Table 3 (*cont.*)

hkl	$F_{\text{meas.}}$	$F_{\text{calc.}}$	*hkl*	$F_{\text{meas.}}$	$F_{\text{calc.}}$	*hkl*	$F_{\text{meas.}}$	$F_{\text{calc.}}$	*hkl*	$F_{\text{meas.}}$	$F_{\text{calc.}}$
$25\bar{2}$	6·6	− 5·4	$55\bar{6}$	4·8	− 4·2	$16\bar{1}$	0·9	− 0·7	$56\bar{4}$	< 0·8	− 0·5
$25\bar{3}$	6·0	− 5·6	$55\bar{7}$	< 1·0	+ 0·3	$16\bar{2}$	1·7	− 1·0	$56\bar{5}$	< 0·8	+ 0·3
$25\bar{4}$	2·7	+ 2·1	$55\bar{8}$	1·1	+ 0·4	$16\bar{3}$	< 0·9	− 0·3	$56\bar{6}$	< 0·8	+ 0·8
$25\bar{5}$	3·6	+ 3·3	651	0·8	− 0·5	$16\bar{4}$	2·7	+ 0·2	$66\bar{1}$	< 0·4	+ 0·1
$25\bar{6}$	1·1	+ 1·0	$65\bar{1}$	0·8	+ 0·5	$16\bar{5}$	0·9	− 1·5	$66\bar{2}$	0·4	+ 0·4
$25\bar{7}$	0·7*	+ 0·8	$65\bar{2}$	3·4	+ 3·4	$16\bar{6}$	< 0·9	− 0·9	$66\bar{3}$	0·4	+ 0·4
$25\bar{8}$	< 0·7	+ 0·6	$65\bar{3}$	2·2	+ 2·5	264	1·1	+ 0·1	$66\bar{4}$	< 0·4	+ 0·4
355	< 0·8	+ 0·5	$65\bar{4}$	0·7*	− 0·2	263	< 0·8	+ 0·1	$66\bar{5}$	2·0	− 1·4
354	< 0·9	+ 0·1	$65\bar{5}$	1·7	+ 1·3	262	4·8	− 3·6	$66\bar{6}$	2·6	− 2·2
353	< 0·8	+ 0·1	$65\bar{6}$	1·3	+ 1·8	261	7·4	− 5·7	071	0·7	− 0·7
352	0·8	− 0·5	$65\bar{7}$	0·5	+ 0·7	$26\bar{1}$	< 1·0	+ 1·0	072	< 0·5	+ 0·3
351	2·7	− 3·1	$65\bar{8}$	< 0·5	− 0·7	$26\bar{2}$	3·5	− 3·4	073	< 0·5	+ 0·4
$35\bar{1}$	1·6	+ 1·4	$75\bar{1}$	< 0·8	− 0·3	$26\bar{3}$	0·7	− 0·9	074	< 0·5	− 0·6
$35\bar{2}$	7·9	− 6·3	$75\bar{2}$	< 0·8	− 0·6	$26\bar{4}$	< 1·2	+ 1·5	170	< 0·6	+ 0·6
$35\bar{3}$	4·3	− 3·2	$75\bar{3}$	< 0·9	− 0·1	$26\bar{5}$	< 1·0	+ 0·2	270	0·7*	+ 0·1
$35\bar{4}$	1·0	+ 0·9	$75\bar{4}$	< 0·9	+ 0·3	$26\bar{6}$	< 0·8	+ 0·4	370	0·6	− 0·7
$35\bar{5}$	5·5	− 4·3	$75\bar{5}$	< 1·0	− 0·5	363	< 0·8	− 0·4	173	< 0·8	+ 0·6
$35\bar{6}$	4·1	− 3·3	$75\bar{6}$	2·5	− 2·2	362	1·8	+ 0·9	172	< 1·0	− 0·1
$35\bar{7}$	< 1·0	+ 0·6	$75\bar{7}$	< 0·8	− 0·5	361	2·5	+ 1·9	171	1·8	− 1·4
$35\bar{8}$	< 0·9	− 0·4	$85\bar{3}$	< 0·7	+ 1·5	$36\bar{1}$	< 0·8	+ 0·1	$17\bar{1}$	1·8	+ 0·4
454	0·4	+ 0·7	$85\bar{4}$	< 0·7	+ 0·1	$36\bar{2}$	1·3	+ 1·1	$17\bar{2}$	< 1·0	− 1·0
453	< 0·6	− 0·5	$85\bar{5}$	< 0·9	− 0·9	$36\bar{3}$	< 0·9	− 0·5	$17\bar{3}$	< 0·8	− 0·4
452	1·8	− 1·8	$85\bar{6}$	< 0·7	− 0·4	$36\bar{4}$	0·9	+ 0·4	$17\bar{4}$	< 0·8	+ 0·1
451	3·6	− 3·3	061	3·6	− 4·0	$36\bar{5}$	0·8	− 0·6	272	2·3	+ 2·0
$45\bar{1}$	0·9	+ 1·5	062	7·5	− 6·7	$36\bar{6}$	< 0·7	− 0·4	271	2·1	+ 2·2
$45\bar{2}$	0·8	+ 1·0	063	1·4	− 0·6	$36\bar{7}$	< 0·7	+ 0·1	$27\bar{1}$	1·9	+ 1·0
$45\bar{3}$	2·8	− 3·2	064	< 2·0	+ 1·4	462	0·7	+ 0·1	$27\bar{2}$	3·2	+ 2·0
$45\bar{4}$	1·1	+ 0·5	065	< 2·0	+ 0·5	461	< 0·8	− 1·0	$27\bar{3}$	1·3	+ 1·2
$45\bar{5}$	5·9	+ 3·6	066	< 1·5	+ 0·3	$46\bar{1}$	1·0	+ 1·4	$27\bar{4}$	< 0·8	− 0·8
$45\bar{6}$	2·5	+ 2·0	160	< 1·0	− 0·1	$46\bar{2}$	0·9	+ 0·6	371	2·2	− 1·0
$45\bar{7}$	< 0·6	+ 0·6	260	1·1**	+ 0·2	$46\bar{3}$	< 0·9	− 0·2	$37\bar{1}$	0·7	+ 1·1
$45\bar{8}$	0·4*	+ 0·3	360	< 0·9	− 0·9	$46\bar{4}$	< 0·9	+ 0·7	$37\bar{2}$	< 0·7	+ 0·2
552	0·4	+ 0·5	460	< 0·9	− 0·7	$46\bar{5}$	2·5	− 1·7	$37\bar{3}$	< 0·7	− 0·5
551	1·0	+ 0·6	560	< 0·9	+ 0·1	$46\bar{6}$	1·7	− 1·6	$37\bar{4}$	< 0·7	− 0·3
$55\bar{1}$	1·0	− 0·3	165	< 0·9	+ 1·2	$46\bar{7}$	< 0·8	+ 0·4	$47\bar{1}$	< 0·8	− 0·3
$55\bar{2}$	2·6	− 2·1	164	< 0·9	+ 0·4	561	0·7	+ 0·6	$47\bar{2}$	< 0·8	+ 0·1
$55\bar{3}$	1·8	− 1·9	163	< 1·0	− 0·8	$56\bar{1}$	< 0·8	− 0·2	$47\bar{3}$	1·3	+ 1·3
$55\bar{4}$	0·7	+ 1·0	162	2·4	+ 1·7	$56\bar{2}$	2·4	+ 1·9	$47\bar{4}$	< 0·7	− 0·4
$55\bar{5}$	3·2	− 2·4	161	2·7	+ 1·9	$56\bar{3}$	2·1	+ 0·7			

