3. *The Crystal and Molecular Structure of Octamethylnaphthalene: A Non-planar Naphthalene Derivative.*

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Crystals of octamethylnaphthalene have been examined by quantitative *X*-ray analysis. They are orthorhombic, space-group D_{2h}^{22}–*Ccca*, with four molecules of $C_{18}H_{24}$ per unit cell. The molecular symmetry is 222, the asymmetric crystal unit consisting of one-quarter of the chemical molecule. In electron-density projections obtained from two-dimensional Fourier syntheses not all the atoms can be resolved, but the molecule is definitely non-planar. The α-methyl groups are displaced from the mean plane by about 0·73 Å, and the β-methyl groups are displaced in an opposite direction by some smaller amount, probably between 0·25 and 0·40 Å. Symmetry requires an alternate up-and-down displacement of all the methyl groups around the molecule. It is also probable that the naphthalene nucleus itself is distorted, to a smaller extent but in a similar way, but this cannot be definitely established from the data.

INTERESTING stereochemical problems arise in the case of fully substituted naphthalene derivatives, and the synthesis of octamethylnaphthalene by Abadir, Cook, and Gibson (see preceding paper) has now made it possible to study the molecular geometry of this derivative by *X*-ray analysis. Hexamethylbenzene (Lonsdale, *Proc. Roy. Soc.*, 1929, *A*, **123**, 494; Brockway and Robertson, *J.*, 1939, 1324) and durene (Robertson, *Proc. Roy. Soc.*, 1933, *A*, **142**, 659) have already been fully studied by this method, and their carbon atoms are found to be strictly coplanar. In naphthalene, however, another situation arises from the overcrowding of substituents in adjacent α-positions. If there is no distortion, the distance between the centres of such groups would be only 2·4 Å, which is well below the limit expected for non-bonded carbon or atoms of similar size.

In the following analysis it is shown that the molecule of octamethylnaphthalene is far from being planar, and the nature of the distortions observed is described later. The unexpectedly high molecular symmetry displayed in the crystal (three mutually perpendicular two-fold axes but no centre or plane) simplifies the analysis and enables fairly definite conclusions to be reached.

Crystal Data.—Octamethylnaphthalene, $C_{18}H_{24}$; *M*, calc. 240·4, found 238·8; m. p. 174°; *d*, calc. 1·109, found 1·102. Orthorhombic, $a = 16{\cdot}66 \pm 0{\cdot}03$, $b = 11{\cdot}31 \pm 0{\cdot}01$, $c = 7{\cdot}64 \pm 0{\cdot}03$ Å. Absent spectra, (hkl) when $h + k$ is odd, $(0kl)$ when k is odd and when l is odd, $(h0l)$ when h is odd and when l is odd, $(hk0)$ when h is odd and when k is odd. Space group, D_{2h}^{22}–*Ccca*. Four molecules per unit cell. Molecular symmetry, 222 (three mutually perpendicular two-fold axes). Volume of the unit cell = 1440 Å^3. Absorption coefficient for *X*-rays ($\lambda = 1{\cdot}54$ Å) $\mu = 5{\cdot}44$ per cm. Total number of electrons per unit cell = F(000) = 528.

Crystals were generally obtained as clusters of very small needles, with occasional flat plates developed on (001). No other well-defined faces were observed.

Structure Analysis.—The crystal data show that the asymmetric unit must consist of one-quarter of the chemical molecule, or $4\frac{1}{2}$ carbon atoms. Four of these atoms must repeat in the 16 general positions defined by $(000;\ \frac{1}{2}\frac{1}{2}0) + xyz;\ \bar{x}\bar{y}z;\ \bar{x}, \frac{1}{2} - y, \frac{1}{2} - z;\ x, \frac{1}{2} + y, \frac{1}{2} - z;\ x\bar{y}\bar{z};\ \bar{x}y\bar{z};\ \bar{x}, \frac{1}{2} + y, \frac{1}{2} + z;\ x, \frac{1}{2} - y, \frac{1}{2} + z;$ while a fifth carbon atom must lie on one of the two-fold axes, with eight-fold multiplicity. The only chemically reasonable position for the intersection of the three mutually perpendicular two-fold axes, which is taken as the origin of co-ordinates, is the middle of the central bond of the naphthalene nucleus (see I). This point recurs with four-fold multiplicity at 000, $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$.

