

A Constrained Refinement of the Structure of Durene

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The crystal structure of durene (1,2,4,5-tetramethylbenzene, $C_{10}H_{14}$) has been refined from three-dimensional, single-crystal neutron-diffraction data. The crystals are monoclinic, $a=11.57$, $b=5.77$, $c=7.03$ Å, $\beta=112.93^\circ$, space group $P2_1/a$, $Z=2$. A conventional refinement, with anisotropic temperature factors and 485 independent, observed reflections measured with a four-circle diffractometer, gave a weighted residual R , on F , of 0.085, but the model contained some physically unreasonable thermal parameters. An alternative refinement in which the molecule was constrained to move as a rigid body, but with the methyl groups permitted to librate around the C–C bond, gave a weighted R of 0.115. All differences in position parameters between the two models were small. All carbon atoms and 6 of the 14 hydrogen atoms in the molecule are essentially coplanar. The ring is somewhat distorted, with bond angles at the corners with no methyl groups of about 123° and those at the other corners of about 118.6° . The C–C bond length between two methylated corners is about 1.425 Å, compared with 1.395 Å for the other bonds in the ring. This long bond, combined with C–C–C bond angles of 121.5° , results in adjacent methyl groups being pushed apart. The methyl groups are in an eclipsed conformation. The eigenvectors of the L tensor correspond very closely to the axes of principal moments of inertia of the molecule. The hydrogen amplitudes derived from the refinement predict a methyl torsional frequency of 130 cm^{-1} , in satisfactory agreement with observed frequencies of 144 and 179 cm^{-1} . The whole molecule amplitudes and frequencies derived from the L and T components of the thermal ellipsoids are also generally consistent with spectroscopic results.

Introduction

The crystal structure of durene (1,2,4,5-tetramethylbenzene, $C_{10}H_{14}$) was first determined by Robertson (1933*a, b*). Using trial and error and then Fourier techniques he determined the general shape of the carbon atom framework and also the packing arrangement of the molecules in the unit cell. He made no attempt to locate the hydrogen atoms, but was able to suggest that the benzene ring was distorted, with larger bond angles at the corners to which only a hydrogen atom was attached than at the corners to which a methyl group was attached, and that adjacent methyl groups were further apart than they would be if all C–C–C bond angles were 120° .

There is considerable interest in the equilibrium conformation of the methyl groups in durene and other methylbenzenes, as well as in the nature of the interaction potential hindering their rotation. The details of the crystal structure and dynamics of aromatic molecular crystals are also of great value in the study of intermolecular potentials. Recently, crystalline durene has been studied extensively by Raman (Sanquer & Meinel, 1972), infrared (Hadni, Wyncke, Morlot & Gerbaux, 1969) and neutron inelastic scattering (Rush, 1967; Livingston, Grant, Pugmire & Strong, 1972) techniques in order to obtain information concerning the details of the crystal vibrations, and the torsional oscillations and rotational barriers of the methyl

groups. Methyl groups attached to adjacent carbon atoms of a benzene ring are 'overcrowded'. In hexamethylbenzene, HMB, this results in the methyl groups being forced out of the plane of the ring (Hamilton, Edmonds, Tippe & Rush, 1969). Neutron inelastic scattering (Rush & Taylor, 1966), neutron diffraction (Hamilton *et al.*, 1969) and n.m.r. (Allen & Cowking, 1967) measurements established a low barrier to internal rotation ($\approx 4\text{ kJ.mol}^{-1}$) of the methyl groups in HMB, which apparently have a cooperative motion much like a series of meshed gears. In durene, however, the barrier to rotation is higher ($\approx 9\text{ kJ.mol}^{-1}$), although there is spectroscopic evidence for an oscillation of considerable amplitude about an axis formed by the C–C bond (Rush, 1967; Livingston *et al.*, 1972).

The purpose of this neutron diffraction investigation was to complete the structure determination of durene by locating the hydrogen atoms (thus determining the conformation of adjacent methyl groups) and to refine the details of the structure. A further purpose was to study the thermal motion information which could be extracted from the diffraction data, and to compare it in detail with the information provided by spectroscopic techniques.

Experimental procedure

Durene crystallizes in the monoclinic system, with cell dimensions (Robertson, 1933*b*) $a=11.57$, $b=5.77$, $c=7.03$ Å, $\beta=112.93^\circ$, space group $P2_1/a$, $Z=2$. Because of the high vapor pressure at room temperature a bottle of the compound which had been on the shelf

* Work performed in part during this author's tenure as a NRC-NBS Postdoctoral Research Associate.

for something more than a year contained many well formed crystals. The crystals were plates, with faces parallel to (001), with thicknesses of the order of 1 mm and other dimensions up to about 5 mm. When the crystals were viewed through a polarizing microscope, the extinctions were invariably sharp, and there was no evidence of twinning.

