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The Crystal and Molecular Structure of Triphenylene, $C_{18}H_{12}$

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The crystal and molecular structure of triphenylene have been determined by quantitative X-ray analysis. The unit cell is orthorhombic with $a = 13{\cdot}20$, $b = 16{\cdot}84$, $c = 5{\cdot}28$ A.; it contains four molecules and the space group is $P2_12_12_1$. The Fourier-transform method was used to estimate the preliminary structure, and the complete determination has been effected by two-dimensional Fourier syntheses on the (001) and (100) planes. The co-ordinates of the atoms, the molecular dimensions, and the intermolecular distances are given. The molecule is planar, and there are variations in bond lengths greater than the probable experimental error of 0·02 A., distances as large as 1·47 A. being found in the central ring. These results agree fairly well with those found theoretically by the method of molecular orbitals (Coulson). Calculations of the bond lengths have been made using the valence-bond pairing method, and comparisons with the experimental values are given.

The most interesting aspect of the structure is found to be in the abnormally close intermolecular approaches (2·7–3·2 A.) which bind the molecules into zigzag chains, between which there are rather large separations (4·3–4·9 A.). This structure appears to be consistent with the crystallographic properties, but there is no ready explanation for the existence of strong intermolecular attractions. Possible bonding mechanisms are discussed, and it appears that the intermolecular forces may be of an entirely new type.

I. X-RAY ANALYSIS

Introduction

A preliminary investigation of the structure of the orthorhombic crystal of triphenylene has been made by Banerjee & Guha (1937), who determined the unit cell, and concluded from observations of the magnetic anisotropy of the crystal that the normals to the planes in which the molecules lie are inclined at 51° to the c axis, and equally inclined at about 57° to the a and b axes. No further work has been reported, and it was therefore decided to undertake an X-ray study of the structure in order to determine more particularly whether the possible steric hindrance between non-bonded atoms in the molecule had any effect on its planarity, and to detect any variable carbon–carbon bond lengths, such as had been reported by Robertson & White in coronene (1945) and pyrene (1947*b*), two other condensed-ring hydrocarbons.

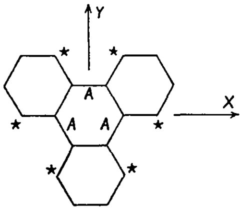

Fig. 1. The triphenylene molecule.

One might perhaps expect the conjugated system of bonds present in the triphenylene molecule to induce a completely coplanar configuration, in order to give the maximum resonance energy, but any such arrangement must be compatible with the van der Waals radii of the CH units, indicated by asterisks in Fig. 1. Relief from steric hindrance between these units might be brought about by deviations from planarity, such as a tilt of the outer rings from the plane of the central ring, or by a non-polar central ring. It will, however, be shown that an energetically stable plane molecule is obtained by the lengthening of the 'open' bonds A.

Preparation and morphology

The material used in the investigations was prepared by Dr W. S. Rapson, by the dehydrogenation of 1:2:3:4:5:6:7:8-octahydrotriphenylene over a palladium catalyst (Rapson, 1941). Suitable crystals were grown by slow cooling from a solution in alcohol. Colourless orthorhombic prisms, elongated in the c direction, were obtained. In most crystals only the (110) and ($1\bar{1}0$) faces occur, although occasionally the small (120) and ($1\bar{2}0$) faces develop as well. The end-faces are not clearly formed. The crystals sublime and evaporate slowly over a period of months; they are, nevertheless, not particularly soft, and under pressure from a needle generally fracture with a cleavage parallel to the (110) and ($1\bar{1}0$) faces.

The unit cell and space group

Oscillation and zero-layer-line Weissenberg photographs were taken with filtered Cu $K\alpha$ radiation. The orthorhombic unit cell has the dimensions

$$a = 13{\cdot}20\text{ A.},\quad b = 16{\cdot}84\text{ A.},\quad c = 5{\cdot}28\text{ A.}$$

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The density of the crystal, determined by flotation, is about 1·3 g.cm.$^{-3}$, and the unit cell therefore contains four molecules, corresponding to a calculated density of 1·28 g.cm.$^{-3}$. Absent spectra determine the space group to be

$$P2_12_12_1-D_2^4,$$

which has a multiplicity of four.

Intensity measurements

For intensity measurements, photographs were taken about the zones [001] and [100]. The linear dimensions of the crystals used for the zone [001] were of the order of 0·25 mm., which is small when considered in relation to the linear absorption coefficient (7·0 cm.$^{-1}$), and, since the crystals were of fairly uniform cross-section, no absorption corrections were made for the *hk*0 reflexions. For the zone [100], the axis of rotation of the crystal is perpendicular to the needle axis, and it was not possible to cut a crystal so short that its length would approximate to its thickness. The effect of absorption was, however, reduced by taking several series of films from different crystals of slightly varying shape and making a comparison of the intensities measured. Nevertheless, the intensity values obtained for the 0*kl* reflexions are not as reliable as those for the *hk*0 reflexions, for which no similar difficulty exists.

Relative intensity measurements were made in two ways: first, visually by comparison with a standard series of spots of varying exposure, and secondly, with a microphotometer calibrated against a standard wedge. At a later stage, the measurements of the *hk*0 intensities on further sets of films were repeated, using the focusing microphotometer of the Royal Observatory of the Cape of Good Hope. The different estimates agreed well, but, since the microphotometer measurements covered the larger intensity range, these were used to calculate the $|F_{\text{obs.}}|$ values by the usual formula applicable to mosaic crystals. The visual estimates were used as a check, particularly in the case of weak reflexions.

In the microphotometer measurements, the assumption is made that the peak intensity recorded by the instrument is proportional to the integrated intensity of the spot on the film, a procedure that has been found in work on crystal material of a similar nature to lead to no inconsistencies. To justify it, however, an attempt was made to estimate the integrated intensity of several reflexions. With a small aperture in the microphotometer, runs were made down the length of the spot at different points of its breadth. The recorded values were plotted graphically, and the integrated intensity was calculated. Although this procedure is rather crude, it was found that the intensity so obtained did bear a fairly constant ratio to the peak intensity over a wide range of spot strengths.

It will be shown below how use was made of the Fourier-transform method to determine the approximate structure. For this, a knowledge of the absolute values of the structure factors is required, so the relative intensities, measured as above, were put on an approximately absolute scale by comparison with a known crystal in the way described by Saunder (1946). *m*-Dinitrobenzene (Archer, 1946) was chosen as the standard, since crystals of convenient shape could be obtained, and since its absorption coefficient (13·5 cm.$^{-1}$) is not very different from that of triphenylene. The method proved to be reliable, for only a very small correction factor was necessary to correlate the *F* values obtained from it with the final calculated values.

Preliminary estimate of the structure

The four molecules of triphenylene occupy general positions in the unit cell. The asymmetric crystal unit thus consists of a complete molecule, or eighteen carbon atoms, if the hydrogen atoms are neglected. It is reasonable to assume as a first approximation a regular planar molecule, in conformity with the usual chemical formula. Simple packing tests, and the results of the magnetic measurements of Banerjee & Guha (1937), which gave the tilt of the molecular plane to the *a b* face of the unit cell as 51°, promised clear resolution of the atoms when projected along the *c* axis, and suggested that the structure might be studied by means of two-dimensional Fourier series.

