

A Refinement of the Structure of the Room Temperature Phase of Phenanthrene, C₁₄H₁₀, from X-ray and Neutron Diffraction Data*

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The structure of the low-temperature phase of phenanthrene, C₁₄H₁₀, has been refined by the use of three-dimensional X-ray and neutron intensity data. The monoclinic lattice parameters are $a = 8.472$ (4), $b = 6.166$ (4), $c = 9.467$ (5) Å, $\beta = 98.01$ (5)°. There are systematic differences in the atomic positions given by the X-ray and neutron refinements respectively. For example, carbon atom positions obtained from the X-ray data are closer to the center of the molecule by an average of 0.006 Å when compared with the neutron results. The carbon skeleton exhibits a rigid-body motion, the hydrogen atoms making riding motions on the skeleton. The effects of crowding caused by the two hydrogen atoms at the open side of the biphenyl configuration are clearly revealed by the bending of the molecule, especially around the central ring. The distance between these overcrowded hydrogen atoms is 2.04 Å, about 0.4 Å less than the usual van der Waals distance.

1. Introduction

The geometrical configuration of the phenanthrene (C₁₄H₁₀) molecule forces a pair of hydrogen atoms to approach each other more closely than their van der Waals radii can allow. In molecules of this type, it is of significance to establish what relationships there are between the effects of such overcrowding and the deviations from the usual resonance-induced configurations. In this case, the hydrogen atoms on C(4) and C(5) (see Fig. 1) are forced towards each other, and if the normal geometry of the molecule were to remain unchanged, the distance between these two hydrogen atoms would be about 0.5 Å less than the normal sum of the van der Waals radii. The present structure analysis of the room-temperature phase of the compound was undertaken in order to study the steric effects caused by the overcrowding by means of both neutron and X-ray diffraction techniques.

Phenanthrene exhibits a phase transition at about 70°C, which is accompanied by a small heat anomaly. This phase change has been studied by various techniques: Arndt & Damask (1966*a*, *b*), Matsumoto (1966), Matsumoto & Tsukada (1965) and Matsumoto & Fukuda (1967). The present diffraction study of the low-temperature phase of the compound is a necessary stage towards an understanding of the phase transformation.

The structure of the low-temperature phase was first studied by Basak (1950) using two-dimensional data. Trotter (1963) then refined the structure using a set of three-dimensional photographic data. The present analyses are based on three-dimensional X-ray diffractometric data and a similar set of neutron data. The results agree well with those of Trotter. They are, however, somewhat more precise and include anisotropic thermal parameters and hydrogen atom positions.

2. Experimental

2.1. Cell data

A redetermination of the lattice constants of phenanthrene on an X-ray diffractometer was found to yield the following values: $a = 8.472$, $b = 6.166$, $c = 9.467$ Å, $\beta = 98.01$ °. The space group is $P2_1$ with one molecule per asymmetric unit.

2.2. Neutron intensity data

A set of three-dimensional neutron diffraction data was collected at the Puerto Rico Nuclear Center reactor at room temperature (24 ± 5 °C) on a crystal grown from a melt at Brookhaven National Laboratory by Drs Damask and Arndt. The crystal was elongated along the *b* direction and had a tabular habit. The distance between (001) faces was 3.0 mm and between (100) faces 4.2 mm. The crystal was 5.6 mm long in the *b* direction. It was encapsulated in aluminum foil to minimize sublimation. A total of 684 reflections were measured with θ - 2θ step scans, of which about 400 were used in the refinement. Those less than 3σ were

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Table 2 (*cont.*)