A crystal with approximate dimensions $5.2 \times 3.6 \times 1.3$ mm was chosen from this collection. Because of its high vapor pressure it was sealed inside a tube of silica glass along with a supply of durene powder, so that the atmosphere inside the tube would be saturated with durene vapor. The crystal was then mounted on a computer-controlled, four-circle, neutron diffractometer (Alperin & Prince, 1970) with the b axis approximately parallel to the ϕ axis. All reflections with $-5^\circ \leq \chi \leq 90^\circ$ and $2\theta \leq 100^\circ$ with a wavelength of 1.232 Å were measured at room temperature (295°K) by a procedure described previously (Prince, 1972). There are 970 independent reflections within the sphere defined by the limiting 2θ angle. Of these 485 had intensities that exceeded background by more than 2σ , where $\sigma = (I_p + I_b)^{1/2}$. The magnitudes of the structure factors for the observed reflections were corrected for the apparent absorption due to incoherent scattering by hydrogen by the method described by Burnham (1966). Because correction for secondary extinction (Zachariasen, 1968) requires the parameter \bar{T} , the absorption-averaged path length through the crystal, and because this is frequently not the same for different members of a set of equivalent reflections, the later stages of refinement were performed with a non-unique data set, formed by averaging only hkl and $\bar{h}\bar{k}\bar{l}$ reflections. In this set there are 1654 reflections of which 832 had significant intensity. In the unique data set the agreement index for equivalent reflections, defined by $R = \sum |F_{hkl} - F_{\bar{h}\bar{k}\bar{l}}| / \sum F_{hkl}$, was 0.028.

Refinement of the structure

A set of idealized hydrogen positions was calculated on the basis of a model for the methyl group conformation similar to that found in HMB (Hamilton *et al.*, 1969) and combined with the carbon positions given by Robertson (1933*b*) in order to determine a set of signs for a Fourier synthesis using the observed intensities. The resulting three-dimensional density map clearly showed the carbon positions, and there were regions of negative density in suitable positions for most of the hydrogen atoms. The approximate coordinates of these positions were used as the initial parameters for a least-squares refinement, using the program *RFINE* (Finger, 1968), with isotropic temperature factors, ignoring secondary extinction, and using weights determined from counting statistics (Prince, 1972). All refinement sought to minimize the function $\sum w(F_{\text{obs}} - F_{\text{calc}})^2$, where the sum is taken over observed reflections only. The refinement proceeded very slowly; after ten cycles a minimum was reached with a weight-

ed R index of 0.173 ($R_w = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}$). Eight additional cycles, with anisotropic temperature factors, led to a weighted R of 0.104.

At this point some diagrams (Johnson, 1965) showed the general features of the structure, but a number of the details, both of position parameters and thermal parameters, were physically unreasonable. The C-H distances in the methyl groups, before correction for thermal motion, ranged from 0.926 to 1.107 Å, and a number of the hydrogen atoms had components of the longest axes of their thermal ellipsoids parallel to the C-H bond, contrary to the expected small amplitude of C-H stretching motions. On the other hand, all the carbon atoms were coplanar within ± 0.005 Å, and the C-C distances were close to normal values. The resulting position parameters also show that the methyl groups are in an 'eclipsed' configuration similar to that described by Pitzer & Scott (1943) in their discussion of the potential function of *o*-xylene. One hydrogen atom of each group lies very close (within 0.035 Å) to the plane of the carbon atoms, in marked contrast to the structure of HMB (Hamilton *et al.*, 1969).

Various attempts at further refinement, by correcting the calculated structure factors for secondary extinction with the parameter \bar{T} (Zachariasen, 1968) treated as a constant, and by altering the weights with the inclusion of an 'ignorance factor' (Corfield, Doedens & Ibers, 1967), led to somewhat lower values of the weighted R index, but did not remove the unreasonable details. Several attempts to reconcile the thermal parameters with various models of molecular motion (Schomaker & Trueblood, 1968; Johnson, 1970) were also unsuccessful. Therefore all further refinement was carried out using the larger, non-unique data set, with an individual value of \bar{T} for each reflection, and the least-squares program, *RFINE*, was revised (Prince & Finger, 1973) to allow molecular motion parameters to be fitted directly to the data.