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The Crystal and Molecular Structure of Naphthalene. II. Structure Investigation by the Triple Fourier Series Method

By S. C. Abrahams, J. Monteath Robertson and (in part) J. G. White
The University, Glasgow W. 2, Scotland

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A triple Fourier series investigation of the naphthalene structure is described, based on the 612 structure factors listed in Part I. The series for the electron density has been evaluated at 54,000 points over the asymmetric crystal unit (half the chemical molecule), and the results are expressed by giving a number of sections through separate atoms at different levels, and also by giving a section through the plane of the molecule. From this map the bond lengths can be determined by direct measurement and are found to vary from 1·36 A. in the $\alpha\beta$ bond to 1·42 A. in the $o\alpha$ bond. The $\beta\beta$ bond and the central bond, oo, are both measured at 1·395 A. These figures are probably correct to within about 0·01 A., and appear to be in reasonably good agreement with the latest theoretical calculations. The rings are also found to be coplanar to within 0·01 A. The bridge value of the electron density varies in the different bonds; the electron distribution and the effect of the hydrogen atoms are briefly discussed.

1. Introduction

In Part I we have described the measurement and listed the values of all the structure factors of naphthalene that lie within the range of copper radiation. The signs, or phase constants, of 612 of these factors can be determined from the previous approximate structure

(Robertson, 1933*b*), and in the present paper we describe a new determination of the structure by the triple Fourier series method which employs these values as coefficients.

As noted in Part I, a recalculation of the structure factors from the final co-ordinates now obtained indicates a change of sign for six of the coefficients included in the present synthesis. The maximum effect of this error on the electron-density maps given below cannot anywhere exceed a value of about 0·05 e.A.$^{-3}$, and in the present analysis of the results no attempt has been made to apply corrections for this error.