It is clear from (I, that the central bond of the naphthalene nucleus must coincide with one of the two-fold axes, and this molecular direction must therefore be parallel to one of the crystal axes, *a*, *b*, or *c*. Packing considerations eliminate the possibility of its being parallel to *c* (7·64 Å). The two remaining possibilities are easily tested by the calculation of a few orders of the axial structure factors (*h*00) and (0*k*0). The fact that the 200 reflection is very much stronger than the 020 immediately indicates that the molecule probably extends along the *b* direction, with the central bond parallel to *a*, and this conclusion can be verified by more detailed calculations. For these, the molecule may be assumed, in projection at least, to have the configuration indicated by (I) and normal dimensions ($C_{ar.}$–$C_{ar.}$ ~1·4 Å, $C_{ar.}$–$C_{al.}$ ~1·5 Å). When the (*h*00) structure factors were evaluated on this basis, good agreements were obtained for eight orders (to 16,000), and a one-dimensional Fourier synthesis showed the expected distribution of scattering matter. The second possibility, that the central bond is parallel to the *b*-crystal axis, was also tested, but this failed to provide any explanation of the observed intensities.

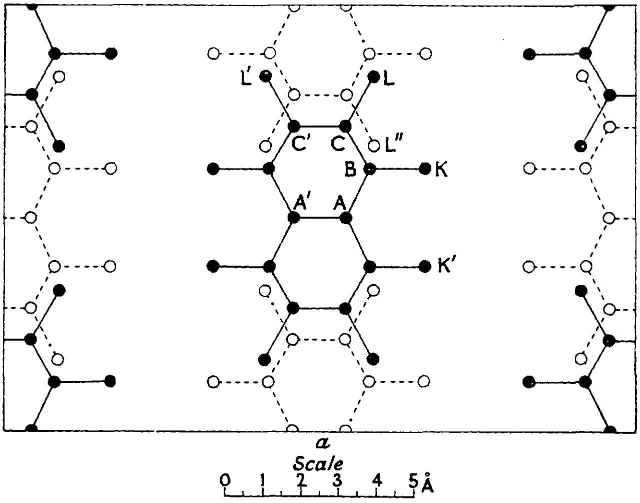
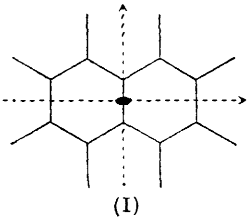


FIG. 1. *Octamethylnaphthalene. Molecular arrangement in projection on* (001).



(I)

The symmetry of the molecules and their orientation in the crystal are now known, but there remains the task of finding the precise position of each atom and hence the details of the molecular geometry. This was studied by trial-and-error methods, the results being refined by means of successive double Fourier syntheses, and difference syntheses, giving projections of the structure along the three axial directions.

The projection along the *c* axis on (001) provides the most detailed information, but even here many of the atoms are obscured by overlap from molecules lying at different levels in the unit cell. The arrangement required on account of the symmetry and the intensity considerations mentioned above is shown in Fig. 1, where the open circles and dotted bonds represent molecules situated half a translation along the *c* axis (perpendicular to the paper) with respect to the standard molecules in the corners and centre. The atoms marked *A*, *B*, *C*, *K*, and *L* may be chosen as the asymmetric unit, with origin at the centre of the molecule. The other atoms are derived from these by obvious symmetry operations. It may be noted that if the molecule is planar then all the carbon atoms of any one molecule must lie strictly in the (001) plane; if it deviates from the planar form, then the distortions must be of a regular type, conforming to the 222 molecular symmetry.

