

The Crystal Structure of Dibiphenylene-ethylene*

By CHARLES P. FENIMORE†

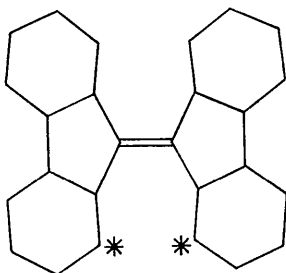
Crystallographic Laboratory, The Johns Hopkins University, Baltimore 18, Md., U.S.A.

(Received 14 June 1948)

Dibiphenylene-ethylene crystallizes in the space group *Pcan*. The data for the unit cell are: $a = 17.2$, $b = 36.9$, $c = 8.23$ Å., $Z = 12$. The strong negative birefringence and marked pleochroism indicate a layer crystal structure, and the morphology suggests an arrangement of molecules compatible with optical data and supported by Fourier syntheses. Satisfactory agreement of calculated with observed structure amplitudes is obtained with a centrosymmetric, planar molecular model constructed on customary C-C distances and angles. The anomalous reactivity and color of dibiphenylene-ethylene are discussed as steric effects of molecular planarity.

Introduction

Dibiphenylene-ethylene is interesting because it is difficult to guess its detailed structure intelligently.



The molecule is conjugated throughout, and the possibility of drawing many resonance forms might lead one to anticipate planarity; but when customary C-C bond lengths and angles are substituted in the planar structural formula, the distance between the starred carbons is found to be only about 2.5 Å. This close approach would represent a serious steric conflict, and in view of the usual covalent and van der Waals radii for hydrogen, or even if the van der Waals radii of matter about the starred carbons were assumed to be no greater than the half thickness of the benzene ring (1.8 Å.), there is reasonable doubt that the molecule could be planar.

Chemical and spectral evidence shows dibiphenylene-ethylene to be anomalous. Its first reduction potential measured at the dropping mercury electrode is smaller in magnitude by several tenths of a volt than that found for other ethylenic compounds which react apparently by the same mechanism, but is equal to the reduction potential observed for triphenylmethyl (Wawzonek & Fan, 1946). Furthermore, it has been shown recently (Fuson & Porter, 1948) that Grignard reagents will add

to dibiphenylene-ethylene to form the corresponding alkyl-dibiphenylene-ethane, although attempts to add Grignard reagents to many other olefins have yielded only negative results. The deep color of the crystals is also unexpected. Generally, a shift in the electronic absorption maximum towards longer wave-lengths is observed on ascending any vinylenic-homologous series (Brooker, 1942). Accordingly, one would expect dibiphenylene-butadiene to absorb further towards the red than dibiphenylene-ethylene. However, while crystals

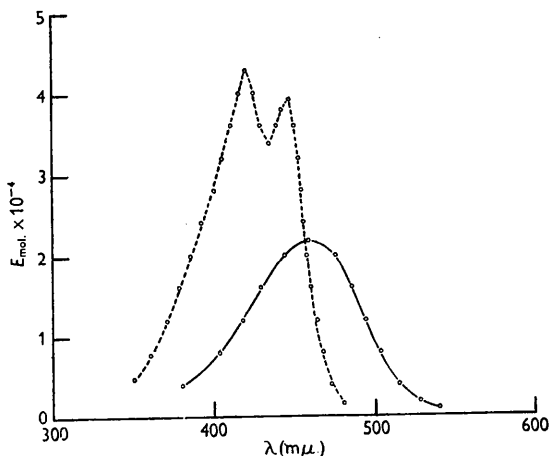


Fig. 1. Absorption of dibiphenylene-ethylene (full line) and dibiphenylene-butadiene (broken line).

of the latter are red, those of the former are only reddish yellow (Wislicenus, 1915). Spectrophotometric examination shows the longest wave-length absorption maxima to be (see Fig. 1):

	λ_{\max}	$E_{\text{mol.}} \times 10^{-4}$
For dibiphenylene-ethylene	460 m μ	2.2
For dibiphenylene-butadiene	446	3.9
(two maxima)	420	4.3

$$E_{\text{mol.}} \text{ (in cm.}^{-1} \text{ L mole}^{-1}\text{)} = \frac{1}{ct} \log_{10} \frac{I_0}{I}$$

where c = concentration, t = thickness of absorbing layer, I_0 = incident light intensity, I = transmitted light intensity.

