

Benzene Crystals at Low Temperature: a Harmonic Lattice-Dynamical Calculation

BY GIUSEPPE FILIPPINI

Centro del CNR c/o Dipartimento di Chimica Fisica ed Elettrochimica, Università di Milano, via Golgi 19, 20133 Milano, Italy

AND CARLO MARIA GRAMACCIOLI

Dipartimento di Scienze della Terra, Sezione di Mineralogia, Università di Milano, via Botticelli 23, 20133 Milano, Italy

(Received 30 March 1988; accepted 7 October 1988)

Abstract

A harmonic lattice-dynamical model has been used to calculate vibrational frequencies and crystallographic atomic displacement parameters (a.d.p.) for benzene crystals at 15 and 123 K. The agreement of the frequencies with the experiment is good; the a.d.p.'s are in excellent agreement with data derived from neutron diffraction only at very low temperature. At 15 K, the zero-point contribution is about 90% of the a.d.p.'s, and so further cooling will produce little change. A bond-length correction according to the general-motion formula leads to an average of 1.401 Å for the C–C bonds, which is higher than expected.

Introduction

Benzene is a molecule of fundamental interest in chemistry. Although the structure is apparently simple, some basic problems concerning its nature are still subject to discussion. The problem of evaluating the molecular geometry as accurately as possible has always been a matter of considerable effort. Among the various experimental methods of determining such geometry, those involving X-ray and neutron diffraction are most reliable.

It has long been known that unbiased estimates of bond lengths imply correction for thermal motion (Cruickshank, 1956; Busing & Levy, 1964; Scheringer, 1972; Johnson, 1970, 1980; Willis & Pryor, 1975); such corrections can be performed in several ways depending on different models of molecular libration. The so-called 'rigid-body' fit to atomic displacement parameters (a.d.p.) (Cruickshank, 1956; Schomaker & Trueblood, 1968) is often followed by crystallographers and corrections are made using this scheme.

Although the 'rigid-body' fit is unquestionably useful if accurate results to better than 0.01 Å are needed, deviation from rigidity and inaccuracy in estimating the a.d.p.'s begin to be important when accuracy is increased by another order of magnitude. To improve the situation, two main methods can be followed:

first, temperature effects can be substantially reduced by cooling down to a few kelvin; secondly, a more general bond-length correction formula can be used [Scheringer, 1972, equation (3.6); Johnson, 1980]:

$$d_c = d_o + [\text{tr}(\mathbf{Z}) - \mathbf{d}_o^T \mathbf{Z} \mathbf{d}_o / d_o^2] / 2d_o.$$

Here d_c and d_o are the corrected and observed bond distances, respectively, and \mathbf{Z} is the matrix

$$\mathbf{Z} = \mathbf{U}_i + \mathbf{U}_j - \mathbf{U}_{ij} - \mathbf{U}_{ij}^T,$$

where the tensors \mathbf{U} are defined below.

In order to apply this general formula some additional information with respect to the crystallographic data should be available. Such information can be provided as thermal motion tensors between different atoms, $\mathbf{U}_{ij} = \langle \mathbf{u}_i \mathbf{u}_j^T \rangle$, where i and j are the two bonded atoms. These tensors, unlike $\mathbf{U}_i = \langle \mathbf{u}_i \mathbf{u}_i^T \rangle$ and $\mathbf{U}_j = \langle \mathbf{u}_j \mathbf{u}_j^T \rangle$, cannot be obtained from diffraction data. A possible method for their evaluation implies lattice-dynamical calculations: if reliable estimates of the frequencies and of the \mathbf{U} 's are obtained, there are good reasons to believe that satisfactory estimates of the \mathbf{U}_{ij} 's can be derived.

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, 1985a; Filippini & Gramaccioli, 1986). In most substances the agreement between the observed and calculated IR- and Raman-active frequencies, phonon dispersion curves, thermodynamic functions and \mathbf{U} 's is very good. However, for benzene, the agreement (at 138 K) is worse than for other hydrocarbons. An explanation of this disagreement, which becomes even worse at higher temperatures, has been suggested by Filippini *et al.* (1974) on the grounds of large vibration amplitudes. Recently, accurate neutron diffraction data have been obtained by Jeffrey, Ruble, McMullan & Pople (1987) at 123 and 15 K on deuterated benzene. The very low-temperature data are of particular interest

because of the reduced amplitude of motion. Moreover, it would be interesting to test most atom-atom semiempirical potentials at a temperature considerably lower than 290 K: anharmonic (or quasi-harmonic) effects are partially taken into account by varying the potentials, so that different coefficients should be used at different temperatures. Such a point of view seems to be supported by a systematic disagreement between observed and calculated U's at low temperature in the few instances where such data are available.

Results and discussion

Lattice-dynamical calculations in the harmonic approximation have been performed following our procedure described previously (Gramaccioli & Filippini, 1983, 1985a). Empirical atom-atom van der Waals potentials have been chosen according to Williams (1967), and the internal field has been 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 is 5.5 Å and the C-H bond lengths have been taken as 1.09 Å.