Any such distortion from a planar form will have very little effect on the (001) projection, and the simple model shown in Fig. 1, with normal bond lengths, was found to give a good account of all the (*hk*0) reflections. Evaluation of the corresponding double Fourier series consisting of 35 terms (see Table 3) gave the electron-density map shown in Fig. 2. The atoms *A* and *K* are clearly resolved, but *B*, *C*, and *L* coalesce with symmetry-related peaks to give unresolved doublets. The *x* and *y* co-ordinates of all the atoms can, however, be estimated with some accuracy from this projection, and the results are collected in Table 1.

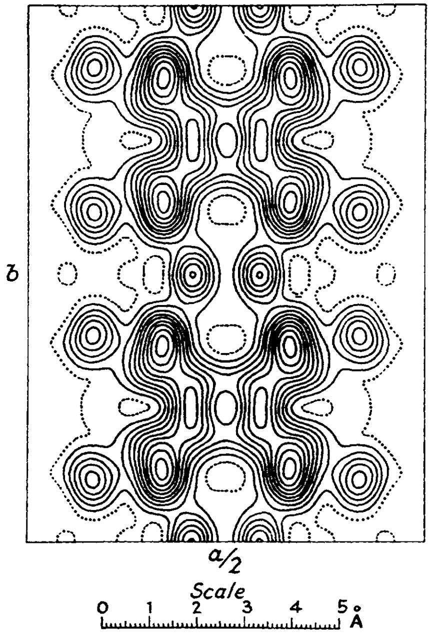


FIG. 2. *Electron-density projection of the octamethylnaphthalene structure on* (001). *Contour lines drawn at intervals of* 1e . Å^{-2}, *the one-electron line being dotted.*

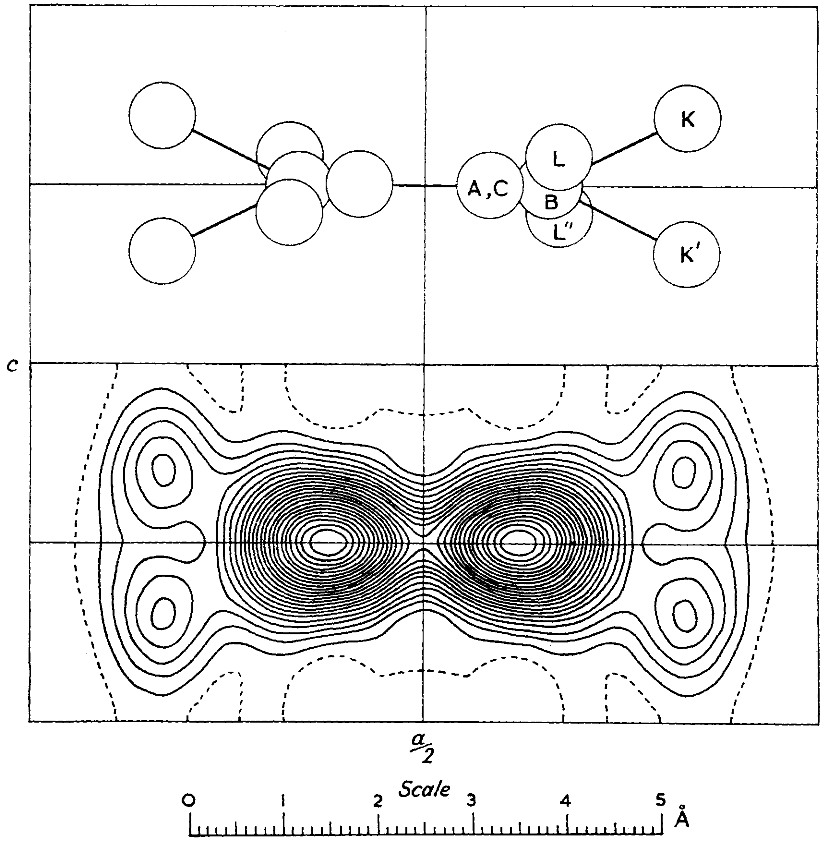
TABLE 1. *Co-ordinates. Origin at intersection of two-fold axes.*