* Presented to the School of Higher Studies, Faculty of Philosophy, The Johns Hopkins University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

† Now at Ballistic Research Laboratories, Aberdeen Proving Ground, Md., U.S.A.

The difficulty of conjecturing the detailed structure, the reactivity, and the color suggest the desirability of attempting an X-ray crystal structure determination of dibiphenylene-ethylene.

Unit cell and space group

Orthorhombic, acicular, red crystals of dibiphenylene-ethylene were furnished by McLain (1946). Rotation and oscillation pictures around the a , b , and c axes gave the identity periods

$$a = 17.22, \quad b = 36.9, \quad c = 8.23 \text{ \AA}.$$

The c axis is the needle axis. The cell contains twelve molecules. Density: calculated 1.28, observed 1.26 g.cm.⁻³. The axial ratios obtained (0.467:1:0.223) are not in agreement with those given by Groth (0.487:1:0.527), nor can they be reasonably transformed to those ratios (Groth, 1906-19, pt. 5, p. 431).

Weissenberg pictures were taken of the zero layer and of the first four layer planes around the c axis, and of the zero layer around the a axis. Both the Weissenberg (c axis) and the a axis rotation pictures showed additional reflections, weak and diffuse, which have been considered spurious. With this limitation, the reflection orders observed were

$$\begin{array}{ll} hkl \text{ all orders,} & h0l \text{ for } h \text{ even,} \\ 0kl \text{ for } l \text{ even,} & hk0 \text{ for } (h+k) \text{ even.} \end{array}$$

They indicate the space group $Pcan$, uniquely determining the point group as holohedral. The data for the cell and space group confirm those given by Senti and quoted by McLain (1946).

It can be demonstrated that the additional reflections do not demand a larger cell by taking oscillation pictures around the a axis. Under these circumstances they appear as weak diffuse layer lines. For oscillations 5° on either side of the b axis, the diffuse reflections are relatively strong. They appear only extremely weakly for oscillations 20° on either side of the c axis, while surely it would be expected that a true identity period for this large cell would show clearly in any 40° oscillation picture.

The space group $Pcan$ allows an eightfold general position and three fourfold special positions. Two of the special positions (at 0, 0, 0 and at $\frac{1}{2}$, 0, 0) require a center of symmetry and one (at x , 0, $\frac{1}{2}$) requires a twofold axis. Considerations of available space forbid simultaneous occupancy of the three special positions; consequently the twelve molecules must be placed in one general and one special position. It is necessary that four molecules (and by reasonable assumption, the remaining eight also) must either be centrosymmetric or contain a twofold axis.

In the rotation pictures taken about the c axis, the layer lines display a moderate alternation of intensity. This suggests a weak pseudo halving in the c direction. The c period (8.23 Å.) is somewhat greater than twice

the thickness of the benzene ring (2×3.6 Å.) and would allow a superposition of two molecules if the molecular structure were approximately planar.

Optics

The optical properties of the crystal, although known only qualitatively, suggest a layer crystal structure with layers roughly normal to the c axis. The crystals are strongly optically negative ($n_x = 1.55$, n_y and $n_z > 1.7$; n_x parallel to the c axis, the needle axis). Furthermore, the crystals are pleochroic, appearing yellow in transmitted plane-polarized light when the vibration direction lies parallel to the needle axis, red when this direction is perpendicular to the needle axis. There is no difference to the eye for different orientations of the vibration direction in the plane normal to the needle axis. On attempting a semi-quantitative measure of the pleochroism by spectroscopic means, it was not found possible to prepare a specimen thin enough to transmit appreciably at the longest wavelength absorption maximum of dibiphenylene-ethylene (460 m μ) because of the high molecular absorption coefficient (10^4) in this region. The thinnest crystal prepared (20 μ thick) was opaque in either orientation for wave-lengths shorter than 520 m μ . However, from 534 to 560 m μ the absorption was seven or eight times as great for light vibrating perpendicular to the needle axis as for light vibrating parallel to this axis. This absorption ratio may be compared with the pleochroism of hexamethyl-benzene, whose carbon atoms all lie nearly in one crystallographic plane (Lonsdale, 1929) and whose absorption of polarized ultra-violet light is approximately ten times as great when the vibration direction is parallel to the plane of the ring as when the direction is perpendicular to this plane (Schiebe, Hartwig & Müller, 1943).