	X	Y	Z
C(12)	0.1908 (4) 0.1904 (6)	0.2279 (6)	-0.0633 (4) -0.0629 (5)
C(13)	0.2554 (5) 0.2552 (6)	0.2422 (7) 0.2405 (15)	0.0873 (4) 0.0880 (6)
C(14)	0.3484 (5) 0.3468 (7)	0.4245 (7) 0.4237 (15)	0.1356 (5) 0.1367 (6)
H(1)	0.198 (2)	0.516 (3)	-0.375 (2)
H(2)	0.028 (2)	0.197 (4)	-0.465 (2)
H(3)	-0.040 (2)	-0.090 (5)	-0.304 (2)
H(4)	0.061 (2)	-0.071 (3)	-0.053 (1)
H(5)	0.162 (2)	-0.068 (3)	0.155 (1)
H(6)	0.271 (2)	-0.027 (4)	0.404 (1)
H(7)	0.432 (1)	0.288 (4)	0.487 (1)
H(8)	0.488 (2)	0.584 (4)	0.314 (2)
H(9)	0.448 (1)	0.724 (3)	0.079 (2)
H(10)	0.348 (2)	0.701 (4)	-0.174 (2)

Intramolecular distances and angles are given in Table 4. The former have been corrected for rigid libra-

tion by transforming coordinates to the principal axis system of the libration matrix and then applying the correction given by Schomaker & Trueblood (1968). Values for the translational, vibrational and screw tensors are given in Table 5. The origin is at the center of mass of the carbon atoms.

It may be noted that eleven of the sixteen C-C distances determined from the neutron data are greater than or equal to the corresponding X-ray results, the average difference being 0.005 Å. The distances of the carbon atoms from their center of mass calculated from the neutron refinement are correspondingly greater by an average of 0.006 Å than the comparable X-ray values. The carbon atom mean-square principal components range from 0.0384 to 0.1366 (average 0.074) for X-ray results and 0.0375 to 0.1270 (average 0.066) for neutron results. Although our results are too imprecise to discuss bonding effects with confidence, the above-mentioned differences in the carbon positions and ther-

Table 3. *Thermal parameters (β_{ij}) used in a temperature factor of the form*
 $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2(hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$

For carbon atoms, X-ray results are given first with neutron results under them. Standard deviations in parentheses refer to the least significant figures.