Atom (cf. Fig. 1)	x/a	y/b	z/c	X (Å)	Y (Å)	Z (Å)
A	0·041	0	0	0·690	0	0
B	0·079	0·110	0·034	1·319	1·241	0·259
C	0·042	0·212	−0·012	0·708	2·400	−0·095
K	0·168	0·115	0·095	2·795	1·301	0·726
L	0·086	0·331	−0·034	1·430	3·745	−0·259

The projection of the structure along the *b* axis on (010) was next considered. A planar model would require the *z* co-ordinates of all the carbon atoms to be zero, but it was found that the intensities of the (*h*0*l*) reflections could not be explained on this basis. A consideration of the geometry of the molecule shows that in a planar model the methyl groups *K* and *K′* (Fig. 1) attached to the α-positions are over-crowded, the separations being about 2·4 Å, as against 2·9—3·0 Å in hexamethylbenzene and in durene (*locc. cit.*). The most likely distortion therefore consists of a displacement of the group *K* out of the molecular plane. A trial structure giving the group a displacement of about 0·7 Å from the mean molecular plane led to a reasonable measure of agreement between calculated and observed (*h*0*l*) reflections, and enabled a double Fourier synthesis to be effected. The resulting electron distribution is shown in Fig. 3. In this projection the α-methyl groups are quite clearly resolved and the displacement out of the mean plane is very distinct. No other atoms are resolved but the distribution found is hardly compatible with a strictly coplanar arrangement of these other atoms, and corresponds rather to the displaced arrangement shown in the explanatory diagram (upper part of Fig. 3).

Measurement of the projection (Fig. 3) shows that the α-methyl group is displaced by 0·73 Å out of the mean plane. If the z co-ordinates of all the other atoms are given zero values, the average discrepancy between calculated and observed values of the ($h0l$) structure factors is about 21%. If, however, the β-methyl group (atom L) is given an opposite displacement of about 0·38 Å, as shown in the upper part of Fig. 3, then the average discrepancy in the structure factor calculations falls to about 12%. This displacement may therefore be taken as definite, although its precise amount is uncertain.

FIG. 3. *Octamethylnaphthalene structure projected on* (010), *showing displacement of the α-methyl groups. Electron-density contour scale as in Fig. 2.*



Further calculation revealed another possibility, which led to equally good structure factor agreements and provided a more reasonable account of the bond lengths within the molecule, as calculated from the assigned co-ordinates. This was that the atoms in the naphthalene nucleus itself, as well as the methyl groups, may be displaced from a strictly coplanar arrangement. From the symmetry, atom A (Fig. 1) must remain in the (001) plane. If atom B is now moved out of the plane by about 0·2 Å, in the same sense as K, and atom C by about 0·1 Å, in the same sense as L, and the displacement of L reduced from 0·38 Å to about 0·26 Å, then equally good structure-factor agreements are obtained, and these co-ordinates give much more reasonable bond lengths (Table 2).

Although the displacement of the methyl groups out of the mean molecular plane is definite, the indicated distortion of the naphthalene nucleus cannot be regarded as fully established. It does not seem possible to obtain further evidence from the existing data, as the third projection, along the *a* axis, does not provide any useful information. A full three-dimensional analysis will be required to establish the positions of all the atoms to within narrower limits. In the meantime we have provisionally adopted the model with distorted nucleus in giving the tables of co-ordinates and dimensions above.

TABLE 2. *Interatomic distances* (*in* Å) (*see* Fig. 1).