First a conventional refinement was run, with anisotropic temperature factors and an isotropic, secondary extinction parameter. Weights were assigned by the formula $w = 1/\sigma_{F_{\text{obs}}}^2$ and $\sigma_{F_{\text{obs}}} = [\sigma_s^2 + (0.03F)^2]^{1/2}$ where σ_s is computed from counting statistics. The weighted R index was 0.085. Next a constrained refinement was performed. The entire molecule was permitted to translate and librate, and in addition each methyl group was permitted to oscillate independently around its C-C bond. Because non-zero third cumulants are implied by the rigid-body model, these were included in the structure-factor calculations. In the first four cycles all parameters except the molecular motion parameters were held fixed at their values from the conventional refinement. Then position parameters were allowed to vary for four cycles, and finally all parameters, including the extinction parameter and the scale factor, were allowed to vary for four cycles. The maximum parameter shift in the last cycle was 0.02 of its standard deviation. The final weighted R

index was 0.115. The parameters resulting from both the constrained and the unconstrained refinements are shown in Table 1. The final values of the extinction parameter r^* were $1.9(2) \times 10^{-5}$ and $1.8(2) \times 10^{-5}$ for the constrained and unconstrained refinement, respectively. Table 2 gives the values of the molecular motion parameters from the constrained refinement, and Table 3 gives the observed and calculated structure factors from the constrained refinement. The largest correlation coefficient, with a value of 0.8024, was between the scale factor and the extinction parameter. Other correlation coefficients with values greater than 0.60 included those between the scale factor and the diagonal elements of **T**, those relating L_{11} and L_{22} with L_{12} , and those between the x and z position parameters of H(5) and H(6).

Discussion

1. Molecular geometry

Fig. 1 shows two views of the molecule, drawn using the parameters from the unconstrained refinement, while Fig. 2 shows the same views using parameters from the constrained refinement. It is apparent that the two are extremely similar but for the constrained model, the physically unreasonable thermal ellipsoid orientations, particularly for hydrogen atoms H(4) and H(7) (Fig. 1) are not allowed. The R -index ratio (Hamilton, 1965) is 1.34. For 485 independent reflections, 110 parameters in the unconstrained model, and 52 parameters in the constrained model the ratio required

Table 2. Rigid body thermal parameters, as determined from the constrained refinement

The system designated 'crystal axes' is an orthonormal coordinate system with x parallel to the a axis, y parallel to the b axis and z parallel to $a \times b$. The molecular system has x parallel to the longer C(2)-C(4) vector in the ring and z perpendicular to the plane of the ring. The θ values are the amplitudes of hydrogen motion around the C-C axis, for the methyl groups including C(1) and C(5) respectively.

Parameter	Orthonormal systems	
	Crystal axes	Molecular axes
T_{11}	0.044 (1)*	
T_{22}	0.049 (1)	
T_{33}	0.064 (1)	
T_{12}	0.010 (1)	
T_{13}	-0.003 (1)	
T_{23}	-0.001 (1)	
L_{11}	0.0098 (4)	0.0115
L_{22}	0.0102 (4)	0.0034
L_{33}	0.0034 (3)	0.0085
L_{12}	0.0015 (4)	0.0003
L_{13}	0.0003 (2)	0.0000
L_{23}	0.0004 (2)	0.0003
θ_1	0.153 (7)	
θ_5	0.132 (7)	

* Units are \AA^2 for **T**, radians² for **L** and θ .

for significance at the 0.005 level is 1.12. The unconstrained model therefore does give a significantly better fit to the data. This is not too surprising, because the constrained model absorbs into the rigid-body par-

Table 1. Position ($\times 10^4$) and thermal ($\times 10^4$) parameters for the constrained and unconstrained refinements of durene

For each pair of numbers the upper one refers to the constrained refinement and the lower one to the unconstrained refinement. Standard deviations for the last significant figures are given in parenthesis. The errors for the thermal parameters have been approximated by the formula

$$\sigma\beta = \left[\sum_i (\sigma_i \frac{\partial \beta}{\partial p_i})^2 \right]^{1/2},$$