The triple Fourier series has been evaluated at 54,000 points distributed over the asymmetric crystal unit (one-quarter of the unit cell, covering half a chemical molecule). It is difficult to present concisely all the structural information contained in this three-dimensional analysis. A number of sections through the various atoms are shown below, and in addition a very detailed picture can be obtained by evaluating a section through the central plane of the molecule. This is shown in Fig. 3 and from this diagram the bond lengths can be measured directly. Small but definite variations in these bond lengths are found in different parts of the molecule (Fig. 5) and the bridge values of the electron density in the different bonds are also found to vary. These results are described more fully in the following sections.

2. Fourier synthesis

Numerical evaluation

For the evaluation of the electron density each crystal axis was subdivided into 60 parts, giving intervals of 0·137 A. along *a*, 0·100 A. along *b*, and 0·144 A. along *c*. The quarter unit cell was then covered by extending the summation from 0 to 30/60ths along *a*, 0 to 30/60ths along *b*, and 0 to 60/60ths along *c*.

The general expression for the electron density is

$$\rho(xyz)=\frac{1}{V}\sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty}F(hkl)\cos 2\pi(hx+ky+lz),$$

where V is the volume of the unit cell and x, y, z the co-ordinates expressed as fractions of the axial lengths (60ths in the present case). This series contains 612 terms and requires to be evaluated at 54,000 points. If no shortening devices are used, the number of separate terms which must be evaluated and added is thus over 33,000,000. The formidable numerical work involved was carried out by the Scientific Computing Service Ltd., of 23 Bedford Square, London, on Hollerith machines, and we are indebted to Dr L. J. Comrie and Miss E. Gittus for the careful planning and supervision which they have given to this work.

For the Hollerith scheme the general expression was reduced to the forms

$$\rho(xyz)=\frac{4}{V}\sum_{0}^{\infty}\sum_{0}^{\infty}\sum_{0}^{\infty}$$

$$\left.\begin{aligned}&\times\{[F(hkl)+F(hk\bar{l})]\cos 2\pi hx\cos 2\pi ky\cos 2\pi lz\\&+[F(hk\bar{l})-F(hkl)]\sin 2\pi hx\cos 2\pi ky\sin 2\pi lz\end{aligned}\right]\begin{matrix}h+k\\ \text{even,}\end{matrix}$$

$$\left.\begin{aligned}&-[F(hkl)+F(hk\bar{l})]\sin 2\pi hx\sin 2\pi ky\cos 2\pi lz\\&+[F(hk\bar{l})-F(hkl)]\cos 2\pi hx\sin 2\pi ky\sin 2\pi\bar{l}z\}\end{aligned}\right]\begin{matrix}h+k\\ \text{odd.}\end{matrix}$$

The structure factors $F(hkl)$ and $F(hk\bar{l})$, which are in general unequal, may thus be combined, with due regard to the multiplicity of the term. Thus, $F(hkl)$ occurs eight times in the different quadrants of the reciprocal lattice, $F(0kl)$ four times, $F(00l)$ twice, and $F(000)$ only once.

Before the summations commenced the F values were multiplied by the factor $1000/V=2{\cdot}765$, so that the final totals gave the densities as electrons per A.$^3\times 1000$ directly. The first summations were taken over the x co-ordinates, the second over the y co-ordinates, and the final summations over the z co-ordinates. Three-figure methods were used throughout the numerical work, with rounding-off deferred to the last stage, the final totals being tabulated to three significant figures.

Graphical representation

A survey of the summation totals showed that the general background of electron density in the regions between the molecules was very uniform, varying between zero and 0·3 e.A.$^{-3}$, with occasional negative regions which never exceeded $-0{\cdot}3$ e.A.$^{-3}$

As the molecular plane is known to be inclined at a fairly small angle (about 30°) to the *bc* plane, the electron density was first plotted graphically along lines parallel to the *a* axis, in order to give as many intersections with the molecular plane as possible. About 750 graphs of this kind were prepared, passing through and near to the atoms in the asymmetric crystal unit, the horizontal scale being 10 cm. to 1 A. and the vertical scale 1 cm. for a density of 0·5 e.A.$^{-3}$.

On the horizontal scales of these graphs the positions of the contour levels, at intervals of 0·5 e.A.$^{-3}$, could be marked accurately. Four sections parallel to (010) and four sections parallel to (001), passing near the atomic centre, were then constructed for each of the five atoms of the asymmetric crystal unit. One pair of sections passing close to the centre of each of the five atoms is reproduced in Fig. 1, and from these diagrams the co-ordinates of the atoms can be obtained with considerable accuracy. The lettering of the atoms and their relation to the crystallographic axes are indicated in Fig. 2.