A–A'	= 1·38	C–C'	= 1·43	K . . . K' (α-CH_3 . . . α-CH_3)	= 2·98
A–B	= 1·42	B–K	= 1·55	K . . . L (α-CH_3 . . . β-CH_3)	= 2·97
B–C	= 1·36	C–L	= 1·54	L . . . L' (β-CH_3 . . . β-CH_3)	= 2·91

Note. Intermolecular distances have not been evaluated in detail, as the z co-ordinates are uncertain. The distance between the mean planes of the molecules whose ends overlie each other (Fig. 1) is $\frac{1}{2}c$ = 3·82 Å.

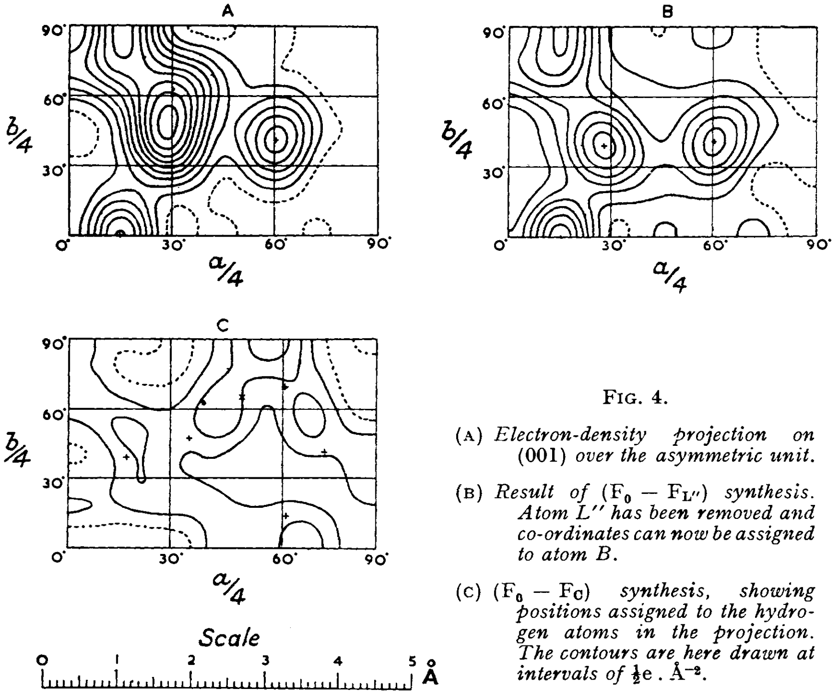


FIG. 4.

(A) *Electron-density projection on* (001) *over the asymmetric unit.*

(B) *Result of* ($F_0 - F_{L''}$) *synthesis. Atom L'' has been removed and co-ordinates can now be assigned to atom B.*

(C) ($F_0 - F_C$) *synthesis, showing positions assigned to the hydrogen atoms in the projection. The contours are here drawn at intervals of* $\frac{1}{2}$e . Å^{-2}.

Difference Syntheses and Hydrogen Effects.—In the course of refining the structure, two types of difference synthesis were employed. The first was used to check the relative values of the y co-ordinates of atoms B and K (Fig. 1), and so obtain information about a suspected mutual displacement of the α-methyl groups relative to the ring atoms, which might arise from steric effects. The position of atom B is obscured by overlap with the atom L''. The atom L'' will not be subject to the same steric effects, and it was therefore considered that the co-ordinates assigned to it were reasonably accurate. Its contribution to the structure factors can thus be calculated, and so it is possible to remove this atom from the electron-density projection by evaluating a double Fourier synthesis with the coefficients (F_0—$F_{L''}$), where F_0 is the observed value of the structure factor and $F_{L''}$ is the calculated contribution of the atom L'' to the structure factor.