Calculated frequencies at $q=0$ for C_6D_6 at two different temperatures are shown in Table 1; they are compared with the corresponding experimental values from IR and Raman spectroscopic measurements (Sataty & Ron, 1976). The agreement is quite good. Calculated values for the deuterated compound at 15 and 123 K are reported for completeness.

The values of the a.d.p.'s at 15 K are quite close to the lattice-dynamical estimates; the discrepancy does not exceed the accuracy of the experimental data (see Table 2). At 123 K there is a much higher disagreement, corresponding more or less to what was already observed with previous experimental data (Bacon, Curry & Wilson, 1964) and calculations (Filippini *et al.*, 1974).

At 15 K, the importance of the zero-point motion is evident from the second line of Table 2. Such a contribution amounts to about 87% of the U's relative to C atoms and 94% of the U's relative to H atoms. This result indicates that no substantial improvement could be achieved by further cooling.*

Calculated T and L tensors are reported in Table 3. Using the experimental data at 15 K and our calculated U's and U_{ij} 's we find that the average C-C bond length corrected by the general-motion formula

* A controversial point is the legitimate application of a classical distribution rather than a Bose-Einstein one when the crystal is practically in the quantum ground state. In our model, the particles are distinguishable because of different atomic coordinates, and this should in our opinion allow the use of classical statistics. If our point of view is wrong, then the problem of temperature factors at low temperatures (even that of liquid nitrogen for crystals with strongly bonded structures) should be paid some attention.

Table 1. Observed and calculated frequencies (cm^{-1})

	Observed (H_6) (Sataty & Ron, 1976)		Calculated (present work)			
	79 K	138 K	H_6	H_6	D_6	D_6
			80 K	138 K	15 K	123 K
A_u	—	—	103	98	104	95
	—	—	70	67	70	65
B_{1u}	—	—	50	57	59	55
	102	98	98	92	98	90
B_{2u}	71	65.5	58	56	59	54
	105	100	109	103	110	100
B_{3u}	59	56	57	54	57	52
	92	88	89	85	90	82
A_g	76	73	76	71	76	70
	97	93	92	89	87	81
B_{1g}	83	78	78	74	73	68
	51	57	39	38	37	34
B_{2g}	132	128	138	131	130	120
	(87)	84	87	83	82	76
B_{3g}	67	61	68	66	64	60
	94	90	102	97	96	88
B_{3g}	83	79	91	87	86	79
	—	—	83	78	78	72
B_{3g}	132	128	140	133	132	122
	105	100	98	93	93	85
	65	57	50	47	47	43

Table 2. Observed and calculated a.d.p.'s ($\text{Å}^2 \times 10^4$)

First line: calculated at 15 K, including zero-point contribution; second line: zero-point contribution; third line: experimental at 15 K; fourth line: internal modes contribution at 15 K; fifth line: calculated at 123 K; sixth line: observed at 123 K. Values are multiplied by 10^4 . Carbon and deuterium atoms are labelled in the same way as in Table 6 of Jeffrey *et al.* (1987).

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	90	66	89	0	7	3
	77	58	77	7	0	3
	79	67	88	6	7	4
	12	14	11	-4	6	3
C2	388	279	377	-6	-15	-10
	232	200	262	17	-13	-12
	84	87	82	6	17	-2
	71	79	70	7	17	-2
C3	74	81	79	9	17	0
	13	15	10	1	2	2
	368	352	360	1	40	-21
	218	255	242	14	33	-16
D1	86	79	82	-6	11	10
	73	72	70	-5	11	10
	81	75	82	-3	14	10
	10	15	13	2	2	1
D2	376	325	350	-50	14	26
	230	237	233	-22	17	19
	216	173	212	38	39	11
	202	165	199	38	39	11
D3	224	114	239	46	25	12
	76	117	71	16	26	6
	678	376	636	27	37	11
	472	262	519	83	2	-2
D4	184	226	215	56	56	5
	170	217	202	56	55	5
	183	204	208	35	88	-8
	65	106	92	32	-2	-13
D5	618	574	612	39	186	-47
	400	469	449	69	168	-32
	228	208	171	-2	37	60
	215	199	158	-1	36	59
D6	214	171	199	-18	61	58
	96	110	57	-16	1	25
	655	519	536	-99	111	85
	450	400	428	-63	98	124

$R = 0.14$ at 15 K
 $R = 0.41$ at 123 K

becomes 1.401 Å, with e.s.d.'s of 0.001 Å. Discussion is omitted for C–D bond lengths, since anharmonicity is present (Craven & Swaminathan, 1985; Jeffrey *et al.*, 1987).

With higher-temperature data (123 K) and the same general-motion corrections the average C–C bond length increases to 1.404 Å. This difference in the corrected bond lengths points to an inadequacy in our thermal-motion correction at higher temperature. Such a situation is already evident from the poor fit between calculated and observed U's, the former being noticeably higher (by 40%) than the latter. Because of this, the correction is too large.