where the sum is taken over the 14 rigid body parameters, and p_i and σ_i denote the parameters and their standard deviations.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	1893 (4)	3205 (8)	2655 (8)	124 (3)	501 (11)	527 (14)	-42 (5)	62 (4)	-151 (9)
	1894 (3)	3195 (8)	2660 (9)	114 (4)	503 (16)	556 (18)	-40 (6)	69 (6)	-172 (13)
C(2)	918 (3)	1558 (5)	1269 (5)	89 (2)	339 (7)	356 (7)	11 (3)	63 (3)	-40 (5)
	920 (2)	1559 (4)	1267 (4)	94 (3)	370 (9)	344 (9)	-1 (4)	67 (4)	-32 (7)
C(3)	378 (3)	-111 (5)	2086 (5)	109 (2)	398 (7)	305 (7)	19 (3)	68 (3)	-3 (4)
	379 (2)	-109 (4)	2095 (6)	107 (3)	379 (9)	315 (10)	26 (4)	71 (4)	1 (8)
C(4)	-524 (3)	-1667 (5)	899 (5)	98 (2)	327 (6)	369 (8)	22 (3)	90 (3)	18 (5)
	-529 (2)	-1664 (4)	885 (5)	102 (3)	323 (8)	374 (9)	33 (4)	88 (4)	37 (7)
C(5)	-1060 (4)	-3403 (8)	1907 (8)	164 (5)	451 (10)	580 (16)	6 (5)	178 (8)	100 (9)
	-1065 (4)	-3422 (7)	1912 (5)	160 (5)	415 (12)	548 (15)	13 (7)	175 (7)	75 (12)
H(1)	2673 (9)	3112 (19)	2317 (22)	137 (3)	979 (22)	979 (24)	-164 (7)	171 (6)	-486 (18)
	2744 (8)	3123 (17)	2396 (21)	146 (8)	998 (46)	1131 (53)	-164 (16)	203 (17)	-525 (41)
H(2)	1657 (9)	4868 (15)	2417 (21)	192 (5)	451 (10)	952 (21)	-47 (6)	18 (8)	-229 (11)
	1661 (8)	4932 (16)	2413 (20)	205 (10)	525 (32)	971 (51)	-29 (15)	90 (17)	-217 (29)
H(3)	2048 (13)	2878 (22)	4139 (19)	295 (6)	1063 (32)	470 (11)	-268 (11)	51 (5)	-223 (12)
	2101 (12)	2848 (21)	4195 (19)	300 (16)	1106 (65)	487 (28)	-298 (27)	53 (19)	-180 (39)
H(4)	687 (7)	-198 (12)	3786 (11)	177 (5)	645 (15)	309 (7)	2 (7)	80 (3)	4 (4)
	693 (6)	-202 (11)	3781 (13)	183 (7)	674 (28)	384 (24)	5 (12)	104 (10)	64 (20)
H(5)	-2026 (9)	-3233 (17)	1497 (21)	172 (5)	790 (19)	1079 (29)	26 (7)	277 (10)	359 (19)
	-2048 (10)	-3250 (16)	1464 (19)	199 (11)	843 (42)	1086 (57)	-49 (17)	271 (21)	308 (36)
H(6)	-911 (12)	-5102 (14)	1573 (24)	335 (9)	396 (8)	1102 (27)	7 (5)	431 (14)	124 (9)
	-922 (11)	-5151 (13)	1559 (21)	359 (16)	433 (29)	1143 (56)	62 (17)	438 (27)	206 (30)
H(7)	-730 (12)	-3282 (19)	3411 (19)	329 (8)	905 (20)	570 (16)	-152 (12)	229 (10)	145 (13)
	-680 (12)	-3317 (19)	3504 (19)	315 (17)	943 (58)	703 (40)	-68 (23)	225 (24)	271 (45)

rameters motions due to internal modes of oscillation, including 'wagging' of the methyl groups, which would be expected to be significant. The constrained refinement appears to provide physically reasonable thermal parameters and we shall use these parameters here for a comparison with spectroscopic results.

The refinement of libration parameters permits corrections to bond distances and angles to be made in accordance with the rigid-body model [Prince & Finnger, 1973, equation (13)]. The uncorrected and corrected values are summarized in Table 4 and the corrected

values are shown in Fig. 3. The benzene ring is stretched along the direction parallel to the long axis of the molecule, the C(2)-C(4) bond appears to be significantly longer than the C(2)-C(3) and C(3)-C(4) bonds. The C-C bonds from the ring to the methyl groups are somewhat short (1.51 Å), possibly due to neglect of the wagging motions of the methyl groups. It is difficult to assess the significance of the departures from an ideal tetrahedral configuration of the methyl groups (with angles of 109.5°). The average of the methyl group C-H bond lengths derived from our

Table 3. Observed and calculated structure factors for the constrained refinement of durene
Columns are h , $100F_{obs}$, $100F_{calc}$, and $100\sigma_{Fobs}$. Unobserved reflections are marked by an asterisk and strongly extinct reflections by E.