The measurements on the sections and the averaged co-ordinates are collected in Table 1. It will be seen from this table, and also from an inspection of the sections which are reproduced in Fig. 1, that although

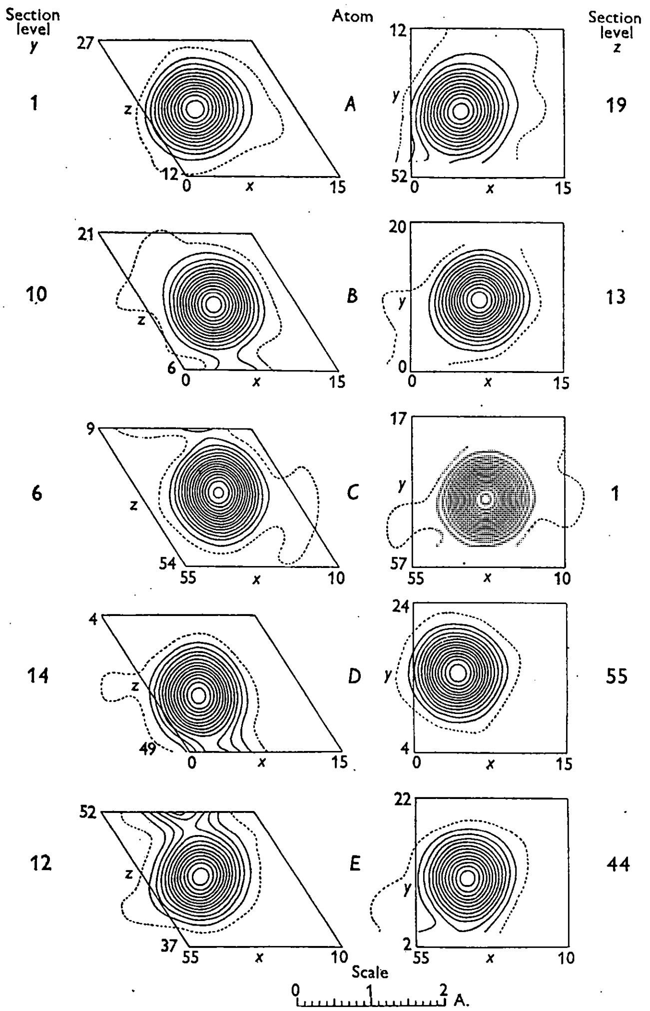


Fig. 1. Crystal sections parallel to (010) and (001) drawn near the centre of each of the five carbon atoms in the naphthalene asymmetric unit. Each contour line represents a density increment of $\frac{1}{2}$ e.A.$^{-3}$, the half-electron line being dotted. Co-ordinates are given in 60ths.

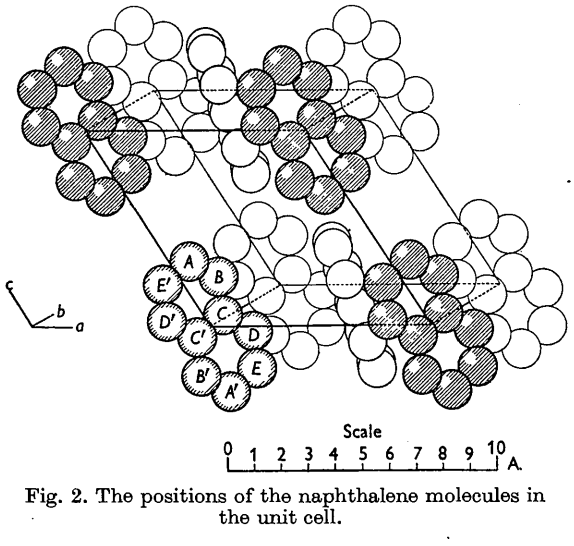


Fig. 2. The positions of the naphthalene molecules in the unit cell.

the co-ordinates can be determined with a high degree of precision yet the electron distributions are not truly spherical. This is partly due to the relatively high bridge values of the density between adjacent carbon atoms in the aromatic rings, and partly to other causes which are still somewhat obscure. Various experimental errors must apply to a different degree in different parts of the diagrams, but in addition there will be the effect of thermal movement of the atoms and of the molecule as a whole. It has not yet been possible to analyse these effects in any detail.

As a result of the non-spherical distribution it will be noted that for some of the co-ordinates there is a progressive drift in value as the sections move away from the centre of the atom. It seems likely that if only a few arbitrarily evaluated sections are available in three-dimensional work of this kind, these estimated co-ordinates may be considerably in error. A good two-dimensional analysis might in fact be preferable.