	$\beta_{11}(\times 10^4)$	$\beta_{22}(\times 10^4)$	$\beta_{33}(\times 10^4)$	$\beta_{12}(\times 10^4)$	$\beta_{13}(\times 10^4)$	$\beta_{23}(\times 10^4)$
C(1)	233 (9) 195 (12)	510 (24) 533 (36)	135 (6) 119 (11)	1 (14) 27 (19)	44 (6) 44 (9)	47 (12) 88 (18)
C(2)	237 (10) 233 (13)	604 (27) 475 (30)	132 (6) 146 (12)	-17 (15) -58 (18)	12 (6) 40 (11)	-15 (13) 5 (17)
C(3)	211 (9) 180 (12)	521 (25) 496 (33)	162 (7) 150 (11)	-47 (13) -69 (16)	1 (6) 3 (9)	-55 (13) -40 (11)
C(4)	186 (7) 160 (10)	348 (18) 338 (24)	153 (6) 113 (9)	-25 (11) -43 (15)	37 (5) 9 (8)	-13 (11) -44 (13)
C(5)	190 (7) 192 (12)	362 (18) 353 (25)	158 (6) 114 (9)	27 (11) -16 (15)	47 (6) 32 (8)	29 (11) 58 (13)
C(6)	265 (10) 285 (15)	597 (27) 487 (30)	123 (6) 107 (11)	92 (15) 73 (19)	45 (6) 31 (9)	70 (12) 46 (15)
C(7)	227 (10) 240 (14)	669 (34) 602 (40)	140 (7) 99 (10)	50 (17) 60 (19)	9 (6) 2 (9)	-56 (14) -45 (17)
C(8)	198 (8) 189 (12)	561 (27) 556 (40)	169 (7) 149 (13)	68 (14) 33 (21)	-26 (6) 0 (11)	-106 (14) -88 (22)
C(9)	176 (8) 192 (14)	378 (19) 282 (26)	200 (7) 167 (12)	-35 (11) 32 (16)	42 (6) 35 (10)	-29 (12) -23 (14)
C(10)	202 (8) 184 (11)	310 (16) 243 (24)	195 (7) 200 (13)	-9 (11) -10 (16)	55 (7) 43 (11)	28 (11) 59 (16)
C(11)	149 (7) 123 (9)	330 (77) 272 (21)	155 (6) 148 (9)	28 (10) -16 (14)	33 (5) 32 (7)	8 (7) 23 (13)
C(12)	134 (6) 118 (8)	283 (15) 253 (18)	130 (5) 92 (8)	-17 (9) -11 (12)	34 (5) 18 (6)	24 (9) -14 (12)
C(13)	134 (6) 125 (8)	317 (8) 271 (23)	133 (5) 108 (9)	32 (9) -20 (12)	38 (5) 16 (7)	-15 (10) -35 (12)
C(14)	141 (6) 130 (19)	397 (21) 339 (26)	154 (6) 120 (8)	27 (11) 59 (14)	25 (5) 6 (7)	-34 (11) -8 (15)
			$\beta_{ij}(\times 10^3)$			
H(1)	37 (3)	58 (7)	17 (2)	0 (4)	1 (2)	10 (3)
H(2)	38 (4)	77 (9)	16 (2)	-6 (5)	0 (2)	-3 (4)
H(3)	45 (4)	65 (8)	26 (3)	-17 (6)	-1 (3)	-10 (5)
H(4)	32 (3)	42 (5)	17 (2)	-14 (3)	1 (2)	1 (3)
H(5)	39 (3)	35 (5)	16 (2)	-8 (4)	0 (2)	0 (3)
H(6)	43 (4)	90 (10)	16 (2)	8 (5)	5 (2)	20 (4)
H(7)	35 (3)	104 (11)	10 (2)	9 (5)	-4 (2)	1 (3)
H(8)	28 (3)	79 (8)	21 (3)	-7 (5)	-1 (2)	-10 (4)
H(9)	15 (2)	48 (6)	27 (3)	-12 (3)	2 (2)	-3 (4)
H(10)	26 (3)	40 (6)	31 (3)	-6 (3)	9 (2)	4 (4)

mal parameters for the X-ray and neutron cases are consistent with bonding effects of the type discussed by Coppens (1968).

Table 4. *Intramolecular distances and angles*

Results from X-ray data are given on top, those from neutron data underneath. Standard deviations are given in parentheses and refer to the least significant figure. The first column of distances contains uncorrected values. The second column has lengths corrected for rigid body motion.