h	$100F_{obs}$	$100F_{calc}$	$100\sigma_{Fobs}$
0 0 0	0	0	0
1 0 0	100	100	100
2 0 0	200	200	200
3 0 0	300	300	300
4 0 0	400	400	400
5 0 0	500	500	500
6 0 0	600	600	600
7 0 0	700	700	700
8 0 0	800	800	800
9 0 0	900	900	900
10 0 0	1000	1000	1000
11 0 0	1100	1100	1100
12 0 0	1200	1200	1200
13 0 0	1300	1300	1300
14 0 0	1400	1400	1400
15 0 0	1500	1500	1500
16 0 0	1600	1600	1600
17 0 0	1700	1700	1700
18 0 0	1800	1800	1800
19 0 0	1900	1900	1900
20 0 0	2000	2000	2000
21 0 0	2100	2100	2100
22 0 0	2200	2200	2200
23 0 0	2300	2300	2300
24 0 0	2400	2400	2400
25 0 0	2500	2500	2500
26 0 0	2600	2600	2600
27 0 0	2700	2700	2700
28 0 0	2800	2800	2800
29 0 0	2900	2900	2900
30 0 0	3000	3000	3000
31 0 0	3100	3100	3100
32 0 0	3200	3200	3200
33 0 0	3300	3300	3300
34 0 0	3400	3400	3400
35 0 0	3500	3500	3500
36 0 0	3600	3600	3600
37 0 0	3700	3700	3700
38 0 0	3800	3800	3800
39 0 0	3900	3900	3900
40 0 0	4000	4000	4000
41 0 0	4100	4100	4100
42 0 0	4200	4200	4200
43 0 0	4300	4300	4300
44 0 0	4400	4400	4400
45 0 0	4500	4500	4500
46 0 0	4600	4600	4600
47 0 0	4700	4700	4700
48 0 0	4800	4800	4800
49 0 0	4900	4900	4900
50 0 0	5000	5000	5000
51 0 0	5100	5100	5100
52 0 0	5200	5200	5200
53 0 0	5300	5300	5300
54 0 0	5400	5400	5400
55 0 0	5500	5500	5500
56 0 0	5600	5600	5600
57 0 0	5700	5700	5700
58 0 0	5800	5800	5800
59 0 0	5900	5900	5900
60 0 0	6000	6000	6000
61 0 0	6100	6100	6100
62 0 0	6200	6200	6200
63 0 0	6300	6300	6300
64 0 0	6400	6400	6400
65 0 0	6500	6500	6500
66 0 0	6600	6600	6600
67 0 0	6700	6700	6700
68 0 0	6800	6800	6800
69 0 0	6900	6900	6900
70 0 0	7000	7000	7000
71 0 0	7100	7100	7100
72 0 0	7200	7200	7200
73 0 0	7300	7300	7300
74 0 0	7400	7400	7400
75 0 0	7500	7500	7500
76 0 0	7600	7600	7600
77 0 0	7700	7700	7700
78 0 0	7800	7800	7800
79 0 0	7900	7900	7900
80 0 0	8000	8000	8000
81 0 0	8100	8100	8100
82 0 0	8200	8200	8200
83 0 0	8300	8300	8300
84 0 0	8400	8400	8400
85 0 0	8500	8500	8500
86 0 0	8600	8600	8600
87 0 0	8700	8700	8700
88 0 0	8800	8800	8800
89 0 0	8900	8900	8900
90 0 0	9000	9000	9000
91 0 0	9100	9100	9100
92 0 0	9200	9200	9200
93 0 0	9300	9300	9300
94 0 0	9400	9400	9400
95 0 0	9500	9500	9500
96 0 0	9600	9600	9600
97 0 0	9700	9700	9700
98 0 0	9800	9800	9800
99 0 0	9900	9900	9900
100 0 0	10000	10000	10000

structure analysis is $1.086 \pm 0.024 \text{ \AA}$, where the error is the r.m.s. deviation of the individual values from the mean. It appears that the adjacent 'eclipsed' CH_3 groups are pushed apart slightly with $\text{C}=\text{C}-\text{C}$ angles

of about 121.5° and minimum $\text{H}-\text{H}$ distances of 2.5 \AA between groups. The minimum distance between methyl and ring protons is 2.3 \AA and the smallest intermolecular $\text{H}-\text{H}$ distance is 2.6 \AA .