The orientation of the plane of the molecule in the unit cell is known from the magnetic data, but to specify its position completely, four degrees of freedom remain, one of rotation of the molecular axes *X*, *Y* (see Fig. 1) in this plane, and the three co-ordinates (x_c, y_c, z_c) of the centre of the molecule with respect to the crystallographic origin. These could not be fixed from the packing, and it was decided to use a molecular structure factor, in the way suggested by Knott (1940). As the molecule is probably plane, or nearly so, and two of the six parameters defining its position were known, it proved possible to apply the method, using an idealized model of the molecule as planar, regular and of side 1·40 A. An account of this work is given elsewhere (Klug, 1950), but, briefly, the Fourier transform of the molecule is constructed, a projection of the reciprocal lattice is superposed on it, and one of them is rotated about their common centre until the lattice points pick out structure amplitudes of the observed magnitudes. The *h*00, 0*k*0 and 00*l* point-rows are particularly suited for this determination, since, for these reflexions, the Fourier transform of the whole unit cell bears a fairly simple relationship to that of one molecule.

In this way, the orientation of the molecular axes *X*, *Y* with respect to the *a* and *b* axes was found, and also the parameters of the centre of the molecule. These are

$$x_c = 0{\cdot}175 \text{ (or } 2{\cdot}32\text{ A.)}, \quad y_c = 0{\cdot}140 \text{ (or } 2{\cdot}36\text{ A.)}.$$

A reliable estimate of the *z* parameter is not possible, since there are only three 00*l* spectra on which to base the determination. The molecule lies in the plane specified by Banerjee & Guha but is rotated about its centre so that its X axis is not quite parallel to the (001) plane but makes an angle of about 3° with it.

Origin of co-ordinates

The origin of co-ordinates adopted in the *Internationale Tabellen...* (1935) was not used in calculating the structure factors. For the projection along the c axis, the origin is taken at the point $(\frac{1}{4}a, 0, 0)$ referred to the origin adopted in the tables, since this choice makes the origin of the projection a centre of symmetry. The co-ordinates of the four equivalent points then become

$$\text{(I)}\ x, y, z; \quad \text{(II)}\ \tfrac{1}{2}+x, \tfrac{1}{2}-y, \bar{z};$$
$$\text{(III)}\ \tfrac{1}{2}-x, \tfrac{1}{2}+y, \tfrac{1}{2}-z; \quad \text{(IV)}\ \bar{x}, \bar{y}, \tfrac{1}{2}+z.$$

This origin is retained throughout the rest of this paper, and the x, y and z values in Table 1 refer to it. In evaluating the Fourier projection along the a axis, however, the origin was taken on the screw axis at $(\frac{1}{4}a, -\frac{1}{4}b, 0)$ with respect to the origin used in the *Internationale Tabellen...*, i.e. at $(0, -\frac{1}{4}b, 0)$ with respect to the origin of the c-axis projection. For this reason, alternate $0k0$ structure factors in Table 3 have signs opposite to those in Table 2.

Table 1. *Atomic co-ordinates expressed as fractions of the corresponding lattice translations*

(Origin on 2_1 axis parallel to c)

Atom (cf. Figs. 3, 4 (*b*))	x/a	y/b	z/c
C_1	−0·051	0·260	0·105
C_2	0·029	0·258	−0·058
C_3	0·203	0·256	−0·419
C_4	0·280	0·259	−0·590
C_5	−0·063	0·203	0·283
C_6	0·103	0·200	−0·057
C_7	0·185	0·202	−0·235
C_8	0·351	0·197	−0·574
C_9	0·009	0·145	0·289
C_{10}	0·089	0·142	0·128
C_{11}	0·262	0·139	−0·228
C_{12}	0·341	0·140	−0·398
C_{13}	0·166	0·078	0·135
C_{14}	0·249	0·077	−0·037
C_{15}	0·155	0·019	0·319
C_{16}	0·315	0·013	−0·003
C_{17}	0·226	−0·043	0·338
C_{18}	0·306	−0·046	0·170

The Fourier projection on the *ab* plane

Calculations of the $hk0$ structure factors based on the atomic co-ordinates, derived from the molecular position and orientation found by the Fourier transform method, led to fair agreement with the observed F values; it was thus possible to proceed immediately with the Fourier synthesis. The first projection on the (001) plane, incorporating about 80 terms, showed the essential structure clearly, with most of the atoms defined, and established the success of the Fourier-transform method in the preliminary estimate of the structure. The parameters of the atoms were refined by successive approximations, and the final projection, in which 110 terms were used, is shown in Fig. 2.

Successive projections improved but slowly, and the slow convergence towards a stable state is probably due to the large number of atomic parameters, and the comparative smallness of the values of most of the structure factors relative to the maximum values possible if all atoms made contributions in phase. To refine the structure, the method of steepest descents (Booth, 1947) could have been used, but no computing aids were available, and the labour involved in applying it to a structure containing so many parameters would have been considerable.

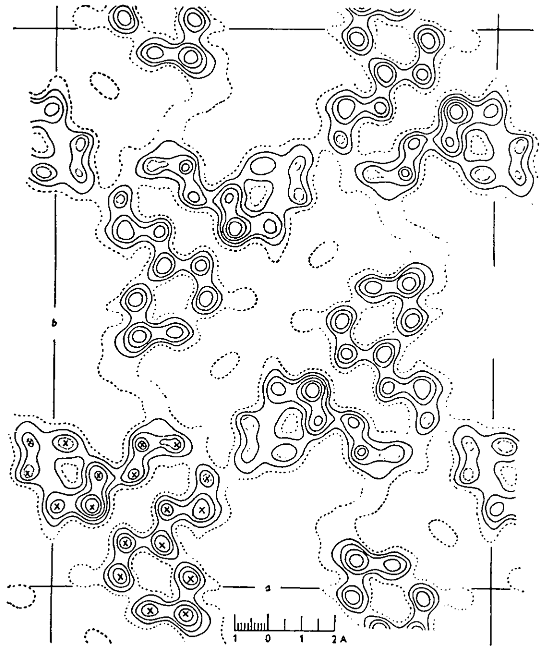

Fig. 2. Fourier projection of the structure along the c axis on to the (001) plane. Contours are drawn at arbitrary levels of 50 (dotted), 100, 150, 200, 250, etc. For some atoms whose peaks are rather low, the 225 level is shown as a dotted line. The co-ordinates assigned in the reference molecule are marked by crosses.

Since, however, a comparatively large number, 25, of fairly large-spacing reflexions of zero or very low observed intensity occur (excluding absences due to the symmetry elements), a variant on the method, also due to Booth (1947), was adopted. This involves minimizing the expression

$$\Sigma F^2_{\text{calc.}} = O_2,$$

taken over all planes of observed zero intensity. If the original co-ordinates of the atoms x_{rj} correspond to a value O_2, then the formula

$$\delta x_{rj} = -2O_2\left(\frac{\partial O_2}{\partial x_{rj}}\right) \Big/ \sum_{rj} \left(\frac{\partial O_2}{\partial x_{rj}}\right)^2$$

gives the corrections to be applied to these co-ordinates.

For the $hk0$ reflexions of the space group $P2_12_12_1$ this expression reduces to a tractable form, which was applied to the x and y co-ordinates derived from the third Fourier projection. The average change in the fractional co-ordinates was 0·002, the maximum being 0·007; the value of O_2 for the 25 reflexions fell correspondingly from 93 to 60.