The ratio of seven or eight as compared with ten in the case of hexamethyl-benzene demands that the crystal be at least approximately a layer structure. It can also be asserted that if dibiphenylene-ethylene is planar the planes of the molecules are tilted from the plane $z = 0$ in the crystal. It would be unreasonable to attempt a quantitative estimate of the tilt from these ratios, however, because the relative absorption for light vibrating in the plane of the molecule to light vibrating perpendicular to this plane might be far greater for dibiphenylene-ethylene than for hexamethyl-benzene.

Morphology

The crystal violates the generalized law of Bravais (Donnay & Harker, 1937) and an additional structural suggestion is afforded by the morphological anomaly. The generalized law states that observed crystal faces should be parallel to net planes of greatest interplanar distances if the faces are given *multiple indices* compatible with the space-group symmetry. For example, for dibiphenylene-ethylene in the case of $\{hk0\}$ forms, only forms with $(h+k)$ even are to be considered. With

the known ratio of $a:b$ (0.467 by X-ray observations, 0.471 by optical goniometry), the interplanar distances are in decreasing order those of $\{020\}$, $\{110\}$, $\{130\}$, and $\{200\}$, and the generalized law states that this should be the order of decreasing predominance of the observed forms. However, an examination of the crystal forms shows $\{130\}$ dominant, $\{200\}$ small, $\{020\}$ and $\{110\}$ absent.

Violations of the law of Bravais appear not to be rare, and can often be interpreted in terms of strong structural features of the crystal. It might prove rewarding, then, to attempt to distribute molecules within the cell in such a way that the absence of $\{020\}$ and $\{110\}$ will be accounted for. Since $\{h k 0\}$ forms are normal to the structural layer planes, the anomaly cannot be due to the extreme departure of the molecules from spherical symmetry, as in the cases considered by Wells (1946), and it will be sufficient to consider point molecules.

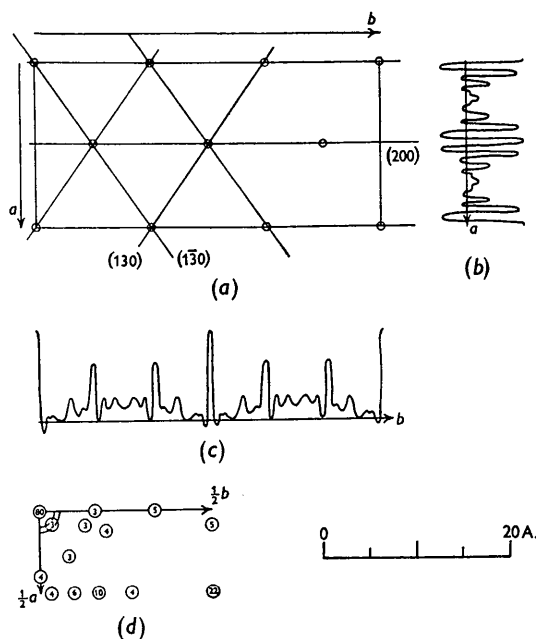


Fig. 2. (a) Approximate placement of molecules suggested by morphology and optics. (b, c) x and y co-ordinates from one-dimensional Patterson-Harker syntheses. (d) $z=0$ section through Patterson space.