The result of this synthesis, taken over the asymmetric unit, is shown in Fig. 4(B), while Fig. 4(A) shows for comparison the original synthesis over the same area. The atom B is now clearly resolved and its co-ordinates can be estimated with some accuracy. The y co-ordinate is found to differ from that originally assigned by 0·06 Å. As it had earlier been given the same y co-ordinate as atom K, there is now evidence that the methyl groups

K and K' are mutually displaced by about 0·06 Å, in the b direction. The correctness of the co-ordinates obtained from this synthesis, of course, depends upon the accuracy of the co-ordinates and scattering curve assigned to the atom L''. These are probably reliable, and it is noteworthy that the $(F_0—F_{L''})$ synthesis reproduces the positions of the previously resolved atoms A and K to within 0·01 Å.

A normal difference synthesis employing the coefficients $(F_0—F_C)$, where F_0 is the measured structure factor and F_C the value calculated from the combined carbon contributions, was also carried out for this zone. The object was to estimate the hydrogen contributions, which must be considerable in this compound, as 18% of the scattering matter consists of hydrogen electrons. The result of this synthesis is shown in Fig. 4(c), where some well-defined ridges at the 1—1·5 electron level in the neighbourhood of the methyl groups probably indicate the average hydrogen positions. For purposes of calculation, the six hydrogen atoms which must be associated with the asymmetric unit have been assigned mean positions which are indicated by the small crosses in Fig. 4(c). These are compatible with a tetrahedral distribution about the methyl groups, at distances of about 1·08 Å from the carbon centres. Apart from these features, the electron-density diagram obtained from the $(F_0—F_C)$ synthesis is comparatively flat, indicating that no large errors have been made in assigning the atomic co-ordinates.

The contributions of the hydrogen atoms to the structure factors were now calculated in a manner similar to that adopted in investigating the structure of hexamethylenediamine (Binnie and Robertson, *Acta Cryst.*, 1950, **3**, 424). The scattering curve used is of similar shape to that employed for carbon, but of one-sixth the height, and falls rapidly to zero at about $\sin\theta = 0{\cdot}6$. The effect of these additions to the structure factors of the $(hk0)$ zone is, however, considerable, the average discrepancy between calculated and observed values falling from 20% to 14·7% with the inclusion of the hydrogen contributions. The results of the structure-factor calculations are given in Table 3.

Discussion.—The most striking result of this analysis is the large extent to which the carbon atoms of octamethylnaphthalene deviate from a coplanar arrangement. The displacement of the methyl groups attached to the α-carbon atoms can be measured directly on one of the electron-density maps (Fig. 3), and amounts to about 0·73 Å. This corresponds to a deviation of about 28° of the $C–CH_3$ bond from the mean molecular plane. There is also evidence that these bonds are not quite parallel, when projected on the mean molecular plane, but show a slight outwards mutual displacement, amounting to about 0·06 Å for each methyl group. It is highly probable that the methyl groups attached to the β-positions also deviate from the planar arrangement, but the amount of the displacement in this case cannot be estimated with certainty. It probably lies between 0·25 and 0·40 Å.

There is an ambiguity concerning the sense of these displacements, which arises from the form of the structure-factor expressions, when the calculations are confined to the two-dimensional data employed in this investigation. However, a study of the model shows that the only feasible movements for the adjacent α- and β-methyl groups are in opposite sense, one above and one below the mean molecular plane. When this is decided for any two groups, say K and L (Fig. 1), then the crystal symmetry demands that all the eight methyl groups should likewise be displaced alternately above and below the mean plane. It is noteworthy that these displacements now give a clearance between adjoining methyl groups around the naphthalene nucleus which is almost exactly equal to that found in durene and in hexamethylbenzene (*locc. cit.*). The separations are given in Table 2.