As only a fraction of the observed data can be used in this method, it was not considered worth while to employ it to correct projections beyond the fourth. On the whole, the shifts were in the correct direction, and in the fifth projection hardly any terms changed sign. It is probably correct to say that this limited application of the method of steepest descents hastened the convergence of the ordinary Fourier-series method.

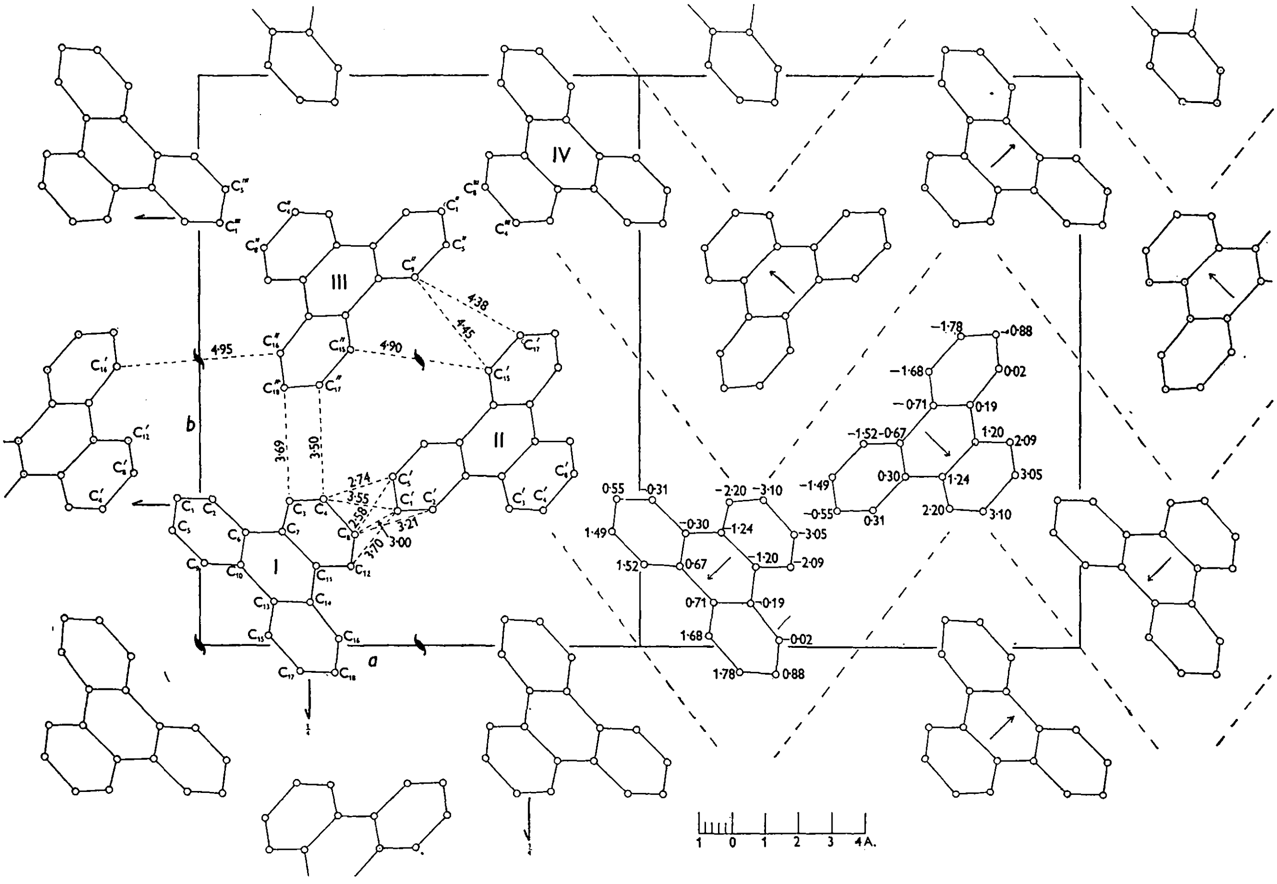

Fig. 3. Projection of the structure along the c axis on to (001). Two unit cells are shown. In the left-hand cell are shown the symmetry operations and the intermolecular distances in A. On the right the z co-ordinates in A. are given, the direction of tilt of the molecules up out of the (001) plane is indicated by the arrows, and the broken lines represent the traces of the (110) and $(1\bar{1}0)$ planes.

From the fifth and final projection in Fig. 2, to which Fig. 3 is the key diagram, it can be seen that all the atoms are clearly resolved. The heights of the peaks in the contour map are not all equal, being rather large for atoms C_{10} and C_{18}, and small for C_1, C_2, C_4, C_5 and C_8. The differences appear to be a little too great to be attributed to random experimental errors in the measurement of F values (see Robertson & White, 1947*a*), and it is difficult to see how any systematic errors could have arisen, although it must be noted that (i) no corrections have been made for absorption; (ii) the convergence of the series may not be quite complete, since some quite strong reflexions occur at high values of θ; (iii) extinction errors have not been allowed for. Variations in peak values of electron density have indeed been observed in other structures, e.g. anthracene (Robertson, 1933) and geranylamine hydrochloride (Jeffrey, 1945), but in these cases the variation is regular, the peaks diminishing from atom to atom, and this may be due to varying thermal motion in different parts of the molecules. The differences found in triphenylene are probably partly real for atoms C_1, C_2, C_4, C_5 and C_8, and in some way related to the abnormally short intermolecular approaches in which, as will be shown, these atoms are involved.

The most probable positions for the centres of the resolved atoms were assigned without using any standard molecular model. The x and y co-ordinates adopted are marked by small crosses in the reference molecule in Fig. 2, and their values are listed in Table 1. The projection is consistent with a planar molecule, with a rather large central ring, tilted at an angle of about 51° to the ab plane. The agreement of position of the molecule with that found from the Fourier-transform method is in fact remarkably good, and this is probably not merely fortuitous, but because this method made use of all $h00$ and $0k0$ spectra.

The Fourier projection on the *bc* plane

The evaluation of the third co-ordinate of the atoms is a matter of considerable difficulty. Even if a regular planar structure is assumed, there is still an unknown parameter for the molecule as a whole along the *c* axis, which must be determined by considering other reflexions. The zone [100] was examined in detail, since the *a*-axis projection promised at least a view of the molecular arrangement, if not actual resolution of the atoms.

The *z* co-ordinates, relative to some fixed point in the molecule, which was assumed to be planar, were calculated for various angles of tilt in the neighbourhood of 51°. The possible translations of the molecules along the *c* axis were confined by packing considerations to very small limits, and it was impossible to find a structure such that the adjacent molecules cleared each other by the normal intermolecular distances of 3·4–3·7 A. Figs. 3 and 4 (*b*) make this clear. On arranging the molecules I and II so that atoms C'_1 and C'_5 of II clear C_4 and C_8 of I comfortably, atom C'_2 of II is hindered by atom C_8 of the molecule I* corresponding to I, but situated at a translation *c* above it. Even when the best possible compromise is made, abnormally short approaches of about 2·7–3·0 A. are still involved.