	Bond lengths (Å)	
	Uncorrected	Corrected for rigid body motion
C(1)—C(2)	1.357 (7)	1.365
C(2)—C(3)	1.400 (12)	1.407
C(3)—C(4)	1.385 (7)	1.393
C(3)—C(4)	1.385 (11)	1.393
C(3)—C(4)	1.385 (6)	1.391
C(4)—C(12)	1.391 (9)	1.397
C(4)—C(12)	1.400 (6)	1.408
C(12)—C(11)	1.409 (9)	1.416
C(12)—C(11)	1.404 (6)	1.412
C(11)—C(1)	1.419 (6)	1.427
C(11)—C(1)	1.426 (6)	1.433
C(11)—C(10)	1.421 (9)	1.427
C(11)—C(10)	1.438 (6)	1.446
C(10)—C(9)	1.428 (11)	1.435
C(10)—C(9)	1.335 (7)	1.341
C(9)—C(14)	1.352 (9)	1.358
C(9)—C(14)	1.445 (7)	1.453
C(14)—C(13)	1.465 (11)	1.474
C(14)—C(13)	1.412 (6)	1.420
C(13)—C(12)	1.411 (7)	1.419
C(13)—C(12)	1.457 (5)	1.464
C(13)—C(5)	1.460 (7)	1.465
C(13)—C(5)	1.408 (6)	1.416
C(5)—C(6)	1.388 (9)	1.395
C(5)—C(6)	1.400 (6)	1.406
C(6)—C(7)	1.401 (9)	1.407
C(6)—C(7)	1.371 (7)	1.379
C(7)—C(8)	1.401 (11)	1.409
C(7)—C(8)	1.375 (8)	1.382
C(8)—C(14)	1.382 (13)	1.389
C(8)—C(14)	1.418 (7)	1.424
C(8)—C(14)	1.400 (9)	1.406
H(1)—C(1)	1.10 (2)	1.10
H(2)—C(2)	1.04 (2)	1.05
H(3)—C(3)	1.10 (3)	1.11
H(4)—C(4)	1.06 (2)	1.07
H(5)—C(5)	1.09 (2)	1.10
H(6)—C(6)	1.10 (2)	1.10
H(7)—C(7)	1.07 (2)	1.07
H(8)—C(8)	1.11 (3)	1.11
H(9)—C(9)	1.04 (2)	1.04
H(10)—C(10)	1.06 (2)	1.07
Non-bonded intramolecular distances (Å)		
H(1)—H(2)	2.52 (3)	2.53
H(2)—H(3)	2.45 (3)	2.47
H(3)—H(4)	2.41 (2)	2.42
H(4)—H(5)*	2.04 (2)	2.04
H(5)—H(6)	2.42 (2)	2.44
H(6)—H(7)	2.44 (3)	2.45
H(7)—H(8)	2.54 (3)	2.56
H(8)—H(9)	2.37 (2)	2.38
H(9)—H(10)	2.43 (2)	2.44
H(10)—H(1)	2.42 (2)	2.43

* Crowded H—H distance.

Table 4 (cont.)

Bond angles °	
C(11)—C(1)—C(2)	119.8 (5)
C(11)—C(1)—C(2)	119.1 (8)
C(11)—C(1)—H(1)	119.3 (11)
C(2)—C(1)—H(1)	121.6 (10)
C(1)—C(2)—C(3)	120.5 (5)
C(1)—C(2)—C(3)	120.2 (8)
C(1)—C(2)—H(2)	121.2 (13)
C(3)—C(2)—H(1)	118.6 (14)
C(2)—C(3)—C(4)	120.7 (5)
C(2)—C(3)—C(4)	121.3 (8)
C(2)—C(3)—H(3)	121.3 (13)
C(4)—C(3)—H(3)	117.4 (14)
C(3)—C(4)—C(12)	120.7 (5)
C(3)—C(4)—C(12)	120.5 (8)
C(3)—C(4)—H(4)	119.0 (10)
C(12)—C(4)—H(4)	120.5 (9)
C(4)—C(12)—C(11)	118.1 (4)
C(4)—C(12)—C(11)	118.3 (5)
C(4)—C(12)—C(13)	123.2 (4)
C(4)—C(12)—C(13)	122.6 (6)
C(11)—C(12)—C(13)	118.7 (4)
C(11)—C(12)—C(13)	119.2 (5)
C(1)—C(11)—C(12)	120.2 (5)
C(1)—C(11)—C(12)	120.6 (7)
C(1)—C(11)—C(10)	119.1 (5)
C(1)—C(11)—C(10)	118.6 (7)
C(10)—C(11)—C(12)	120.7 (5)
C(10)—C(11)—C(12)	120.7 (6)
C(12)—C(13)—C(5)	122.3 (4)
C(12)—C(13)—C(5)	122.2 (6)
C(12)—C(13)—C(14)	118.8 (4)
C(12)—C(13)—C(14)	118.5 (5)
C(5)—C(13)—C(14)	118.9 (5)
C(5)—C(13)—C(14)	119.2 (5)
C(13)—C(5)—C(6)	119.1 (5)
C(13)—C(5)—C(6)	119.7 (7)
C(13)—C(5)—H(5)	123.5 (9)
C(6)—C(5)—H(5)	116.8 (9)
C(5)—C(6)—C(7)	122.0 (5)
C(5)—C(6)—C(7)	121.2 (8)
C(5)—C(6)—H(6)	119.0 (12)
C(7)—C(6)—H(6)	119.8 (11)
C(6)—C(7)—C(8)	120.0 (6)
C(6)—C(7)—C(8)	119.1 (8)
C(6)—C(7)—H(7)	117.4 (15)
C(8)—C(7)—H(7)	123.5 (14)
C(7)—C(8)—C(14)	120.1 (5)
C(7)—C(8)—C(14)	120.3 (9)
C(7)—C(8)—H(8)	121.0 (11)
C(14)—C(8)—H(8)	118.6 (12)
C(8)—C(14)—C(13)	120.0 (5)
C(8)—C(14)—C(13)	120.5 (7)
C(8)—C(14)—C(9)	119.8 (5)
C(8)—C(14)—C(9)	119.2 (7)
C(13)—C(14)—C(9)	120.2 (5)
C(13)—C(14)—C(9)	120.2 (5)
C(14)—C(9)—C(10)	120.7 (5)
C(14)—C(9)—C(10)	120.5 (8)
C(14)—C(9)—H(9)	116.4 (11)
C(10)—C(9)—H(9)	123.2 (11)
C(9)—C(10)—C(11)	120.9 (5)
C(9)—C(10)—C(11)	120.8 (8)
C(9)—C(10)—H(10)	118.8 (12)
C(11)—C(10)—H(10)	120.3 (12)