A possible arrangement is obtained by placing molecules in one of the two special positions with $x=y=0$, and in the general position with $x=0$, $y=\frac{1}{3}$ (see Fig. 2a). If no distinction is made between positions, this arrangement makes the projection of the unit cell on the x, y plane equivalent to three two-dimensional centered cells; and the law of Bravais now requires $\{130\}$ to be dominant and $\{200\}$ to rank second, as is observed. Furthermore, since the molecules have been placed on c glide planes, this disposition requires that each x, y position represent a superposition of two molecules and, in view of the c axial length of only 8.23 Å., forces an approximately layer structure, which is compatible

with the optical properties. It should be emphasized that non-equivalence of positions might still be consistent with the observed crystal morphology (Bunn, 1945, p. 230).

In order to test the tentative placement of the molecules, two one-dimensional Patterson-Harker syntheses were prepared (Harker, 1936). The co-ordinates derived from these are shown graphically in Fig. 2b, c where, barring the trivial maxima at $x=0, \frac{1}{2}$ and at $y=0, \frac{1}{2}$, one finds the largest maxima in the x and y co-ordinates to lie at $x = \pm 0.06, \frac{1}{2} \pm 0.06$ and at $y = n/6$, with n integral. This means that many atoms are located at x and y values consistent with the proposed placement.

If the Patterson function

$$P_{x,y,z} = \sum_h \sum_k \sum_l |F_{hkl}|^2 \cos 2\pi(hx + ky + lz)$$

is evaluated for $z=0$, $P_{x,y,0}$ will have maxima at vector distances from the origin equal to vector distances between atoms at equal z . Again in Fig. 2d, and barring the trivial maxima at $x=y=0$ and at $x=y=\frac{1}{2}$ (the latter being required if any of the special positions is occupied), one finds the largest maximum at $x=\frac{1}{3}$, $y=\frac{1}{6}$ (the maximum of value 10). This would be expected from the placement of the molecules and thus supports that assignment.

Structure

A consideration of the $hk0$ reflections of high indices and great intensity now allows orienting the molecules in x and y as was done for coronene (Robertson & White, 1945). The reflections 0.18.0, 1.15.0, 2.18.0, 3.15.0, 730, 7.11.0, 800, and 860 are all strong and consequently the corresponding planes must all be highly populated by atoms. One may draw the eight sets of planes (with both positive and negative phases) and attempt to place the molecules so that as many atoms as possible lie as near as possible to as many planes as possible, using either the positive or the negative phase only for each set of planes. The attempt is facilitated by the knowledge that the structure is more or less planar and that the molecules are centered at $x=y=0$ and at $x=0, y=\frac{1}{3}$. The result of this study is presented in Fig. 3, where only the phases finally decided upon are retained, and where the usual C-C distances and angles are employed in the trial molecules. The open and closed circles represent atoms in two superposed molecules, though not necessarily indicating which of the two is the upper one. It may be observed that the orientation of the molecules in the special positions is slightly different from that of the molecules in the general positions.

A comparison of observed and calculated structure amplitudes for all $hk0$ reflections, using the atomic positions found above, turns out favorably in most cases. An attempt to give the same orientation to the molecules in the general and in the special positions led to a worsening of this comparison. Three two-dimen-

sional Fourier syntheses with progressive changes in the co-ordinates gave the electron-density projection presented in the right-hand half of Fig. 4 (summed from 130 terms). This projection shows the regions of low electron density at the centers of the five-membered rings and at the centers of the benzene rings. Owing to the superposition of two molecules in every case, it may be difficult to visualize a single molecule.

general position was also centrosymmetric—a rather obvious assumption.

It was observed previously that the molecules are probably tilted. The fact that the planes $x=0$ and $x=\frac{1}{2}$ are c glide planes means that there cannot be much tilt about a line parallel to the y axis. Any tilt in this sense would rapidly move the molecules apart and require more space than is available to contain them. Tenta-