Section through the molecular plane

From the averaged co-ordinates in Table 1 it is found that the carbon atoms lie very closely on a plane whose equation is

$$x' - 0{\cdot}527y + 0{\cdot}369z' = 0,$$

where x', y and z' are the co-ordinates referred to the orthogonal axes a, b and c', c' being taken perpendicular to a and b, and

$$x' = x + z\cos\beta, \quad z' = z\sin\beta.$$

The distances of the atoms from the plane defined above are

$$A,\ +0{\cdot}007\text{ A.},\quad B,\ -0{\cdot}011\text{ A.},$$
$$C,\ -0{\cdot}001\text{ A.},\quad D,\ -0{\cdot}006\text{ A.},$$
$$E,\ +0{\cdot}004\text{ A.}$$

It is unlikely that any real significance can be attached to these small deviations of the atoms from a truly coplanar structure.

In view of these results it was decided to evaluate the electron density over the mean plane of the molecule, as defined by the above equation. As this plane does not coincide with any simple crystallographic position it was necessary to evaluate the electron density at an array of points in the plane by interpolation from the existing summation totals, which had been prepared at intervals of 60ths along each axial direction. For this purpose the existing 750 graphs of the electron density along lines parallel to the a axis were used. The points of intersection of these lines with the molecular plane were easily found from the above equation, and the electron densities at these points were read off from the graphs. In this way an array of electron densities in the molecular plane was tabulated.

From this array of densities a contour map showing the electron distribution in the plane of the molecule was prepared in the usual manner, by making graphs

Table 1. *Co-ordinates estimated from crystal sections*

Monoclinic crystal axes, centre of symmetry as origin. *x* and *z* are obtained from sections parallel to (010) and *y* from sections parallel to (001), at levels along the *b* and *c* axes as indicated.

Atom	Level of sections					Average		
	b/60	*c*/60	*x* (A.)	*y* (A.)	*z* (A.)	*x* (A.)	*y* (A.)	*z* (A.)
A	0	18	0·710	0·090	2·815	0·716	0·092	2·816
	1	19	0·713	0·094	2·812			
	2	20	0·718	0·093	2·819			
	3	21	0·722	0·091	2·816			
B	8	12	0·934	0·963	1·893	0·934	0·960	1·892
	9	13	0·934	0·961	1·893			
	10	14	0·934	0·961	1·893			
	11	15	0·934	0·956	1·889			
C	5	0	0·385	0·611	0·298	0·390	0·611	0·297
	6	1	0·391	0·610	0·294			
	7	2	0·395	0·612	0·298			
	8	3	0·399*	0·611	0·298			
D	13	54	0·612	1·476	−0·692	0·614	1·483	−0·685
	14	55	0·615	1·479	−0·681			
	15	56	0·609	1·487	−0·686			
	16	57	0·619	1·491	−0·680			
E	10	43	0·081	1·114	−2·201	0·083	1·121	−2·195
	11	44	0·081	1·119	−2·193			
	12	45	0·083	1·123	−2·194			
	13	46	0·087	1·128	−2·191			

* Omitted from average; section elliptical.