This difficulty could not be avoided by varying, even considerably, the tilt of the molecular plane, or by abandoning the assumption that the molecule is plane. The calculated $0kl$ structure factors agreed best with the observed values when a planar molecule, with its centre at $z = -0{\cdot}05$, was used. The calculated structure factors are particularly sensitive to the angle of tilt of the molecule to the *ab* plane, and the best value was found to be $50\frac{1}{2}°$, in close agreement with Banerjee & Guha's estimate of 51°. Moreover, nothing could be gained by abandoning their finding that the molecular plane made equal angles with the *a* and *b* axes.

The result of the second Fourier synthesis, based on these preliminary assumptions, and incorporating 65 terms, is shown in Fig. 4 (*a*). Although all the atoms are not clearly resolved, the general molecular arrangement is obvious, and the position of the molecule along the *c* axis can be determined with some accuracy. The atomic positions obtained using *y* co-ordinates from the *c*-axis projection and *z* co-ordinates calculated for a planar model tilted at $50\frac{1}{2}°$ to the (001) plane, are marked with crosses; and it is clear that the projection is consistent with them. Atoms C_1, C_2, C_3 and C_4 are obscured by the overlap of atoms from an adjoining molecule (marked +) lying at a different depth in the unit cell, and atoms C_6 and C_8 are swamped by their closeness to the large peaks formed by this overlap; but the general distribution of the contours in the projection shows very clearly that the structure assigned must be nearly correct.

It is not practicable to deduce the *y* co-ordinates of the more clearly resolved atoms from the contour map, for most atoms in the projection approach one another within 1 A. or less, at which distance the distortion produced in projecting two atoms on the same plane becomes appreciable. From the estimates made by Booth (1948), the deviation *d* of one atom in terms of the projected interatomic distance *s* is $d = 0{\cdot}010, 0{\cdot}026, 0{\cdot}066$ A. for $s = 1{\cdot}0, 0{\cdot}9, 0{\cdot}8$ A. respectively. The *y* co-ordinates estimated from the $hk0$ projection have in any case been retained unaltered, because this projection incorporates more terms depending on more accurately measured intensities than the $0kl$ projection.

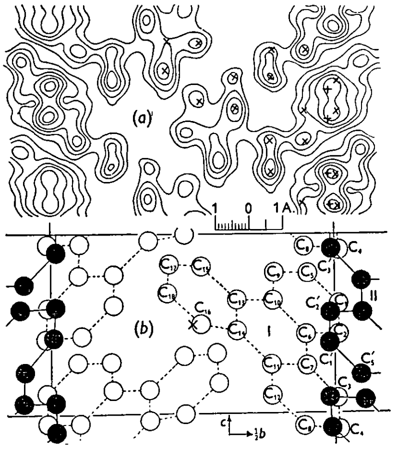

Fig. 4. (*a*) Fourier projection along the *a* axis on to the (100) plane. Contours drawn at arbitrary heights. Co-ordinates consistent with a planar molecule are marked by crosses. (*b*) The structure projected on to (100). The molecules denoted by the dark circles lie at a height $\frac{1}{2}a$ relative to those denoted by plain circles. The origin of the *c*-axis projection (Figs. 2 and 3) is indicated by a cross.

The final atomic parameters of the reference molecule with respect to the origin used for the *c*-axis projection are collected in Table 1. The atomic centres given by these co-ordinates are coplanar, although small departures of about 0·03 A. in *z* from a planar arrangement are within the limits of experimental error. The other three molecules in the unit cell are derived from the reference molecule by the symmetry operations of the space group, and the arrangement of the molecules in the structure is illustrated in Fig. 3. The reference molecule I is tilted out of the (001) plane so that the lines joining C_4 and C_{10}, and C_8 and C_{13}, make an angle of about 50° with this plane. The molecule is, however, not disposed exactly symmetrically with respect to the *a* and *b* axes, as might appear, but is rotated about 3° in its own plane; this is clear from the gradual decrease in the *z* co-ordinates (indicated in the figure) in the directions C_{17}–C_5, C_{18}–C_1 and so on.

Reliability factor

The structure factors were calculated from the final values of the co-ordinates, using the atomic scattering factors given by Robertson (1935). The results are given in Tables 2 and 3, and it can be seen that on the whole the agreement with $F_{\text{obs.}}$ is fair. When the discrepancies are expressed as

$$\frac{\Sigma\{|F_{\text{calc.}}|-|F_{\text{obs.}}|\}}{\Sigma|F_{\text{obs.}}|}=R,$$

the result is 0·20 for the [001] zone and 0·32 for the [100] zone. The first figure compares favourably with the values of R found in other crystal analyses, although it is slightly higher than those found in the work of Robertson and his collaborators on other condensed ring hydrocarbons. The comparatively large value of the discrepancy in the [100] zone may be partly due to the less reliable intensity measurements, but is probably due more to the small average values of the

Table 2. *Observed and calculated values of the* ($hk0$) *structure factors*

(Origin on 2_1 axis parallel to c.)

$hk0$	$\|F_{\text{obs.}}\|$	$F_{\text{calc.}}$
200	80	−82
400	16	+24
600	19	+21
800	17	−22
10,0,0	< 6	− 8
12,0,0	38	+38
020	63	−68
040	60	+61
060	24	−26
080	16	+20
0,10,0	25	−33
0,12,0	12	−15
0,14,0	29	+33
0,16,0	13	+10
0,18,0	26	−35
0,20,0	13	+17
110	41	+35
120	76	−84
130	56	−39
140	49	+32
150	38	+21
160	27	+23
170	16	+12
180	9	+ 6
...		
1,13,0	13	−10
1,14,0	14	− 9
1,15,0	< 4	− 3
1,16,0	54	−56
1,17,0	18	−23
1,18,0	13	− 9
210	23	−19
220	70	−67
230	26	−25
240	17	−17
250	6	− 8
260	16	+16
270	15	− 8
280	16	+17
290	< 4	+ 2
2,10,0	17	+14
2,11,0	12	+12
310	61	+20
320	33	−25
330	54	−28
340	46	+24
350	19	−10
360	45	−40
370	57	+55
380	39	−26
390	19	−15
3,10,0	20	−14
3,11,0	18	−19
3,12,0	12	+10
410	< 5	+ 6
420	42	−23
430	< 5	−14
440	38	+15
450	67	+72
460	35	−43
470	14	−14
480	< 5	+11
490	48	−41
4,10,0	38	−44
510	32	−24
520	8	+ 7
530	9	+ 8
540	28	−22
550	23	−17
560	53	+50
570	27	−16
580	< 4	− 2
590	< 4	− 1
5,10,0	12	+16
5,11,0	29	+11
5,12,0	18	+18
610	11	− 8
620	21	+22
630	15	+10
640	14	+14
650	17	+13
660	< 4	+ 6
670	18	+15
680	14	+11
690	< 4	+ 5
6,10,0	14	+14
6,11,0	13	+15
710	11	+ 6
720	31	+29
730	12	+10
740	< 4	+ 4
750	< 4	− 5
760	9	−11
770	< 4	− 4
780	15	−13
...		
7,12,0	19	−17
810	14	+13
820	< 4	+ 4
830	33	−27
840	49	−38
850	32	−29
860	15	+13
...		
8,13,0	11	−11
910	< 6	+ 7
920	< 6	− 2
930	19	−16
940	16	−14
950	< 6	+ 3
960	16	+13
...		
9,10,0	14	+10
10,4,0	12	+ 8
11,1,0	< 6	− 7
11,2,0	25	+23
11,3,0	36	−40
11,4,0	29	+21
...		
11,14,0	9	+10
11,15,0	11	+15
12,1,0	25	−36
12,2,0	< 6	+ 7
12,3,0	< 6	− 1
12,4,0	17	−19
12,5,0	14	−15
...		
12,13,0	15	+18
12,14,0	17	+20
13,1,0	18	+22
13,2,0	26	−30
13,3,0	17	+21