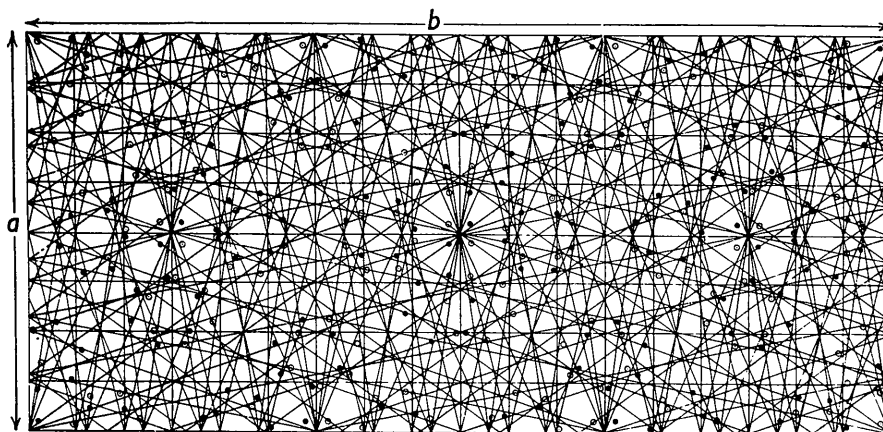


Fig. 3. Molecular orientation in x and y .

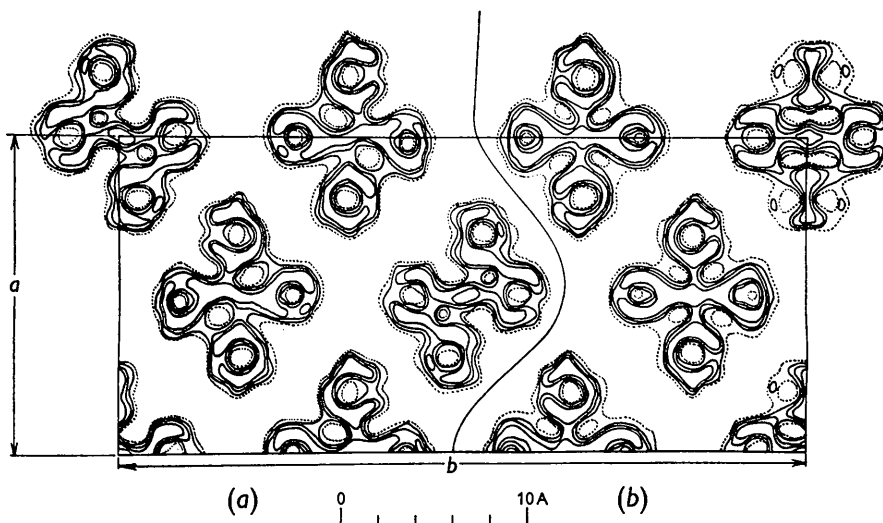


Fig. 4. (a) Electron-density projection of half unit cell (from $z = -\frac{1}{4}$ to $z = +\frac{1}{4}$) on x, y plane. (b) Electron-density projection of whole unit cell on x, y plane. Contours in (a) drawn at intervals only half as great as in (b).

The molecular symmetry falls out of the solution at this point. If the molecule at $x=y=0$ occupies the special position with $z=0$, it is centrosymmetric; if it occupies the special position with $z=\frac{1}{4}$, it possesses a twofold axis along the line $y=0$. But the molecule, as oriented at $x=y=0$, cannot have a twofold axis along the line $y=0$. Consequently, the molecule must be centrosymmetric, and the z co-ordinate of its center must be $z=0$. From this point on it was assumed that the crystallographically independent molecule in the

tively, it is assumed that no tilt at all occurs about a line parallel to the y axis. On the other hand, there is no reason why there could not be considerable tilt about an axis parallel to the x axis, and the fact that the reflections 052 and 062 are exceedingly strong suggests that the molecules lie near these planes. Assuming this tilt for the molecules, and solving the one-parameter problem for the center of the molecule in the general position, one obtains the approximate value $z=0.434$. An electron-density projection of the cell contents on the

plane $x=0$ (Fig. 5) shows the approximately planar molecules to have about the tilt expected. This projection is presented only to show the general lay of the molecules. It probably cannot do more since only forty terms were summed in its construction.