As briefly mentioned above, the carbon rings were assumed to act as a rigid body. If the hydrogen atoms are included, the root-mean-square (r.m.s.) deviation between the observed values of U_{ij} and those calculated

from the rigid body model increased from 0.0064 to 0.0100 Å². It therefore appears that the hydrogen thermal parameters do not fit the carbon rigid body model too well. The r.m.s. deviations between observed and calculated tensor components is 0.0036 Å² for the X-ray data. The average value of the C–H distance from the neutron diffraction data was 1.076 Å before correction for rigid body motion, and 1.082 Å after correction. The tensor components of the rigid body mean-square amplitudes were subtracted from the measured mean-square amplitudes at the hydrogen position. The remaining amplitudes should be due to internal hydrogen modes. Twenty-five out of the thirty diagonal elements (U_{ii}) for hydrogen were positive and four out of the other five were only very slightly negative. While only three hydrogen temperature factors remained positive definite, addition of 1 to 2σ to some of the mean-square amplitude components would make all the results positive definite. The addition of the quantity

$$\frac{2}{3} \sum_{j=1}^{10} \sum_{i=1}^3 [U_{ii}^j(\text{total}) - U_{ii}^j(\text{rigid body})] / 2 \sum_{j=1}^{10} r_{C-H}^j$$

where j runs over the 10 hydrogen atoms and i the 3 orthogonal directions, to r_{C-H} gives a rough 'riding correction' of 0.017 (Busing & Levy, 1964). This correction is too small since the components should be, and indeed are, greater perpendicular to the C–H bond than parallel to it. However, the average remainders are too close to the standard deviations to make a 'correction' except in the average sense. The average correction results in an average C–H distance of 1.099 Å. The isotropic analog of $\frac{2}{3}$ was used since the components parallel to the bond are not negligible. The somewhat long average C–H distance may be due to a poor choice of assumptions for corrections for vibrations.

Table 5, part 2, shows that the general agreement between the rotation tensors for the X-ray and neutron

results is excellent, although the principal axes are about 10° apart. Most of the systematic differences in temperature factors between the X-ray and neutron results affect the translation and screw tensors. The translation amplitudes seem to be somewhat larger in the X-ray case, possibly because the X-ray data give larger thermal parameters. Differences in screw components are not significant. The agreement between the X-ray and the neutron results indicates that the rotation and screw tensors are probably significant to their standard deviations, while the translation tensor is somewhat less significant in view of the systematic discrepancies between X-ray and neutron data.