Table 3. *Observed and calculated values of the* ($0kl$) *structure factors*

(Origin on 2_1 axis parallel to a)

$0kl$	$\|F_{\text{obs.}}\|$	$F_{\text{calc.}}$
000	—	480
020	69	+68
040	60	+61
060	24	+26
080	16	+20
0,10,0	25	+33
0,12,0	12	−15
0,14,0	29	−33
0,16,0	13	+10
0,18,0	26	+35
0,20,0	13	+17
002	15	− 6
004	6	−11
006	12	−17
011	< 4	− 9
021	22	− 6
031	< 4	+20
041	25	+16
051	13	−21
061	14	−15
071	3	− 2
081	12	+ 7
091	16	+16
0,10,1	< 3	− 8
0,11,1	10	− 7
0,12,1	7	−10
0,13,1	9	− 6
0,14,1	6	+12
0,15,1	18	+15
0,16,1	11	−19
0,17,1	< 3	− 4
0,18,1	5	+ 6
0,19,1	4	+ 5
0,20,1	7	− 8
012	13	+ 6
022	15	+16
032	19	− 5
042	33	+34
052	17	+36
062	30	+35
072	22	+19
082	5	+14
092	13	+12
0,10,2	< 4	− 4
0,11,2	20	−15
0,12,2	26	−34
013	< 3	− 7
023	3	− 1
033	11	− 3
043	< 3	+ 2
053	19	−14
063	6	− 3
073	10	+12
083	< 3	+ 1
...		
0,15,3	7	+ 9
014	6	− 6
024	< 3	− 3
034	3	− 2
044	4	− 3
054	16	− 6
064	17	−20
074	10	+26
084	11	−10
094	7	− 6
0,10,4	18	−28
015	5	− 3
025	3	− 2
...		
075	5	− 5

observed $0kl$ structure factors than to serious errors in the atomic co-ordinates. In fact, the validity of R as an index of the reliability of a structure has been questioned on the grounds of the discontinuous nature of the moduli, and because the value obtained appears to depend very much on the number of reflexions considered, and on the treatment given to reflexions too weak to be observed (Smare, 1948). Thus the value 0·32 obtained may be compared, for example, with the values 0·33 and 0·32 found by Smare, and 0·27 found by Pitt (1948).

It should be noted that there is a great divergence between $|F_{\text{obs.}}|$ and $|F_{\text{calc.}}|$ for certain individual spectra, notably those from 310 to 340, 410 to 440 and 011 to 041. This is probably not attributable to experimental inaccuracies or extinction effects, and may well arise from departures from spherical symmetry in the atomic scattering factors, although the possibility of differential thermal effects cannot be excluded. For instance, the 011 and 031 spectra were not observed, yet it was found impossible to bring the calculated F values to zero by considering slight changes in co-ordinates. The only way in which the discrepancies could be reduced was by assigning slightly smaller scattering factors to the atoms of the central ring than to the other atoms. This may be purely fortuitous, but it does perhaps indicate the direction in which the treatment may lie, especially in view of the variations in the effective electronic charge present in atoms of the same molecule that have been found in applying quantum-mechanical methods to the study of the electronic structure of molecules by Coulson, and by Daudel & Pullman.

II. BOND LENGTHS AND INTER-MOLECULAR DISTANCES

The molecular dimensions

It has already been shown that the triphenylene molecule is planar to within the limits of experimental error. The X-ray analysis shows further that the 'open' bonds, marked A in Figs. 1 and 5, are long, and this gives a clearance of about 3·1 A. between the non-bonded CH units of the molecule, which is of the same order as the distances found between hindered CH groups in *cis*-azobenzene (Robertson, 1939) and in *o*-diphenylbenzene (Lonsdale & Clews, 1937), so that a planar molecule is possible without steric hindrance. It should be noted that the wave-mechanical theory of the bonding in triphenylene, which will be discussed below, indicates a lengthening of these open bonds.

Further, Rapson, Schwartz & Stewart (1944) have compared the ultra-violet absorption spectra of triphenylene and *o*-diphenylbenzene. The presence of the central hexatriene ring in the former causes a profound difference between its absorption spectrum, which is typical of a polynuclear aromatic compound containing a planar resonant formation, and that of the non-planar *o*-diphenylbenzene.

The bond lengths found experimentally and illustrated in Fig. 5 (a) show definite variations which may be compared with those hitherto reported for condensed-ring hydrocarbons (see Robertson, 1948). The bond angles all approximate to 120°, the largest discrepancies being 6° in the angles $C_6H_{10}C_9$ and $C_7C_{11}C_{12}$. There is an apparent lack of trigonal symmetry in the molecule, but this may be due partly to an unavoidable element of arbitrariness in fixing the atomic centres from the non-circular contours of the Fourier projection. On the assumption that the molecule is symmetrical, and that only five types of bonds, A, B, C, D, E, exist, the mean bond lengths are given in Fig. 5 (b). The individual deviations from these mean values are nowhere greater than 0·02 A., and it is felt that no significance can be attached to them, although the close intermolecular approaches discussed below might conceivably give rise to some asymmetry.

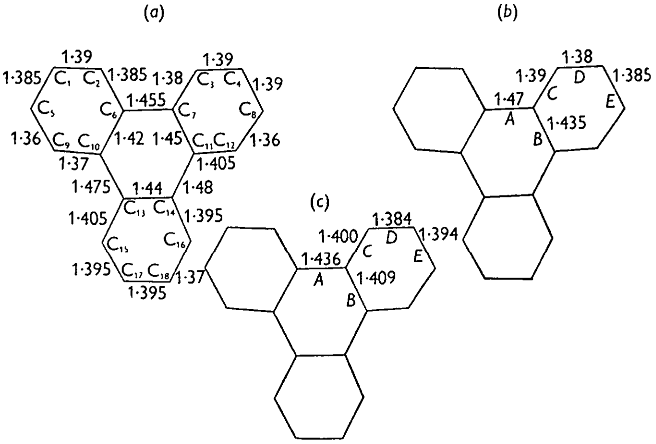

Fig. 5. (a) Observed molecular dimensions to the nearest 0·005 A. (b) Averaged bond lengths. (c) Bond lengths calculated by method of molecular orbitals.

The same accuracy cannot be claimed here as in the work of Robertson & White (1945) on coronene, the analysis which this problem most closely resembles, and the errors in placing individual atoms are probably of the order of 0·03 A.; but, as a complete molecule constitutes the asymmetric crystal unit, every bond length in the molecule has been determined, and the lengths of the five bond types represent the mean either of three or of six such determinations. The errors in the mean bond lengths should thus not be greater than about 0·02 A., and are probably less.

Theoretical study of the bond lengths

The variations in bond lengths are undoubtedly real and the bonds A and B are both long, B being the shorter of the two. Bonds C, D and E all lie closer to the normal benzene distance of 1·39 A., but it might possibly be claimed that D is significantly shorter than C and E, which are really indistinguishable.