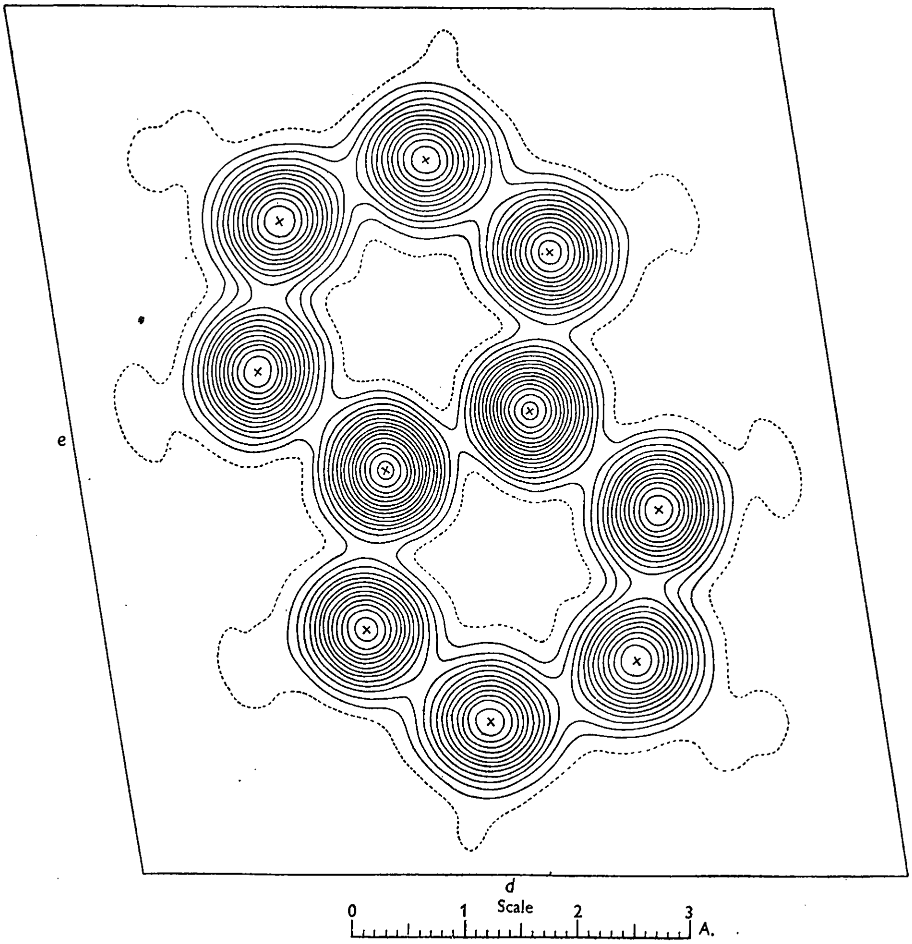


Fig. 3. A crystal section through the plane of the naphthalene molecule. Each contour line represents a density increment of ½ e.A.$^{-3}$, the half-electron line being dotted.

of the rows and columns and interpolating the positions of the contour levels. The result is shown in Fig. 3 as a crystal section through the plane of the molecule. All the carbon atoms are perfectly resolved and it is possible to mark their centres with a high degree of precision. The bond lengths can, of course, be measured directly from the diagram. On the half-electron contour level (dotted line) there is distinct evidence of the presence of the hydrogen atoms, but the outlines are vague and certainly subject to large errors.

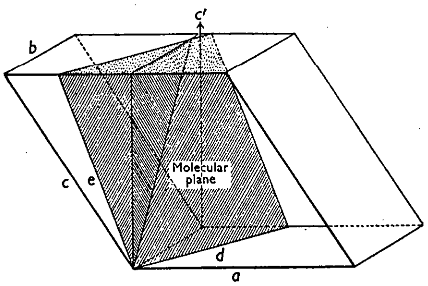


Fig. 4. Relation of the molecular plane boundary lines to the crystal axes and unit cell.

The boundary lines in Fig. 3 are: d, the intersection of the molecular plane with the plane $z'=0$; and e, the intersection of the molecular plane with the plane $y=0$. Substituting in the equation of the molecular plane we have

$$x'=0{\cdot}527y,$$

from which the angle between the b crystal axis and d is

$$\tan^{-1} 0{\cdot}527=27{\cdot}8^\circ.$$

Similarly the angle between c' and e is

$$\tan^{-1}(-0{\cdot}369)=-20{\cdot}25^\circ.$$

The lengths of the lines d and e are

$d=b/\cos 27{\cdot}8^\circ=6{\cdot}792$ A. (interval, $d/60=0{\cdot}113$ A.),

$e=c'/\cos 20{\cdot}25^\circ=7{\cdot}761$ A. (interval, $e/60=0{\cdot}129$ A.).

Table 3. *Co-ordinates referred to crystal axes*

(Origin at centre of symmetry.)

Atom	x (A.)	x' (A.)	$2\pi x/a$	y (A.)	$2\pi y/b$	z (A.)	z' (A.)	$2\pi z/c$
A	0·716	−0·814	31·3°	0·092	5·5°	2·816	2·363	117·0°
B	0·934	−0·094	40 8	0·960	57·6	1·892	1·589	78·7
C	0·390	0·229	17·1	0·611	36·6	0·297	0·249	12·4
D	0·614	0·986	26·8	1·483	88·9	−0·685	−0·575	−28·5
E	0·083	1·275	3·6	1·121	67·2	−2·195	−1·842	−91·3

From these relations the angle θ between d and e is given by

$$\cos\theta=-\sin 27{\cdot}8^\circ \sin 20{\cdot}25^\circ,$$
$$\theta=99{\cdot}3^\circ.$$

The relation of the molecular plane boundary lines d and e to the crystal axes and the unit cell will be clear from Fig. 4.

3. Molecular dimensions, co-ordinates and orientation

The dimensions of the molecule obtained by direct measurement from the crystal section given in Fig. 3 are shown in Fig. 5 and Table 2. These dimensions correspond with great precision to the dimensions deduced independently from the averaged co-ordinates obtained from the crystal sections collected in Table 1, the maximum deviation being 0·005 A. in bond length and 0·4° in valency angle.

The co-ordinates referred to the monoclinic crystal axes and to the orthogonal axes are collected in Table 3, expressed in Ångström units and in angular measure.

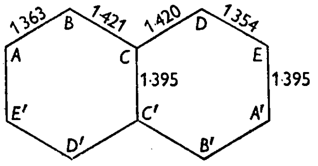


Fig. 5. Dimensions of naphthalene molecule.