The unfavourable situation at higher temperature is very probably connected with the large amplitude of vibration: the behaviour at 15 K should accordingly be more favourable; moreover, since the U's are in closer agreement, there is good reason for expecting physically meaningful bond-length corrections. Nevertheless, the average of 1.401 Å for C–C bonds seems to be definitely longer than other experimental measurements and the best theoretical calculations (Jeffrey *et al.*, 1987).

A reason for the disagreement between bond-length corrections is also evident from Table 3. In spite of the excellent agreement (at 15 K) of the a.d.p.'s, the interpretation in terms of T and L is substantially different (the lattice-dynamical estimation being smaller for T and larger for L). Since for a rigid-body model the bond-length correction depends on L only, this explains why the lattice-dynamical correction is larger than the 'rigid-body' one.

We conclude that there is a systematic disagreement between theoretical and experimental measurements for benzene: this disagreement is linked to this particular case, since for other hydrocarbons involving phenyl rings bond-length corrections based on the same lattice-dynamical treatment give quite acceptable results [see for instance *o*-terphenyl and tetraphenylmethane (Gramaccioli & Filippini, 1985*b*; Filippini & Gramaccioli, 1986)]. Such disagreement probably arises for two main reasons. First, the amplitude of vibration is very large, and this may imply a considerable correction not only to the lattice-dynamical algorithm, but also to the Schomaker–Trueblood (ST) rigid-body treatment. Secondly, the ST fit to the benzene C–C skeleton leads to indeterminacy, solved only by introducing the peripheral D

Table 3. *Calculated and observed T and L tensors (referred to the axes of inertia) × 10⁴ at 15 K*

	T (Å ²)			L (rad ²)		
51	–2	–3	22	2	0	calc.
	53	0		18	0	
		43			12	
59	1	–2	2	1	0	obs.
	61	0		5	0	
		89			8	

atoms, which, in turn, seem to be affected by non-rigid and anharmonic behaviour (see line 4 of Table 2).

References

- BACON, G. E., CURRY, N. A. & WILSON, S. A. (1964). *Proc. R. Soc. (London) Ser. A*, **279**, 98–110.
- BONADEO, H. & BURGOS, E. (1982). *Acta Cryst.* **A38**, 29–33.
- BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142–146.
- Craven, B. M. & Swaminathan, S. (1985). *Trans. Am. Crystallogr. Assoc.* pp. 133–135.
- CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 747–753, 754–756, 757–758.
- FILIPPINI, G. & GRAMACCIOLI, C. M. (1986). *Acta Cryst.* **B42**, 605–609.
- FILIPPINI, G., GRAMACCIOLI, C. M., SIMONETTA, M. & SUFFRITTI, G. B. (1973). *J. Chem. Phys.* **59**, 5088–5101.
- FILIPPINI, G., GRAMACCIOLI, C. M., SIMONETTA, M. & SUFFRITTI, G. B. (1974). *Acta Cryst.* **A30**, 189–196.
- FILIPPINI, G., GRAMACCIOLI, C. M., SIMONETTA, M. & SUFFRITTI, G. B. (1976). *Acta Cryst.* **A32**, 258–264.
- FILIPPINI, G., SIMONETTA, M. & GRAMACCIOLI, C. M. (1984). *Mol. Phys.* **51**, 445–459.
- GRAMACCIOLI, C. M. & FILIPPINI, G. (1983). *Acta Cryst.* **A39**, 784–791.
- GRAMACCIOLI, C. M. & FILIPPINI, G. (1985*a*). *Acta Cryst.* **A41**, 356–361.
- GRAMACCIOLI, C. M. & FILIPPINI, G. (1985*b*). *Acta Cryst.* **A41**, 361–365.
- JEFFREY, G. A., RUBLE, J. R., McMULLAN, R. K. & POPLE, J. A. (1987). *Proc. R. Soc. London Ser. A*, **414**, 47–57.
- JOHNSON, C. K. (1970). *Crystallographic Computing*, edited by F. R. AHMED, pp. 207–226. Copenhagen: Munksgaard.
- JOHNSON, C. K. (1980). *Computing in Crystallography*, edited by R. DIAMOND, S. RAMASESHAN & K. VENKATESAN, pp. 14.01–14.19. Bangalore: Indian Academy of Sciences.
- NETO, N., SCROCCO, M. & CALIFANO, S. (1966). *Spectrochim. Acta*, **22**, 1981–1998.
- PAWLEY, G. S. (1967). *Phys. Status Solidi*, **20**, 347–360.
- SATATY, Y. A. & RON, A. (1976). *J. Chem. Phys.* **65**, 1578–1580.
- SCHERINGER, C. (1972). *Acta Cryst.* **A28**, 616–619.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- WILLIAMS, D. E. (1967). *J. Chem. Phys.* **47**, 4680–4684.
- WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*. Cambridge Univ. Press.