5. Discussion

The present results confirm that the distance between H(4) and H(5) is only 2.04 Å, well below the van der Waals distance of 2.4 Å, and that this close approach forces the distortion from planarity.

Several planar calculations were carried out in an attempt to determine the nature of the distortions. Since the positional parameters of the carbon atoms are more accurately known and the thermal parameters are smaller than those of the hydrogen atoms, and the former are more likely to be rigidly constrained, planes were fitted to various sets of carbon atoms. Figs. 1 and 2 show the deviations of the atoms from some of these planes as evaluated by unweighted least-squares analyses. The X-ray results are given above the neutron results. Fig. 1 gives distances from the plane of the six central carbon atoms. Fig. 2 shows distances from the plane of the ten carbon atoms which are least likely to be involved in the overcrowding (*i.e.* C(3), C(4), C(5), C(6) omitted from the calculation). Fig. 1 indicates that the top ring (I) is twisted about the C(2)–C(12) axis with C(3), C(4), H(3), and H(4) bent out of the plane of the Figure. The same is true of ring (III) which is twisted

Table 5. *Rigid body analysis of the carbon skeleton of phenanthrene*

Components are in a^* , b , c system. The origin is at the center of mass of the carbon atoms. The mean square displacement tensor U , for atom K is given by $U^K = T + G^K L + H^K S$, where T , L , and S are the translation, rotation, and cross tensors. G^K and H^K are tensors containing orthogonal coordinates for atom K (see Schomaker & Trueblood, 1968).

1. Translation tensor with e.s.d.s in Å².

	T_{11}	T_{22}	T_{33}	T_{12}	T_{13}	T_{23}
X-ray	0.044 (2)	0.056 (2)	0.057 (1)	0.006 (2)	0.007 (1)	–0.002 (1)
Neutron	0.041 (4)	0.048 (2)	0.048 (2)	0.004 (3)	0.005 (2)	0.000 (2)

2. Rotation tensor, L_{ij} terms in same order as above in radians².

X-ray	0.0054 (4)	0.0038 (3)	0.0065 (9)	–0.0002 (3)	0.0000 (4)	0.0007 (3)
Neutron	0.0052 (6)	0.0037 (5)	0.0064 (15)	–0.0001 (4)	0.0002 (8)	0.0008 (5)

3. Cross tensor in usual matrix order referred to orthogonal coordinates in radian.Å. $S(1,1) = -[S(33) + S(22)]$.

X-ray results

	0.0011	0.0010 (4)	–0.0020 (4)
	0.0003 (3)	–0.0018 (6)	0.0009 (4)
	–0.0007 (5)	–0.0005 (7)	0.0007 (8)

Neutron results

	0.0009	0.0013 (6)	–0.0029 (8)
	–0.0008 (5)	–0.0017 (10)	0.0004 (8)
	–0.0010 (9)	0.0015 (12)	0.0008 (15)

about C(13)–C(7), but also shows additional bending about C(13)–C(14); C(6) and C(7) are further out of the plane of ring (II) than are C(5) and C(8). These results agree with Trotter's (1963) results to within about 0.01 Å except for C(6), which, according to his results, is 0.089 Å out of the plane, and C(8) which he places 0.041 Å out of the plane of ring (II). Since the deviations derived from the three sets of data are consistent, it follows that the two ends of the phenanthrene molecule are probably not equivalent. All carbon atom positions in rings (I) and (III) are planar to within 0.01 Å. The angles between the plane of rings (I) and (II), (II) and (III), and (I) and (III) are (X-ray/neutron) respectively: 1.2°/1.3°; 1.2°/0.7°; 2.4°/2.0°.