The orientation of the molecule in the crystal is expressed by the angles χ_L, ψ_L, ω_L; χ_M, ψ_M, ω_M; and χ_N, ψ_N, ω_N, which the molecular axes L, M and N make with the crystal axes a, b and c'. The molecular axis N is taken normal to the plane of the molecule ($x'-0{\cdot}527y+0{\cdot}369z'=0$). L lies in this plane and passes through the point midway between the atoms A and E', while M is perpendicular to N and L. All the molecular axes pass through the origin. These values are collected in Table 4. The comparison with the values obtained earlier (Robertson, 1933*b*) is of interest in showing an extremely close agreement, and indicates that the two-dimensional Fourier series method is thoroughly reliable in determining the orientation of

Table 2. *Dimensions of molecule*

$AB=1{\cdot}363$ A.	$BAE'=121^\circ\ 5'$
$BC=1{\cdot}421$ A.	$ABC=119^\circ\ 35'$
$CC'=1{\cdot}395$ A.	$BCC'=118^\circ\ 55'$
$CD=1{\cdot}420$ A.	$C'CD=120^\circ\ 10'$
$DE=1{\cdot}354$ A.	$CDE=119^\circ\ 30'$
$EA'=1{\cdot}395$ A.	$DEA'=120^\circ\ 50'$

Table 4. *Orientation*

		1933 values
$\cos\chi_L=-0{\cdot}4350$	$\chi_L=115{\cdot}8^\circ$	$\chi_L=115{\cdot}3^\circ$
$\cos\psi_L=-0{\cdot}2128$	$\psi_L=102{\cdot}6$	$\psi_L=102{\cdot}6$
$\cos\omega_L=0{\cdot}8750$	$\omega_L=29{\cdot}0$	$\omega_L=28{\cdot}7$
$\cos\chi_M=0{\cdot}3217$	$\chi_M=71{\cdot}2$	$\chi_M=71{\cdot}2$
$\cos\psi_M=0{\cdot}8709$	$\psi_M=29{\cdot}45$	$\psi_M=28{\cdot}8$
$\cos\omega_M=0{\cdot}3718$	$\omega_M=68{\cdot}2$	$\omega_M=69{\cdot}1$
$\cos\chi_N=0{\cdot}8410$	$\chi_N=32{\cdot}8$	$\chi_N=32{\cdot}4$
$\cos\psi_N=-0{\cdot}4428$	$\psi_N=116{\cdot}3$	$\psi_N=115{\cdot}05$
$\cos\omega_N=0{\cdot}3102$	$\omega_N=71{\cdot}9$	$\omega_N=71{\cdot}2$

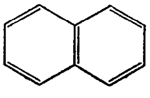
planar molecules in crystals on the basis of averaged dimensions, even although, as in the case of the earlier naphthalene work, all the atoms may not be separately resolved.

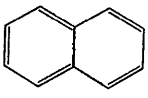
4. Discussion

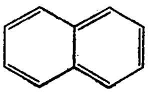
Theoretical aspects

The theoretical applications of the work described in this paper are of considerable interest in view of the large amount of work which has already been expended in deriving the bond lengths of the naphthalene molecule from calculations based on wave-mechanical treatments (Sherman, 1934; Pauling, Brockway & Beach, 1935; Penney, 1937; Lennard-Jones & Coulson, 1939; Coulson, 1939; Coulson, 1941; Daudel & Daudel, 1948; Gold, 1949). It is not intended to discuss these applications fully in the present paper. We are at present engaged on a similar determination of the bond lengths in the anthracene molecule, and it will be better to discuss the theoretical treatments of these two molecules together in a later contribution. It may be noted here, however, that the latest determinations of the bond orders in naphthalene, mentioned above, lead to estimations of the individual bond lengths which are in very promising agreement with our present measurements.

It is also clear that our results can be correlated with the outstanding chemical properties of naphthalene. The chemically reactive $\alpha\beta$ bond (AB or DE in Fig. 5) is not only much the shortest bond but also possesses a relatively high bridge value for the electron density. To a first rough approximation these results are compatible with the three non-excited (Kekulé) structures if it is assumed that each of these structures makes a contribution to the normal state of the molecule.







Accuracy

With regard to the accuracy of the present bond-length measurements, the internal consistency of the results and the methods of computation and interpolation employed lead to the assignment of atomic centres which are reproducible to within 0·005 A. The Fourier series used is very extensive and the limiting coefficients are small. The small number of terms omitted and the few included with signs which are probably incorrect or doubtful are almost negligible in comparison with the others. It can be shown also that the experimental errors in the F values (not greater than about 10%) will have very little effect on the positions of the atomic centres. Taking all these factors into account it is estimated that the bond-length errors should not exceed 0·01 A.