The evidence concerning corresponding movements of the atoms in the naphthalene nucleus itself is very indirect. It can only be said that such displacements, of about 0·1—0·2 Å and in the same sense as the displacements of the methyl groups, are compatible with the X-ray evidence, but are not as yet conclusively proved by that evidence. It is known that in naphthalene itself the atoms are very rigidly coplanar (see, *e.g.*, Coulson, Daudel, and Robertson, *Proc. Roy. Soc.*, 1951, *A*, **207**, 306). However, when the bonds to the methyl groups are forced out of the naphthalene plane, the state of regular trigonal hybridization around each carbon atom will be destroyed. If an attempt is made to maintain a coplanar arrangement for the three bonds emanating from each ring-carbon atom, and at the same time to displace the methyl groups in the way that has been observed, then it is necessary to displace the ring-carbon atoms from the mutually coplanar arrangement in just the way that is suggested by the X-ray data. In this way the regular trigonal symmetry of the bonds about each ring atom can be retained, but the bonds between adjoining ring atoms become twisted. These relations become evident when one examines a rigid molecular model and tries to impose on it the required distortions.

TABLE 3. *Measured and calculated values of the structure factor.*

(Hydrogen contributions are included in the (*hk*0) zone for planes with 2 sin θ <1·20.)

hkl	2 sin θ (λ = 1·542)	F, meas.	F, calc.	*hkl*	2 sin θ (λ = 1·542)	F, meas.	F, calc.	*hkl*	2 sin θ (λ = 1·542)	F, meas.	F, calc.
200	0·185	170	162	14,6,0	1·530	<7	−2	804	1·094	17	−22
400	0·370	70	−67	16,6,0	1·690	<6	−5	10,0,4	1·226	<10	−6
600	0·555	43	−47	18,6,0	1·854	7	−4	12,0,4	1·371	10	−12
800	0·739	100	−109	280	1·106	12	−1	14,0,4	1·524	<8	−1
10,0,0	0·924	23	−24	480	1·150	<7	−2	16,0,4	1·684	<9	−7
12,0,0	1·109	22	−28	680	1·222	<7	13	18,0,4	1·848	<7	−9
14,0,0	1·294	14	−12	880	1·316	14	−11	206	1·224	24	33
16,0,0	1·479	11	−20	10,8,0	1·428	11	−8	406	1·265	14	13
18,0,0	1·664	<6	−7	12,8,0	1·554	<7	8	606	1·332	<10	−21
20,0,0	1·849	<5	−4	14,8,0	1·691	<6	−2	806	1·418	<10	−6
020	0·272	59	−57	16,8,0	1·837	<5	−1	10,0,6	1·522	<10	−5
040	0·545	82	−90	18,8,0	1·989	<1	1	12,0,6	1·641	<9	−14
060	0·817	21	20	2,10,0	1·374	9	14	14,0,6	1·772	<7	−2
080	1·089	23	26	4,10,0	1·411	<7	2	16,0,6	1·910	<5	−2
0,10,0	1·362	19	32	6,10,0	1·471	<7	2	208	1·624	<9	8
0,12,0	1·634	<7	−5	8,10,0	1·550	<7	−13	408	1·654	<9	6
0,14,0	1·906	<4	−4	10,10,0	1·646	<7	−11	608	1·705	<8	2
220	0·329	48	−43	12,10,0	1·756	<6	−1	808	1·774	<7	1
420	0·459	5	7	14,10,0	1·879	<4	−4	10,0,8	1·859	<6	−6
620	0·618	11	24	2,12,0	1·644	<7	2				
820	0·787	7	5	4,12,0	1·675	<6	−2	022	0·486	39	−41
10,2,0	0·963	<6	2	6,12,0	1·726	<6	−8	042	0·678	26	−25
12,2,0	1·142	<6	3	8,12,0	1·793	<5	3	062	0·911	9	19
14,2,0	1·322	<7	3	10,12,0	1·877	<5	6	082	1·161	17	11
16,2,0	1·504	<7	4	12,12,0	1·975	<2	1	0,10,2	1·420	19	22
18,2,0	1·686	<6	3					0,12,2	1·683	<10	−2
20,2,0	1·869	<5	−2	002	0·403	291	266	0,14,2	1·948	<5	−1
240	0·576	30	35	004	0·806	76	73	024	0·851	14	−22
440	0·659	69	76	006	1·210	20	18	044	0·973	25	23
640	0·778	34	23	008	1·613	<9	9	064	1·148	<11	18
840	0·918	26	23	202	0·444	156	137	084	1·355	<12	−5
10,4,0	1·073	22	−25	402	0·547	11	−18	0,10,4	1·583	12	8
12,4,0	1·236	50	−56	602	0·686	65	−66	0,12,4	1·822	<9	2
14,4,0	1·404	14	−15	802	0·842	61	−65	026	1·240	<11	−8
16,4,0	1·576	<7	2	10,0,2	1·008	16	−16	046	1·327	16	21
18,4,0	1·751	<6	2	12,0,2	1·180	<9	11	066	1·460	<12	10
20,4,0	1·928	7	7	14,0,2	1·355	<10	−7	086	1·628	<11	−4
260	0·838	19	21	16,0,2	1·532	<10	−15	0,10,6	1·822	<9	3
460	0·897	5	−6	18,0,2	1·711	<8	−9	028	1·636	<11	−1
660	0·988	16	−18	20,0,2	1·891	<6	−2	048	1·703	<10	7
860	1·102	<6	2	204	0·827	78	80	068	1·808	<9	1
10,6,0	1·233	13	6	404	0·887	16	13	088	1·946	<5	1
12,6,0	1·377	14	−3	604	0·979	42	−53				