These experimental results receive rather striking support from a quantum-mechanical study of this molecule by the method of molecular orbitals, in which the bond orders have been calculated by Coulson (1948). The theoretical bond lengths could then be easily found from the formula of Coulson (1939) relating bond order to length. The results are shown in Fig. 5(*c*) and in Table 4; the agreement from a qualitative point of view is good.

Table 4. *Comparison of calculated and observed bond lengths*

	Bond orders				Bond lengths (A.)				Observed bond lengths (A.)
Bond	1	2	3	4	1′	2′	3′	4′	
A	0·428	0·111	0·123	0·163	1·436	1·485	1·481	1·490	1·47
B	0·562	0·444	0·482	0·550	1·409	1·399	1·404	1·405	$1{\cdot}43_5$
C	0·603	0·444	0·394	0·592	1·400	1·399	1·408	1·396	1·39
D	0·690	0·555	0·609	0·681	1·384	1·382	1·375	1·379	$1{\cdot}37_5$
E	0·637	0·444	0·394	0·561	1·394	1·399	1·408	1·402	$1{\cdot}38_5$
Mean	0·602	0·428	0·429	0·547	1·401	1·408	1·408	1·407	$1{\cdot}40_5$

1. Mobile bond orders (Coulson, 1948).
2. Double-bond characters.
3. Weighted double-bond characters.
4. Penney bond orders.

The last decimal in columns 1′–4′ is unreliable but is inserted for comparison purposes. The observed bond lengths are given to the nearest 0·005 A.

The method of molecular orbitals is undoubtedly the most satisfactory for the study of electronic structure and bond lengths of aromatic molecules, but the problem may be approached by less refined methods, and an account of their application to triphenylene follows.

A rough calculation of the bond distances can be made by considering the nine non-excited valence-bond, or Kekulé, structures of triphenylene shown in Fig. 6. By the method that has been described for other polycyclic hydrocarbons (Pauling, Brockway & Beach, 1935; Robertson, 1948), the percentage double-bond character can be calculated for each bond in the molecule, and the bond distances can be obtained from the empirical curve of Pauling & Brockway (1937). The results are given in columns 2 and 2′ of Table 4, and it can be seen that the bond *A* may be expected to be rather longer, and *D* slightly shorter, than the others.

In the simplified calculation just discussed, equal weights were assigned to the nine stable valence-bond structures. The relative contributions of the different structures can be found by the Heitler–London–Slater–Pauling or pairing method (Pauling, 1933), in which the complete wave function for the unsaturation electrons of an aromatic molecule is obtained as a linear combination of many-electron functions representing the independent canonical structures. The application of this method to naphthalene is given by Pauling & Wheland (1933).

The full solution along these lines is virtually impossible, since the number of canonical structures for triphenylene runs into four figures. It may, however, be simplified by neglecting all ionic and excited structures, as Moffit & Coulson (1948) have done for coronene and pyrene, and confining the treatment to the nine non-excited structures. This procedure is highly questionable; for Daudel & Pullman (1946*a*, *b*, *c*) have found that the contribution of excited structures to the ground states of polynuclear molecules far outweighs that of the non-excited structures. The fact that reasonable results are obtained at all is probably due to the high symmetry of the molecules dealt with. In the case of triphenylene, it is evident from the molecular diagrams of Pullman (1946) that the weights to be attached to the individual bonds are roughly proportional in the non-, mono- and di-excited formulae.

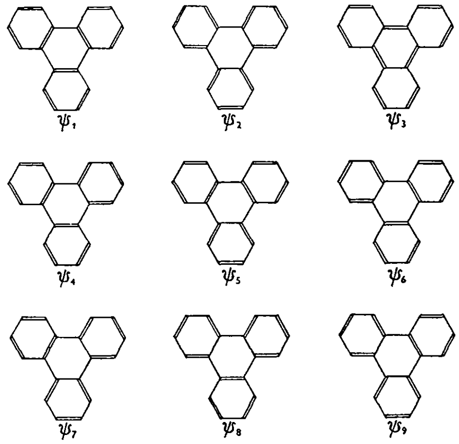

Fig. 6. The nine Kekulé structures of triphenylene.

The wave-function of the triphenylene molecule is written as the linear sum of the nine wave-functions ψ_i corresponding to the nine non-excited structures (see Fig. 6),

$$\Psi = \sum_i a_i \psi_i.$$

Following Pauling's (1933) symbolic technique, the corresponding matrix coefficients $(\psi_i \,|\, H-E \,|\, \psi_k)$ are readily evaluated in terms of Q and α, the Coulomb and exchange integrals respectively. The secular equation can then be set up, but it may be factorized, and reduced to an equation of the fifth degree, by writing

$$\Psi = r\psi_1 + s\psi_2 + t\psi_3 + u(\psi_4 + \psi_5 + \psi_6) + v(\psi_7 + \psi_8 + \psi_9)$$

from symmetry considerations. The secular equation was solved by a numerical method (Margenau & Murphy, 1943, p. 483), and for the ground state, α being negative, it was found that $E = Q + 6{\cdot}59\alpha$, the unnormalized coefficients corresponding to this being

$$r:s:t:u:v = 1{\cdot}0:0{\cdot}72:0{\cdot}83:0{\cdot}61:0{\cdot}55,$$

and the resonance energy $3{\cdot}59\alpha$.

The bond orders may now be defined in one of two ways. The first is due to Pauling *et al.* (1935) as mentioned above, and is merely the usual double-bond character weighted as the squares of the coefficients of the structures. A more satisfactory definition is that of Penney (1937) based on a vector model due to Dirac, by means of which problems involving permutation degeneracy may be dealt with.

The bond orders were calculated in this way, and the bond lengths found from the empirical curves appropriate to each case. The results are shown in columns 3, 4 and 3′, 4′ of Table 4. There is no significant improvement on the values obtained from the rough method (columns 1, 1′); the bond *A* is again long and *D* a little short, but the pairing method fails to predict the length of *B* as appreciably greater than the lengths of *C*, *D* and *E*. In this respect it falls short of the molecular-orbital method which is undoubtedly superior, giving results that agree well with the measured bond lengths, although the spread of values does not appear to be sufficient—an effect also found for coronene and pyrene (see Moffitt & Coulson, 1948).

The chemical properties of polynuclear hydrocarbons can sometimes be roughly expressed by stating a preference for some of the Kekulé structures. The Fries rule states that those structures with the greatest number of benzenoid rings should be given the greatest weight in taking the linear sum. It has been suggested by Moffitt & Coulson (1948) that a better rule is to give preference to those structures which show the greatest number of double bonds in the 'exposed' positions, i.e. those in which each end of the bond is attached to only one other aromatic carbon (e.g. bonds *D* and *E* of triphenylene).

These rules have been applied to triphenylene and the results are shown in Table 5. Both rules are valid in a rough sort of way and give greatest weight to ψ_1. For ψ_3 the 'exposed position' rule agrees better, but it is doubtful whether anything definite can be inferred from this example.

Table 5. *Application of Fries and Moffitt & Coulson rules*

Structures	Coefficients	N_b	N_e
ψ_1	1	4	6
ψ_2	0·72	3	3
ψ_3	0·83	1	6
ψ_4, ψ_5, ψ_6	0·61	3	5
ψ_7, ψ_8, ψ_9	0·55	3	4

N_b = number of benzenoid rings. N_e = number of exposed bonds.