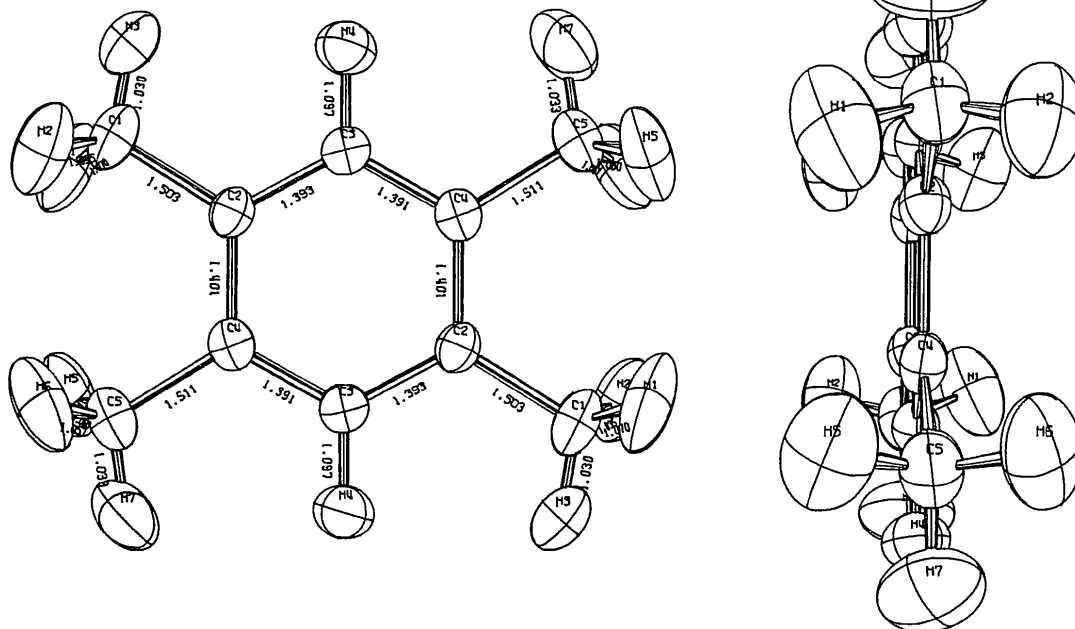


Table 4. Bond distances and angles for the constrained refinement before and after applying the libration correction

Errors in the last significant figures are given in parenthesis. It has been assumed that the contribution to the error due to the uncertainty in the parameters used in the libration correction is negligible.

Distances	Uncorrected	Corrected
C(1)–C(2)	1.506	1.517 (5) Å
C(1)–H(1)	1.020	1.100 (11)
C(1)–H(2)	0.994	1.068 (12)
C(1)–H(3)	1.005	1.086 (16)
C(2)–C(3)	1.388	1.397 (4)
C(2)–C(4)	1.412	1.426 (5)
C(3)–C(4)	1.382	1.392 (4)
C(3)–H(4)	1.107	1.118 (9)
C(4)–C(5)	1.495	1.505 (5)
C(5)–H(5)	1.043	1.111 (11)
C(5)–H(6)	1.038	1.106 (12)
C(5)–H(7)	0.977	1.043 (15)

Angles	Uncorrected	Corrected
C(2)–C(1)–H(1)	108.9	107.6 (6)°
C(2)–C(1)–H(2)	114.4	112.7 (6)
C(2)–C(1)–H(3)	109.8	108.6 (6)
H(1)–C(1)–H(2)	102.8	104.2 (10)
H(1)–C(1)–H(3)	114.6	116.0 (12)
H(2)–C(1)–H(3)	106.4	107.9 (7)
C(1)–C(2)–C(3)	121.0	120.7 (4)
C(1)–C(2)–C(4)	121.0	121.2 (4)
C(3)–C(2)–C(4)	118.0	118.1 (3)
C(2)–C(3)–C(4)	123.8	123.6 (3)
C(2)–C(3)–H(4)	118.0	118.1 (4)
C(4)–C(3)–H(4)	118.2	118.3 (5)
C(3)–C(4)–C(5)	120.3	120.1 (3)
C(2)–C(4)–C(5)	121.5	121.6 (3)
C(2)–C(4)–C(3)	118.2	118.3 (3)
C(4)–C(5)–H(5)	113.8	112.4 (6)
C(4)–C(5)–H(6)	112.9	111.5 (6)
C(4)–C(5)–H(7)	113.9	112.7 (6)
H(5)–C(5)–H(6)	106.3	107.8 (9)
H(5)–C(5)–H(7)	102.5	104.1 (11)
H(6)–C(5)–H(7)	106.4	108.0 (11)