Some interesting stereochemical possibilities are suggested by these results, which we hope to examine in other simple naphthalene derivatives and related compounds.

EXPERIMENTAL

Copper-K_α radiation, λ = 1·542 Å, was employed in all the measurements. Rotation, oscillation, and moving-film photographs were taken from crystals rotated about all the principal zone axes, and these were analysed in the usual way to determine the cell dimensions and systematic halvings, from which the space-group could be determined uniquely.

The density was accurately determined, in order to check the molecular weight of the compound, by flotation in sodium chloride solution, with evacuation and use of detergent to ensure freedom from trapped air. With four crystals (all very small) the values obtained were 1·098, 1·109, 1·108, 1·092, mean 1·102. Four molecules being assumed in the unit cell, the corresponding molecular weights are 238·0, 240·4, 240·2, 236·7, mean 238·8 [Calc. for $C_{18}H_{24}$: 240·4. Calc. for $C_{17}H_{22}$ (heptamethylnaphthalene), 226·3].

For the intensity measurements, small crystals were employed, with cross-sections normal to the rotation axes of 0·12 × 0·35 mm. for the (*hk*0) zone, and 0·42 × 0·46 mm. for the (*h*0*l*) zone. The crystals were completely bathed in a uniform *X*-ray beam. The absorption coefficient is low (μ = 5·44 per cm.) and no corrections were applied. The multiple-film technique (Robertson, *J. Sci. Instr.*, 1943, **20**, 175) with visual estimation was employed, the total range of intensities covered being about 7500 to 1.

The usual formulæ for mosaic-type crystals being used, the structure factors were evaluated and are listed in Table 3 under " F, meas.". The absolute scale was obtained at a later stage by correlation with the final calculated values. In deriving the calculated values from the co-ordinates in Table 1, the empirical atomic scattering curve derived from the naphthalene analysis (Abrahams, Robertson, and White, *Acta Cryst.*, 1949, **2**, 233) was used. The discrepancies between the calculated and observed structure factors, expressed as a percentage of the total measured structure factors, amounts 14·2% for all planes from which reflections were recorded.

The Fourier syntheses were calculated by the usual formulæ, and by means of the three-figure strip and stencil method (Robertson, *J. Sci. Instr.*, 1948, **25**, 28). The asymmetric unit is of small area, and the axial sub-divisions employed for the calculations were $a/120$ = 0·139 Å, $b/60$ = 0·189 Å, $c/60$ = 0·127 Å.

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[*Received, August* 20*th*. 1952.]