Fig. 2 shows the displacements from the plane of C(1), C(2), and C(7) through C(12). It has been found by Okaya (1966) that in overcrowded silane molecules with aromatic substituents all atoms but those immediately affected by the crowding remain planar. If we consider the average standard deviation to be about 0.008 Å for C and 0.02 Å for H, then the deviations for C(12), C(1) and C(7) are between 2σ and 3σ . In this case, the atoms in ring (III) lie almost in the plane, and the distortions are largely in ring (I).

The main conclusion from the above arguments is that to find the exact nature of the distortion, it is necessary to obtain better data taken at low temperature in order to minimize thermal vibrations - preferably a set of neutron data on a deuterated crystal to eliminate electronic shape effects and incoherent scattering. It should also be pointed out that the choice of the model for the planar parts of the molecule is quite important in any discussion of the molecular configuration, especially when the atomic coordinates are subject to various uncertainties as in the present study.

Table 6 gives bond distances averaged across the quasi-twofold molecular axis. These distances are compared with the molecular orbital values calculated by Trotter (1963). The average difference of the pairs of distances is 0.01 Å for the X-ray results and 0.016 Å for the neutron results. The present C(11)–C(1) distance is much closer to the result of the molecular orbital calculation than the results of the previous determinations. The C(12)–C(13) distance is somewhat longer than Trotter's (1963) theoretical result. According to Coulson & Haigh (1963), who calculated the effects of the H–H repulsion on ring distortion, the presence of H–H overcrowding would increase this bond length by up to 0.02 Å and also C(11)–C(10) and C(9)–C(14) by up to 0.01 Å. The exact increase depends upon the H–H potential chosen, but in any case, these additions do improve the agreement with observation. Coulson & Haigh have concluded that, for what they consider reasonable hydrogen–hydrogen potentials, there should be no out-of-plane distortion. Since there is a distortion, we may conclude that one possible explanation is that the actual potential is harder than their tested values, and probably has an extremely steep slope around the observed H(4)–H(5) distance of 2.04 Å. A second

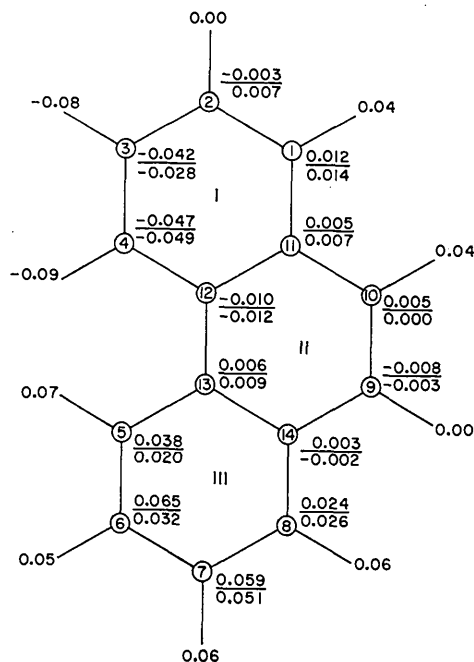


Fig. 1. Distances from the average plane of the carbon atom ring II. Distances from X-ray data are given over neutron results. Distances of hydrogen atoms from the plane are given for neutron results only. The equations in a^*, b, c , system are: $0.8250x - 0.4864y - 0.2878z = 1$ and $0.8272x - 0.4815y - 0.2895z = 1$ for X-ray and neutron results respectively.