Intermolecular distances

The interplanar distance between two parallel molecules separated by a translation *c* is given by

$$5{\cdot}28 \cos 50\tfrac{1}{2}^\circ = 3{\cdot}38\ \text{A.},$$

a value almost identical with those found in graphite, coronene and 1 : 12 benzperylene (White, 1948). Fig. 7 shows the normal projection of one of these molecules on to the plane of the other, and it can be seen that direct overlap of atoms is avoided. The closest approaches are as follows:

C(10)–CH(3)*	3·41 A.
C(14)–CH(8)*	3·44 A.
C(13)–CH(8)*	3·53 A.
CH(15)–C(11)*	3·43 A.
C(6)–CH(4)*	3·55 A.

All other approaches of this kind are greater than 3·55 A., similar to those usually found in hydrocarbon structures.

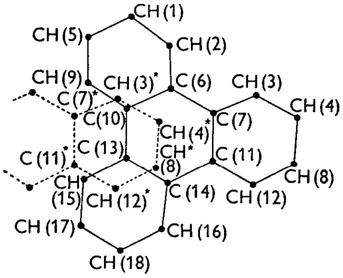

Fig. 7. Normal projection of two parallel molecules.

The most interesting feature of the structure is the occurrence of distances markedly less than the normal van der Waals approach of about 3·5 A. These are found between atoms C_4, C_8 and C_{12} of molecule I and atoms C_5', C_1' and C_2' of molecule II, and of course between their counterparts in molecules III and IV. The values are shown in Fig. 3. Three distances lie between 2·6 and 2·7 A. and two between 3·0 and 3·2 A., indicating rather powerful bonding forces between the molecules. It was previously mentioned that it was not found possible so to pack the molecules that the C_5'–C_1'–C_2' corner of molecule II cleared the C_4–C_8–C_{12} corners of molecules I and I*, which is separated from I by a translation *c*, by the normal van der Waals approach.

The results thus show that molecules I and II approach to within abnormally short distances; but it should be noticed that the distance 3·21 A. between atoms C_2' and C_8 shown in Fig. 3 refers to C_8 of molecule I* at a distance *c* above I, so that there is also a rather weaker intermolecular bond between molecules II and I*.

In virtue of the crystal symmetry the identical relation exists between the C_2–C_1–C_5 corner of molecule I and the C_{12}'–C_8'–C_4' corner of the molecule II adjacent to I but situated in the next unit cell. In this way the strong intermolecular forces extend right through the crystal in the *a* direction, binding the molecules into a sort of zigzag chain, –I–II–I–II–, etc., which has alternate units I and II with their centres at $z = -0{\cdot}05$ (or $-0{\cdot}264$ A.) and $z = 0{\cdot}05$ respectively, the molecules being inclined at $50\frac{1}{2}^\circ$ to the (001) plane in the directions indicated by the arrows in Fig. 3. The arrangement is made clear in this figure, from which it is seen that lying parallel to –I–II–I–, but with alternate molecular centres at $z = 0{\cdot}55$ (or 2·90 A.) and $z = 0{\cdot}45$ (or 2·37 A.) respectively, is the chain –III–IV–III– formed through close approaches between the C''_2–C''_1–C''_5 and C'''_{12}–C'''_8–C'''_4 corners in exactly the same way.

Between the chains, the approach of atoms C_3 and C_4 of molecule I to C''_{17} and C''_{18} of molecule III is about 3·6 A. This is normal, but all the distances between molecules II and III (and, of course, between I and IV) are greater than 4 A. The molecules concerned are related by the screw axes parallel to *c*, and it is the translation of $\frac{1}{2}c$ which is responsible for these large distances. In fact, the structure might well have been arranged according to the space group $P2_12_12$, which has no $\frac{1}{2}c$ translation, without the molecules coming closer than the normal van der Waals distances.

There are thus quite large holes running through the structure, between the parallel chains and perpendicular to their direction, as the contour map in Fig. 2 shows. In spite, therefore, of the close approaches between certain molecules, the structure is on the whole an open one, such as is found, for example, in α-resorcinol (Robertson & Ubbelohde, 1938). In triphenylene we seem to be dealing not only with some kind of intermolecular bond, but with bonds which have considerable directive power and are able to maintain an unusually open structure, as do the hydrogen bonds in α-resorcinol.

Some confirmation of the proposed molecular arrangement can be obtained from the physical properties of the crystal. The broken lines in Fig. 3 represent the traces of the naturally occurring crystal faces (110) and ($1\bar{1}0$), and they are approximately parallel to the zigzags of the molecular chains. One might perhaps expect cleavage planes parallel to (110) and ($1\bar{1}0$), which are, in fact, observed. The slight volatility of the crystal very probably arises from the large separations between the chains; the melting-point (197° C.) is, however, of the order found in other condensed ring compounds, which may be due to a balance between the strong and weak intermolecular bonds that occur.

Unfortunately, little is known about the physical properties of polynuclear aromatic compounds (see Corbin, Alexander & Egloff, 1948), particularly about those of triphenylene, so the relation of the structure to the properties cannot be studied quantitatively. For this purpose measurements of the sublimation energy, the variation of molecular volume with temperature, and other physico-chemical properties are necessary.

The nature of the intermolecular forces

The very short intermolecular distances that occur in the triphenylene crystal are the most interesting result obtained from the study of its structure; and it should be remarked that the conclusions reached as to the general nature of the intermolecular arrangement would not have been seriously modified even if errors as large as 0·1 A. had been made in fixing the positions of the atoms. The shortest distance hitherto recorded between CH groups of different molecules is 3·4 A. in chrysene (Iball, 1934), and distances of this order are due to the operation of normal van der Waals forces. In triphenylene the three short approaches of 2·58, 2·70 and 2·74 A. are very like those found in cases of intermolecular hydrogen bonding, and suggest forces of the same strength. Because carbon is not electronegative they cannot, however, be attributed to this cause.

The arrangement of the molecules in zigzag chains is strongly reminiscent of the structure assumed by some polar molecules in the solid state, for example, solid HF (Gunther, Holm & Strunz, 1939). This is illustrated in Fig. 8, where the head and tail of the arrows represent oppositely charged ends of a polar molecule. Although the triphenylene molecule is not linear, and geometrical complications would arise because of its shape, such a polar hypothesis would explain the close intermolecular approaches in the chains, and also the large separations between the molecules related by the screw axes parallel to *c*, which are apparently separated as widely as possible. Such a separation might conceivably arise in the case of polar molecules, for similarly charged ends of molecules in proximity would repel each other and tend to take up positions far apart in the crystal. (Since this paper was completed, Robertson & Abrahams (1948) have reported short intermolecular approaches of 2·7–3·0 A. in *p*-nitraniline, between the atoms of a nitro-group and the aromatic carbon atoms of an adjoining molecule. These are not hydrogen bonds and, since the molecule is polar, they apparently arise through dipole interaction.)

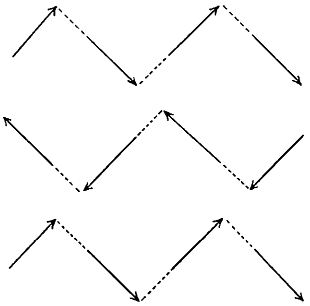

Fig. 8. Schematic arrangement of polar molecules.