In the naphthalene molecule the bonds AB and DE (Fig. 5) are chemically the same but crystallographically independent. The measurements here (1·363 and 1·354 A.) differ by just less than 0·01 A. For chemical reasons it would seem most likely that this difference is due to error, just as the deviations from a strictly coplanar structure, also about 0·01 A., may be due to error. On the other hand, it might be argued that structural distortions of about this order of magnitude could arise from the manner in which the molecules are packed together to form the crystal lattice, even although such distortions may not be present in free molecules, e.g. in the vapour phase. There is some evidence to support this view, derived from the analysis of other structures, but no very definite conclusions can yet be drawn.

Electron distribution

The bridge values of the electron density in the various bonds are of interest, and these values do not seem to be entirely a function of interatomic distance. In the two bonds mentioned above, AB and DE, the shorter one, DE, has a bridge value higher by about 0·5 e.A.$^{-3}$ ($>2{\cdot}0$ instead of $>1{\cdot}5$ e.A.$^{-3}$). The longer bonds BC and CD have a lower and very constant bridge value of between 1·0 and 1·5 e.A.$^{-3}$. The end bond AE, however, although measured at 1·395 A., has a relatively high bridge value of over 1·5 e.A.$^{-3}$. The central bond, CC', also measured at 1·395 A., has a distinctly lower bridge value of just over 1·0 e.A.$^{-3}$.

It seems likely that these bridge values of the electron density may have some chemical significance, but they are complicated by another factor. The peak value of the electron density on the different atoms is found to vary, diminishing progressively as we pass outwards from the centre of the molecule. On atom C the peak value of the electron density is 8 e.A.$^{-3}$, on B and D it is just over 7 e.A.$^{-3}$, and on E and A it is just over 6·5 e.A.$^{-3}$.

This phenomenon is now a fairly common one, and it was first observed in the early two-dimensional work on anthracene (Robertson, 1933*a*), although not to any appreciable extent in the corresponding two-dimensional work on naphthalene (Robertson, 1933*b*). Another very distinct example of the same effect is seen in the three-dimensional analysis of geranylamine hydrochloride (Jeffrey, 1945), where the peak values of the densities decrease steadily on passing outwards from the ionic attachments towards the tail of the molecule. These effects would seem to be connected with some thermal vibration of the molecules as a whole. The effect in naphthalene could to some extent be explained if we imagine the molecule as a rigid body vibrating about its centre. The outlying atoms would then execute the largest movements and the peak values of the averaged electron densities would diminish. The atoms A and E do not seem to have a much greater spread in the molecular plane than the other atoms, but the sections through these atoms parallel to the (010) plane, which are reproduced in

Fig. 1, show a somewhat greater elongation in the direction of the *a* axis (*x* co-ordinate) than do the corresponding sections through the other atoms. (The *a* axis is not perpendicular to the molecular plane, but makes an angle of nearly 60° with it.)

Effects such as those just described tend to obscure the more chemically interesting aspects of the charge distribution. Progress can perhaps be made by a more careful exploration of the outer portions of the atoms, but it may not be profitable to attempt this in detail until further measurements of the structure factors at lower temperatures can be carried out.

Hydrogen atoms

In Fig. 3, the half-electron line makes a distinct bulge on the outer portions of the atoms, *A*, *B*, *D* and *E*. This bulge in each case surrounds the position of the hydrogen atom, if it is assumed to lie at about 1·08 A. (Pauling, 1939, p. 158) from the centre of the carbon atom, on a line drawn from the centre of the hexagon and lying in the molecular plane. The bulge around atom *A* is somewhat suppressed, but there is a notable absence of any effect in the neighbourhood of atom *C* which does not carry a hydrogen atom. Although this contour level is easily susceptible to large errors, it seems very likely that it does indicate the effect of the hydrogen atoms.

From studies which have recently been carried out on aliphatic compounds (Morrison, Binnie & Robertson, 1948) we have the impression that the hydrogen atoms in naphthalene are not so well defined as they would be in a similar analysis of an aliphatic molecule. The comparison is rather difficult at present because so far only two-dimensional studies of the aliphatic compounds are available. This conclusion would be expected, however, if the number of electrons associated with each hydrogen atom in naphthalene were somewhat less than the number associated with each hydrogen atom in the aliphatic compounds; i.e. if the hydrogens were relatively more positive in aromatic molecules than in aliphatic molecules. Other evidence in the same direction may be deduced from the results of dipole-moment measurements and from spectroscopic data, and has recently been summarized by Gent (1948). X-ray studies of the present kind may in the future provide very direct evidence on this chemically important point.

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