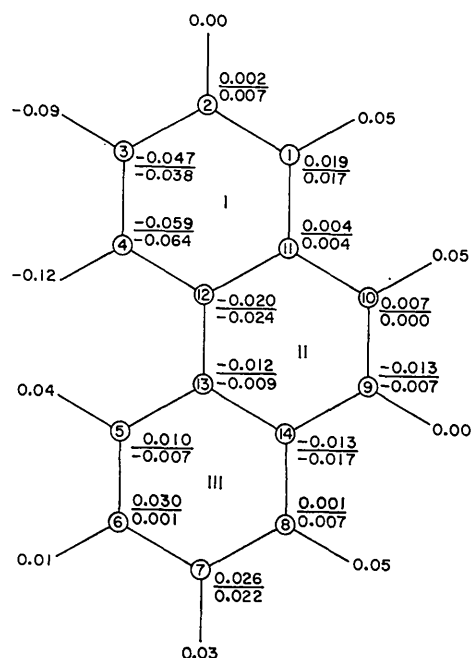


Fig. 2. Distances from the average plane of atoms not involved in overcrowding, C(1), C(2), C(7) through C(14). Arrangement is as in Fig. 1. The equations of the plane are: $0.8253x - 0.4822y - 0.2939z = 1$ and $0.8280x - 0.4773y - 0.2944z = 1$ for X-ray and neutron results, respectively.

Table 6. Average of C–C distances for both X-ray and neutron results across the quasi-twofold axis halfway between C(10) and C(11), and C(12) and C(13), lying in ring II compared with Trotter's (1962) experimental and molecular orbital (MO) results

The difference between two distances where averaged is given in parentheses and refers to the least significant figure.

	X-ray	Neutron	Trotter*	MO
C(1)—C(2)	1.374 (17) Å	1.398 (18) Å	1.381 (2) Å	1.390 Å
C(7)—C(8)				
C(2)—C(3)	1.386 (14)	1.401 (16)	1.398 (13)	1.405
C(6)—C(7)				
C(3)—C(4)	1.399 (15)	1.402 (10)	1.383 (30)	1.391
C(5)—C(6)				
C(4)—C(12)	1.412 (8)	1.406 (21)	1.405 (3)	1.411
C(5)—C(13)				
C(12)—C(11)	1.416 (8)	1.423 (8)	1.404 (28)	1.419
C(13)—C(14)				
C(11)—C(1)	1.428 (9)	1.417 (21)	1.457 (18)	1.413
C(8)—C(14)				
C(11)—C(10)†	1.450 (7)	1.455 (39)	1.390 (22)	1.426
C(14)—C(9)				
C(9)—C(10)	1.341	1.358	1.372	1.378
C(12)—C(13)†	1.464	1.465	1.448	1.434

* Uncorrected for rigid body motion. Add about 0.007 Å for an approximate correction.

† Coulson & Haigh (1963) would add up to 0.01 Å to C(4)—C(12) and 0.02 Å to C(12)—C(13) for overcrowding of H(4)—H(5).

is that the H–H repulsion is anisotropic since the displacements of these hydrogen atoms from the plane do not result in any significant increase in the H–H distance over the values they would have in the plane. It is also probable that omitted non-quadratic energy terms and/or crystal forces play some important role in the molecular configurations. As for the question of whether the bond lengths are different across the quasi-twofold axis, it appears from Tables 4 and 6 that our results are not precise enough to give a definite answer.

It may also be noted that another effect of the overcrowding is to open up the area occupied by H(4), C(4), C(12), C(13), C(5) and H(5). While in some other overcrowded molecules such as orthosubstituted benzoates (*e.g.* Okaya, 1967) similar angles may be as large as 125° because of the effects of overcrowding, in the present case we note an average of 122°. This may be due, in the case of C(12) and C(13) to ring distortions. The relatively 'small' angles of 123° and 120° at C(4) and C(5) respectively, however, indicate that the strain is sufficiently relieved by the out-of-plane distortion, so that no greater angular separation is needed, giving further credence to the hypothesis of anisotropic hydrogen electron density which would lead to anisotropic hydrogen–hydrogen repulsion in the molecule.

The out-of-plane bending is a consistent feature of the three independent determinations and suggests that crystal forces act differently on the two ends of the molecule.

The hydrogen position determination clearly shows the overcrowding; the very large hydrogen vibrations, however, limit the accuracy of the observed C–H bond distances and make them very sensitive to the type of vibrational model assigned to them.

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