A redetermination and group-refinement of the molecular packing of benzene II at 25 kilobars.

By R. Fourme, D. André and M. Renaud, *Laboratoire de Chimie Physique, Université de Paris* VI, 91, *Orsay France*

The molecular packing of benzene II has been redetermined by a Monte Carlo technique using data of Piermarini and co-workers, and then group-refined. The Hamilton tests show a significant improvement of the agreement between observed and calculated structure factors.

Bridgman (1914) put forward the first evidence for the existence of a high-pressure modification of benzene, stable at room temperature above 12 kbar (benzene II). A high-pressure single-crystal X-ray diffraction study has been performed by Piermarini, Mighell, Weir & Block (1969) and can be briefly summarized as follows: Crystals of benzene II were grown in a diamond-anvil pressure cell at elevated temperature and pressure from the transition of solid I to solid II; X-ray precession data were obtained from a single crystal in the high-pressure cell. It was shown that at 21°C and ~25 kbar, benzene II crystallizes in the monoclinic system with $a = 5\cdot417(5)$, $b = 5\cdot376(19)$ and $c = 7\cdot352(7)$ Å; $\beta = 110\cdot00(8)$°.

As the space group is $P2_1/c$ with only two molecules per cell, the centre of the benzene ring may be placed on the origin. Assuming the molecule is undistorted under high pressure, all possible molecular packing configurations were generated by stepping rotation of the molecule about its centre. For each configuration, reliability factors and packing energies were calculated. This procedure produced a unique solution for the molecular packing of benzene II, with an R index of $0\cdot076$ for the 19 observed reflexions. Uncertainties in coordinates were derived on the basis of an assumed simultaneous error of 1° in each of the three rotation angles of the benzene ring but, strictly speaking, a refinement was not attempted. In view of the theoretical importance of this structure, we decided to redetermine and refine it.

We have developed a Monte Carlo technique which has proved efficient for solving molecular structures, even when data are very poor, provided a suitable molecular model is available (André, Fourme & Renaud, unpublished). The molecule is assumed to be a rigid group, its position and orientation being described by n parameters ($n \le 6$) which are randomly generated; the packing configurations are group-refined, using first a few low-angle heavy reflexions. The configurations with a low R index are selected for additional group-refinement cycles. The procedure is made fully automatic by means of a computer program called *PYTHIE*.

In benzene II only three angular parameters θ_1, θ_2, θ_3 need be generated because the centre of the model is fixed.*

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* For a precise definition of those parameters, see André, Fourme & Renaud (1971). Here, the orthogonal system $S_3(Z_1, Z_2, Z_3)$ bound to the molecule is chosen so that its origin is at the centre of the benzene ring. Z_1 is perpendicular to the ring and the atom C(2) is on Z_2.

We have used the molecular model of Piermarini *et al.* (1969) (hexagonal planar ring with C–C = 1·39 and C–H = 0·96 Å), their 19 observed structure factors and an overall temperature factor of 3·0 Å². The number of reflexions used for group-refinement of the trials was between $3n$ and $5n$ (*i.e.* 9 to 15 reflexions). For a UNIVAC 1106 computer, about 20 seconds are required to examine 20 trial structures and the rate of success is rather good since about 1 trial in 6 converges to what is essentially the same configuration as previously reported. This solution was refined with a group-refinement program called *ORION* (André, Fourme & Renaud, 1971). The following five parameters were adjusted: the three rotation parameters, an overall temperature factor and one scale factor. The final R factor is 0·069; the weighted R factor is $R' = 0\cdot785$ with $R' = \sum_i w_i (|F_o|_i - |F_c|_i)^2 / \sum_i w_i |F_o|_i^2$. The corresponding values for the molecular packing found by Piermarini *et al.* (1969) are 0·076 and 0·0940. The lower values of the residual factors are not a proof of a significant improvement of the agreement between observed and calculated structure factors. Hamilton (1965) has developed formulae which allow tests on $\mathcal{R} = R_1/R_0$, where R_0 and R_1 are respectively the generalized weighted residual factors for the structure resulting from the less restrained least-squares refinement and the more restrained refinement. If we can assume Hamilton's treatment to be applicable to a situation such as this with 19 reflexions, then we can make the significance tests. In Piermarini's work, four parameters were adjusted; in ours, an additional parameter is refined (the temperature factor). With the unitary weighting scheme used in both cases, the generalized weighted factors are identical with R' factors hence: $\mathcal{R} = 0\cdot0940/0\cdot0785 = 1\cdot197$. The number of degrees of freedom for the refinement is $19 - 5 = 14$; from the tables given by Hamilton, the structure is significantly improved at the 0·050 level. (With Hamilton's notation:

$$\mathcal{R}_{1,\ 14,\ 0\cdot050} = 1\cdot190 \text{ and } \mathcal{R}_{1,\ 14,\ 0\cdot025} = 1\cdot204).$$

Refined parameters are given below, together with the uncertainties obtained from the variance–covariance matrix:

Angular parameters: $\theta_1 = -145\cdot99(2\cdot66)$°
$\theta_2 = -\ 46\cdot58(0\cdot87)$
$\theta_3 = -134\cdot86(1\cdot32)$

Scale factor: $1\cdot065(39)$

Overall temperature factor: $5\cdot05(1\cdot02)$ Å².

High uncertainties in the angular parameters are connected with poor data; especially, as the k Miller indices of the observed reflexions are ≤ 1, θ_1 and θ_3 are badly determined. The temperature factor is higher than previously assumed. We have found a similar result for a high-pressure crystal structure of chlorobenzene (André, Fourme & Renaud, 1971) and it seems that high pressure has little effect on the amplitude of atomic vibrations.

The atomic coordinates are given in Table 1; the uncertainties are computed according to the formula given by Busing, Martin & Levy (1964). Any error in the model itself is neglected. Table 2 gives the observed and calculated structure factors.

Table 1. *Atomic coordinates of benzene* II

	x	y	z
C(1)	−0·2556 (49)	−0·0397 (101)	−0·1213 (13)
C(2)	−0·0604 (99)	−0·2124 (39)	−0·1119 (82)
C(3)	0·1951 (55)	−0·1726 (68)	0·0094 (84)
H(1)	−0·4321 (83)	−0·0672 (171)	−0·2051 (22)
H(2)	−0·1022 (167)	−0·3590 (65)	−0·1892 (139)
H(3)	0·3299 (94)	−0·2918 (116)	0·0159 (142)

Table 2. *Observed and calculated structure factors*

h	k	l	F_o	F_c
1	0	0	24·8	22·3
2	0	0	12·6	−11·8
0	0	2	19·3	18·1
1	0	2	12·1	−13·5
2	0	2	9·0	−11·1

Table 2 (*cont.*)

h	k	l	F_o	F_c
1	0	−2	31·6	33·1
0	0	4	5·9	−5·8
3	1	0	7·4	−7·2
0	1	1	22·9	23·8
2	1	1	9·8	−7·3
1	1	−1	15·8	16·7
2	1	−1	11·0	−11·1
0	1	2	16·4	−16·6
1	1	−2	25·7	25·7
2	1	−2	11·8	10·0
1	1	−3	11·5	11·2
3	1	−3	7·7	−6·8
1	1	−4	11·1	12·0
2	1	−4	10·4	9·2

Reference

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