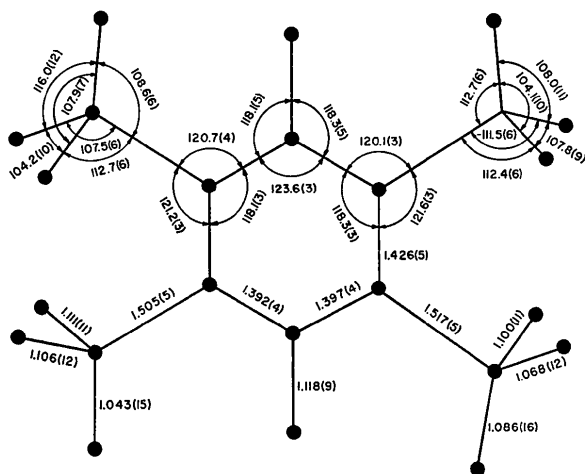


Fig. 3. Bond distances and angles in the durene molecule after correction for libration.

2. Thermal motion

As pointed out in the Introduction, there is considerable spectroscopic information concerning the librational and translational vibrations of durene. In this section we shall compare the vibrational frequencies measured in the spectroscopic studies with frequencies computed from the thermal motion parameters derived from our constrained refinement (see Table 2). Librational and torsional frequencies will be calculated from the thermal parameters, using the expression relating frequencies to mean-squares amplitudes of motion for a harmonic oscillator:

$$\theta^2 = (h/8\pi^2\omega cI) \coth(hc\omega/2kT),$$

where I is the molecular or methyl group moment of inertia, ω is the frequency in cm^{-1} , and θ^2 is the mean-square amplitude of rotational motion in radians.

2.1 Methyl group torsional vibrations. The mean-square amplitudes derived for the torsional motion of the methyl groups (θ_1 and θ_5 in Table 2) are 0.153 and 0.132 rad^2 for methyl groups including C(1) and C(5) respectively (Fig. 2). The torsional frequencies at 148°K for in-phase and out-of-phase oscillation of the methyl groups in durene have recently been measured by neutron inelastic scattering to be 144 and 179 cm^{-1} respectively (Livingston *et al.*, 1972). Previous neutron spectra (Rush, 1967) indicate little shift in the torsional frequency between 292° and 127°K. We have used the average of our values (0.142 rad^2) and the expression above to calculate the 'average' frequency of oscillation predicted from our thermal motion parameters. The resulting frequency is 130 cm^{-1} , which is in reasonable agreement with the observed spectroscopic values. This comparison is shown in Table 5 along with similar results for the molecular librations which will be discussed below.

Table 5. Comparison of librational and torsional frequencies of durene derived from the rigid-body motion analysis with spectroscopic frequencies

Librations are described in the molecular system; OX , OY and OZ refer to the principal axes of inertia (in ascending order of moments of inertia). Moments of inertia (I) calculated from the structural data are also listed.

Axis of libration	$I(10^{-40} \text{ g cm}^2)$	Mean square amplitude (rad^2)	Frequency (cm^{-1})	
			Rigid body	Spectroscopic
Methyl torsion	5.24	0.142	130	144, 179*
OX	390	0.0115	50	72†
OY	803	0.0034	65	103†
OZ	1172	0.0085	34	32†

* From Livingston *et al.* (1972).

† From Sanquer & Meinel (1972).

There are a number of factors which could explain the difference between the 'average' spectroscopic (160 cm^{-1}) and diffraction (130 cm^{-1}) frequency values. These include the inherent uncertainty in the diffraction result (which must be $\sim 10\text{ cm}^{-1}$ even if our correction for rigid-body contributions is assumed to be rigorously correct), the neglect of possible anharmonic character in the torsional oscillations, and the neglect of some of the contribution of bending vibrations of the methyl groups to the proton amplitudes. Another factor, which is potentially very significant in the case of durene and other molecules exhibiting internal rotation with low potential barriers ($\lesssim 10\text{ kJ.mole}^{-1}$), is reorientation of the oscillation group from one equilibrium position to another. One obvious way to test the effect of such re-orientational motions on our thermal motion analysis is to obtain diffraction data at low temperature.

2.2 Molecular librations. There are six modes of libration for the two molecules in the durene unit cell. In a recent Raman scattering study of durene Sanquer & Meinel (1972) have concluded that the molecular librations at the limit of very long wavelengths ($q=2\pi/\lambda=0$) involve rotational displacements which roughly correspond to motions around the three principal axes of inertia of the durene molecules. In addition the six librational modes (which have either A_g or B_g symmetry) break down into three pairs of librations with almost identical frequencies. These frequencies are listed in Table 5 along with the moments of inertia around the corresponding molecular axes. In the table OX is the axis bisecting the durene molecule in a direction perpendicular to the axis OY , which passes through the two benzene ring protons; OZ is the axis which is perpendicular to the benzene ring plane and passes through the center of the ring.

