularly promising in view of the extension

0108-7681/90/050643-03$03.00

of the semiempirical force fields to wider classes of compounds than those considered in the parameter derivation.

Introduction

Lattice-dynamical calculations for crystals of aromatic hydrocarbons have been carried out by several authors with substantial success (Pawley, 1967; Filippini, Gramaccioli, Simonetta & Suffritti, 1973, 1974, 1976; Bonadeo & Burgos, 1982; Gramaccioli & Filippini, 1983, 1985*a*,*b*; Filippini & Gramaccioli, 1986, 1989); in most cases, the agreement between the observed and calculated IR-and Raman-active frequencies, phonon-dispersion curves, thermodynamic functions, and atomic diplacement parameters is very good.

The aim of these calculations is on the one side to extend the range of applicability of the available semiempirical force fields and on the other side to provide a comparison with experimentally determined a.d.p.'s and spectroscopic measurements of internal and external frequencies.

While the former aim is self-explanatory, since potential functions obtained through a best fit of properties on a limited number of compounds ought to be confirmed by enlarging the field of application, the latter aim deserves a closer look. It is well known that large condensed aromatic systems are difficult to synthesize or to crystallize and, even in the best cases, the crystals may not be of high quality. Therefore, the experimental determination of reliable a.d.p.'s is impossible. Their calculation by means of a lattice-dynamical procedure is then extremely helpful. Moreover, the calculated values represent a kind of average along a class of compounds, the differences being due only to the crystal packing of the compound under examination.

Corannulenes or circulenes have been of interest in chemistry over the years, both on theoretical (Kitaigorodskii, Mirskaya & Bereznitskaya, 1970; Boyd, Fyfe & Wright, 1974; Kao & Allinger, 1977; Agranat, Hess & Schaad, 1980; Randic & Trinajstic, 1984) and spectroscopic grounds (Babkov & Kovner, 1973; Cyvin, Cyvin & Brunvoll, 1979; Cyvin, Brunvoll & Cyvin, 1984; Cyvin, 1982), and also because of biological consideration of their carcinogenicity (mainly for coronene).

The structures of the three title compounds have been determined at different levels of accuracy over the years; the most recent data were obtained by X-ray diffraction for corannulene (Hanson & Nordman, 1976) at two different temperatures (203 and 293 K), for coronene (Fawcett & Trotter, 1965) at room temperature, and for [7]-circulene (Yamamoto *et al.*, 1983, 1988), again at two temperatures (163 and 293 K).

Table 1. *Agreement factors*

First line: calculated (only external contribution) *versus* observed a.d.p.'s; second line: calculated (external + internal contribution: no mixing) *versus* observed a.d.p.'s; third line: calculated (external + internal contribution: mixing up to 200 cm^{-1}) *versus* observed a.d.p.'s. $R = \sum|B_o - B_c|/\sum B_o$, $\Delta B = \sum(B_o - B_c)/\sum B_o$.

	R	ΔB
Corannulene at 293 K	20·6	−7·2
	22·4	−11·6
	25·1	−13·3
Corannulene at 203 K	27·3	22·5
	24·6	18·0
	23·9	16·4
Coronene	27·4	0·3
	23·2	−3·8
	21·4	−8·4
[7]-Circulene at 293 K	25·7	20·4
	18·1	13·0
	14·0	5·5
[7]-Circulene at 163 K	40·2	35·8
	30·8	27·6
	24·7	20·4

Neither disorder (Pawley & Rayment, 1979) nor rotational freedom (Boyd *et al.*, 1974) seem to be present in the coronene crystal.

Method of calculation

Lattice-dynamical calculations in the harmonic approximation have been performed following a previously described procedure (Gramaccioli & Filippini, 1983, 1985*a*,*b*; Willis & Pryor, 1975); details of the Brillouin-zone sampling are given in Filippini *et al.* (1976). Empirical atom–atom van der Waals potentials were chosen according to Mirsky (1978); the internal field was assumed following Neto, Scrocco & Califano (1966) for the 'in-plane' movements and Filippini, Simonetta & Gramaccioli (1984) for the 'out-of-plane' displacements. The maximum packing distance in the lattice sums was 5·5 Å and the C—H bond lengths have been taken as 1·09 Å.

Our calculations in the crystal include a number of internal degrees of freedom in the dynamical matrices, corresponding to those normal coordinates of the free molecule whose frequencies are below a preset value (in this case 200 cm^{-1}).

Results and discussion

Table 1 reports agreement factors between observed and calculated a.d.p.'s for the circulenes, while Table 2 collects observed and calculated **T**, **L**, **S** tensors [as in Schomaker & Trueblood (1968)]. Table 3* contains all the U_{ij} values.

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* Table 3 has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52903 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Calculated* **T**, **L** *and* **S** *tensors* (*referred to the axes of inertia*) × 10^4

L_{ii} are the root-mean-square amplitudes of librational motion (*a*) from lattice-dynamical calculations, (*b*) from Schomaker–Trueblood fits to crystallographic a.d.p.'s.

	T (Å²)			L (rad²)			S (Å rad)			L_{ii} (°)	
										(*a*)	(*b*)
Corannulene at 293 K, first molecule	606	30	89	36	5	3	−4	−30	−24	3·2	3·4
		477	34		37	3	33	5	5	3·6	3·6
			421			67	15	−8	7	4·7	4·1
Corannulene at 293 K, second molecule	660	42	−23	53	0	−4	−16	78	21	3·7	2·9
		682	32		42	−4	−30	8	−4	4·1	3·7
			409			58	−7	−18	0	4·5	5·0
Corannulene at 203 K, first molecule	379	22	−51	22	−2	−1	−2	14	10	2·5	2·2
		279	0		20	−2	−22	2	8	2·7	2·9
			247			42	0	−11	−6	3·7	3·9
Corannulene at 203 K, second molecule	385	−2	−30	28	0	−1	−13	42	9	2·8	2·7
		386	20		25	−3	−17	9	−5	3·0	3·2
			240			39	−6	−7	−1	3·6	4·5
Coronene	381	17	21	16	1	−1				2·3	2·1
		482	39		23	−2				2·7	2·6
			263			33				3·3	2·8
[7]-Circulene at 293 K	409	−16	6	10	−1	−4	−9	0	−1	1·7	2·5
		379	11		10	0	0	7	0	1·8	3·2
			189			30	32	0	−1	3·2	3·8
[7]-Circulene at 163 K	159	−6	4	5	0	0	4	0	0	1·2	1·8
		190	−3		5	−2	0	−4	0	1·3	2·4
			93			14	0	14	−2	2·1	2·7

The values of the crystallographic a.d.p.'s are quite close to the lattice-dynamical estimates for coronene, [7]-circulene at 293 K and corannulene at both temperatures: the discrepancy does not exceed the accuracy of the experimental data as determined from the reported *R* index. The agreement is somewhat worse for [7]-circulene at 163 K: a marked improvement is obtained when mixing with internal frequencies up to 200 cm^{-1} is allowed (see Tables 1 and 3).

Applying the general-motion formula (Scheringer, 1972; Willis & Pryor, 1975) to the experimental data and our calculated *U*'s and U_{ij}'s, the average increase in the C—C bond length is 0·01 and 0·007 Å for corannulene at 293 and 203 K, respectively, 0·008 Å for coronene, and 0·008 and 0·005 Å for [7]-circulene at 293 and 163 K, respectively.

This work was supported by CNR (Progetto Strategico 'Metodologie Cristallografiche Avanzate').

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