It is difficult to understand how a molecule as symmetrical as triphenylene could be polar. Polarity in hydrocarbons possessing conjugated systems has, however, been reported (Sirkin & Schott-Lvova, 1944; Hannay & Smyth, 1946), the observed moments being attributed to heteropolar or ionic structures in resonance with the usual homopolar structures. Similar observations have been made by Lumbroso (1947) on acenaphthene and perylene. The latter, a condensed ring hydrocarbon possessing a centre of symmetry, is stated to have a moment of 1·9 D.

If the molecules in triphenylene are indeed polar, then we can regard the crystal as a sort of self-complex in which identical molecules polarize each other. Why this should happen in triphenylene and not in the other condensed ring hydrocarbons, whose crystal structures have been investigated, is puzzling, but the answer may possibly be related to the existence of the large central ring in the molecule, particularly to the long open bonds A which approximate more to single than benzenoid bonds.

The observed deviations from true trigonal symmetry in the molecular dimensions, although small and assumed to be spurious, may indeed arise from the asymmetry consequent upon a polar structure of the molecule. Furthermore, the low peaks in the electron-density maps found for the atoms involved in the close approaches may be related to small displacements of electron charge in the molecules. These questions, however, cannot be settled from the X-ray evidence, and must await a measurement of the dipole moment of triphenylene, although it must be borne in mind that the electronic configuration in the crystal may be different from that in the free state.

A clue to a less obvious but perhaps more plausible mechanism that may produce molecular association in triphenylene is to be found in the processes of bimolecular- and self-quenching of fluorescence in solutions of condensed ring hydrocarbons (Bowen, Barnes & Holliday, 1947). In such cases the molecules seem to be held together not only by the usual van der Waals forces, but by London dispersion forces, which are not a first-order wave-mechanical interaction but a second-order effect arising from the time variation of the wave-functions of the π electrons. For aromatic molecules (and polarizable halogen and nitro-compounds) these forces may be unusually large because of the simultaneous operation of more than one factor. Finally, the theory of Dewar (1947) on π-complex formation, in which π orbitals of aromatic compounds can apparently form molecular bonds, may also have some bearing on the subject of molecular association.

The suggestions put forward in this section to account for the close intermolecular approaches are mainly tentative, and are an attempt to view the unexpected results obtained in terms of existing chemical theory. It may possibly be necessary to assume forces of a new type, but little can be done until the physico-chemical properties of triphenylene have been more fully investigated.

In conclusion, I wish to thank Prof. R. W. James for his constant interest and aid throughout the course of this work. I also wish to thank Dr W. S. Rapson for preparing the crystals, Dr J. Jackson, H.M. Astronomer at the Cape of Good Hope, for the use of the microphotometer at the Royal Observatory, and Prof. C. A. Coulson for the use of his unpublished results on the bond orders of triphenylene. To the South African Council for Scientific and Industrial Research I am indebted for a research grant which made this work possible.

References

Archer, E. M. (1946). *Proc. Roy. Soc.* A, **188**, 51.
Banerjee, S. & Guha, A. C. (1937). *Z. Krystallogr.* **96**, 107.
Booth, A. D. (1947). *J. Chem. Phys.* **15**, 415.
Booth, A. D. (1948). *Fourier Technique in X-ray Organic Structure Analysis.* Cambridge: University Press.
Bowen, E. J., Barnes, A. W. & Holliday, P. (1947). *Trans. Faraday Soc.* **43**, 30.
Corbin, N., Alexander, M. & Egloff, G. (1948). *J. Phys. Chem.* **52**, 387.
Coulson, C. A. (1939). *Proc. Roy. Soc.* A, **169**, 413.
Coulson, C. A. (1948). *C.R. Acad. Sci., Paris*, **226**, 1906.
Daudel, R. & Pullman, A. (1946*a*). *J. Phys. Radium*, **7**, 59.
Daudel, R. & Pullman, A. (1946*b*). *J. Phys. Radium*, **7**, 74.
Daudel, R. & Pullman, A. (1946*c*). *J. Phys. Radium*, **7**, 105.
Dewar, M. J. S. (1947). *Faraday Soc. Discussion*, **2**, 50.
Gunther, P., Holm, K. & Strunz, K. (1939). *Z. phys. Chem.* B, **43**, 229.
Hannay, N. B., & Smyth C. P. (1946). *J. Amer. Chem. Soc.* **68**, 244.
Iball, J. (1934). *Proc. Roy. Soc.* A, **146**, 140.
Internationale Tabellen zur Bestimmung von Kristallstrukturen (1935). Berlin: Bornträger.
Jeffrey, G. A. (1945). *Proc. Roy. Soc.* A, **183**, 391.
Klug, A. (1950). *Acta Cryst.* **3**, 176.
Knott, G. (1940). *Proc. Phys. Soc. Lond.* **52**, 229.
Lonsdale, K. & Clews, C. J. B. (1937). *Proc. Roy. Soc.* A, **161**, 493.
Lumbroso, H. (1947). *C.R. Acad. Sci., Paris*, **225**, 1003.
Margenau, H. & Murphy, G. M. (1943). *The Mathematics of Physics and Chemistry.* New York: van Nostrand.
Moffitt, W. E. & Coulson, C. A. (1948). *Proc. Phys. Soc. Lond.* **60**, 309.
Pauling, L. (1933). *J. Chem. Phys.* **1**, 280.
Pauling, L. & Brockway, L. O. (1937). *J. Amer. Chem. Soc.* **59**, 1223.
Pauling, L., Brockway, L. O. & Beach, J. Y. (1935). *J. Amer. Chem. Soc.* **57**, 2705.
Pauling, L. & Wheland, G. W. (1933). *J. Chem. Phys.* **1**, 362.
Penney, W. G. (1937). *Proc. Roy. Soc.* A, **158**, 306.
Pitt, G. J. (1948). *Acta Cryst.* **1**, 168.
Pullman, A. (1946). *C.R. Acad. Sci., Paris*, **222**, 736.
Rapson, W. S. (1941). *J. Chem. Soc.* p. 15.
Rapson, W. S., Schwartz, H. M. & Stewart, E. T. (1944). *J. Chem. Soc.* p. 73.
Robertson, J. M. (1933). *Proc. Roy. Soc.* A, **140**, 79.
Robertson, J. M. (1935). *Proc. Roy. Soc.* A, **150**, 110.
Robertson, J. M. (1939). *J. Chem. Soc.* p. 232.
Robertson, J. M. (1948). *Acta Cryst.* **1**, 101.
Robertson, J. M. & Abrahams, S. C. (1948). *Acta Cryst.* **1**, 252.
Robertson, J. M. & Ubbelohde, A. R. (1938). *Proc. Roy. Soc.* A, **167**, 122.
Robertson, J. M. & White, J. G. (1945). *J. Chem. Soc.* p. 607.
Robertson, J. M. & White, J. G. (1947*a*). *Proc. Roy. Soc.* A, **190**, 329.
Robertson, J. M. & White, J. G. (1947*b*). *J. Chem. Soc.* p. 358.
Saunder, D. H. (1946). *Proc. Roy. Soc.* A, **188**, 31.
Sirkin, J. & Schott-Lvova, E. (1944). *Acta Physicochim.* **19**, 379.
Smare, D. L. (1948). *Acta Cryst.* **1**, 150.
White, J. G. (1948). *J. Chem. Soc.* p. 1398.