One interesting feature of the spectroscopic results is that the frequency of oscillation around the OY axis is considerably higher than that around the OX

axis, even though the moment of inertia around OY is twice that around OX . This is quite different from the spectroscopic results for HMB (Dumas & Michel, 1971), which show that the librations around the three molecular axes have frequencies in an inverse order to the moments of inertia. Such a result suggests that the force constants for rotational displacements around the OX axis are considerably lower than for displacements around the OY axis.

The librational frequencies calculated from our thermal parameters are also listed in Table 5. It can be seen that only the librational frequency around the OZ axis agrees closely with the spectroscopic result. However, the order of the librational frequencies is consistent with the spectroscopic values. Most particularly, the diffraction data do yield a higher frequency for motions around the OY axis than around the OX axis, which is consistent with the force-field asymmetry reflected in the spectroscopic results. The lack of quantitative agreement between the spectroscopic and diffraction frequencies may be attributed to several factors, including the influence of possible anharmonicity and the fact that the spectroscopic frequencies are measured at $q=0$, and thus do not reflect the dispersion of the librational branches at finite q , which could lead to significantly different 'average' frequencies and displacements. In addition the contribution of 'wagging' vibrations of the methyl groups, which is partly neglected in the rigid body approximation, leads to the derivation of a 'librational' frequency that is systematically too low.

2.3 Translational motions. Frequencies have been assigned at 290°K for the three optical lattice modes involving translational displacements of the durene molecules (Hadni *et al.*, 1969). A frequency of 65 cm^{-1} is assigned to vibrations (species A_u) parallel to the b axis of the crystal while two peaks at 37 and 68 cm^{-1} are assigned to vibrations (both B_u) in the ac plane, without any conclusion about translational directions.

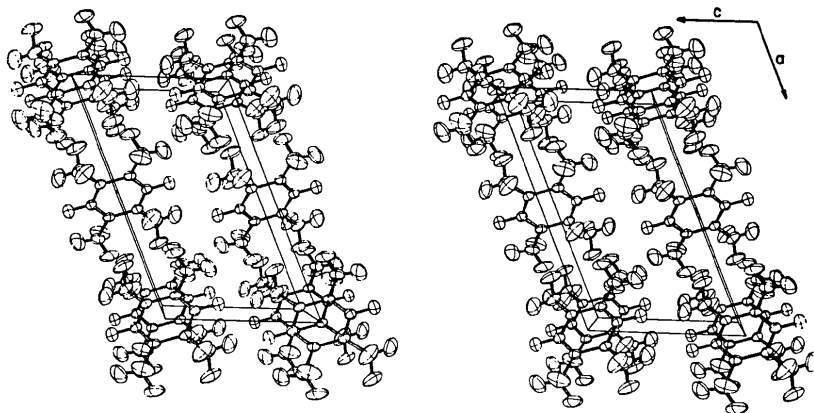


Fig. 4. Stereoscopic pair showing the molecular arrangement in the durene crystal, viewed along the b axis.

The arrangement of the durene molecules in the monoclinic lattice is shown in Fig. 4, which presents a view along the **b** direction.

The calculation of comparative frequencies from our thermal parameters does not seem worthwhile in this case, since the translational motions of the durene molecules in the lattice involve a superposition of displacements from the three (unmeasured) acoustic vibrational branches as well as the three optical branches whose $q=0$ frequencies are given above. Thus any calculated frequencies could not be directly related to the observed frequencies. The spectroscopic data do suggest, however, that there is a significant asymmetry in the thermal motion in the *ac* plane (Fig. 4), which should be reflected in our rigid-body amplitudes. Examination of the parameters in Table 2 does indeed show such an asymmetry. These results yield a mean-square amplitude of 0.049 \AA^2 in the **b** direction and quite different amplitudes in directions parallel to the **a** direction (0.044 \AA^2) and parallel to the **c*** direction (0.064 \AA^2). Thus our diffraction results also clearly indicate dissimilar translational amplitudes in the *ac* plane and suggest that the observed infrared frequencies at 37 and 68 cm^{-1} should be assigned to vibrations approximately in the **c*** and **a** directions respectively. Such a result is reasonable in view of the arrangement of durene molecules in the lattice (Fig. 4) since out-of-phase molecular displacements in a direction perpendicular to the *a* axis will involve less steric interaction than displacements along the **a** direction.

We shall attempt to obtain more information concerning the thermal motions in durene and the validity of the above comparisons by a neutron-diffraction study at a much lower temperature.

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