One may now employ the general hkl terms with some degree of confidence. In the left-hand side of Fig. 4 there is presented a projection of one-half of the cell contents (from $z = -\frac{1}{4}$ to $z = \frac{1}{4}$) on the x, y plane, a slice which contains all but six atoms of one molecule in the special position and a smaller fraction of the atoms in

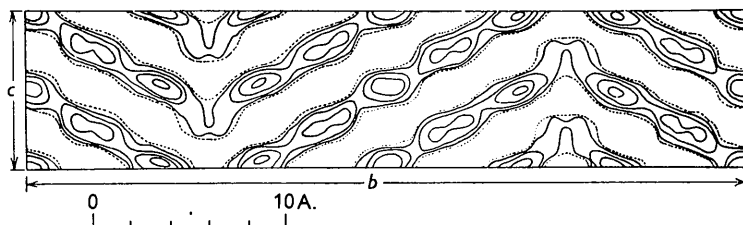


Fig. 5. Electron-density projection on y, z plane. Origin at upper left-hand corner.

one molecule in the general position. The contours are drawn at intervals only one-half as great for the left as for the right-hand portion of Fig. 4. Although the atoms are not resolved, the general features of the molecular structure are evident.

Finally, since the molecular tilt (35.5°) is very close to that of $0\bar{3}1$ (33.8°), the electron density on this plane in the neighborhood of the origin is presented in Fig. 6. In this section all the data (482 terms) were employed and a little more detail is evident than in the other electron-density maps. Since the approximation

that $0\bar{3}1$ is the plane of the molecule is worse the greater the y distance, one should expect that Fig. 6 would be a less accurate molecular representation at large than at small y ; for example, the greater extent of the minima in the centers of the benzene rings at large than at small y is not to be wondered at.

Although the cell contains 12 molecules, and therefore $(12 \times 26)/8 = 39$ crystallographically independent carbon atoms, it is sufficient, since a center of symmetry is assumed in the molecule in the general position, to list only 26 carbon atoms: 13 for the molecule in the

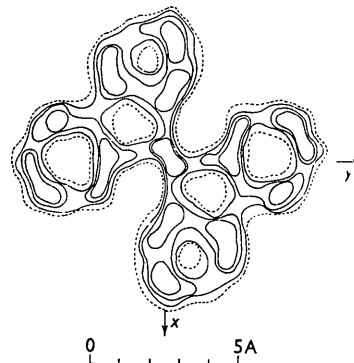


Fig. 6. Electron density on $(0\bar{3}1)$ in the neighborhood of the origin.

special position (at $0, 0, 0$) and 13 for that in the general position (at $\frac{1}{2}, \frac{1}{8}, 0.434$). This is done in Table 1. In the molecule in the general position, atoms lie at $\frac{1}{2} + A, \frac{1}{8} + B, 0.434 + C$, and at $\frac{1}{2} - A, \frac{1}{8} - B, 0.434 - C$, so each value of A, B, C listed places two crystallographically independent atoms. In the molecule in the special position, atoms lie at $\pm(x, y, z)$, so that each value of x, y, z listed places two atoms related by a center of symmetry.

A comparison of observed F_{hkl} 's and calculated values of $0.48 F_{hkl}/8$ is listed in Table 2.

Table 1. List of atomic positions

Atom no.	Special position			General position		
	x	y	z	A	B	C
1	0.024	0.011	0.036	-0.027	0.010	0.033
2	-0.005	0.042	0.135	-0.111	0.002	0.008
3	-0.075	0.058	0.186	-0.160	-0.022	-0.071
4	-0.073	0.089	0.285	-0.240	-0.018	-0.058
5	-0.002	0.104	0.332	-0.272	0.010	0.033
6	0.068	0.088	0.281	-0.223	0.035	0.111
7	0.066	0.057	0.182	-0.142	0.031	0.099
8	0.133	0.036	0.116	-0.081	0.054	0.173
9	0.212	0.043	0.139	-0.092	0.085	0.271
10	0.286	0.021	0.067	-0.027	0.103	0.331
11	0.244	-0.009	-0.028	0.048	0.091	0.292
12	0.165	-0.016	-0.050	0.058	0.061	0.194
13	0.109	0.007	0.022	-0.007	0.042	0.135

Planar molecules are centered at $0, 0, 0$ and at $\frac{1}{2}, \frac{1}{8}, 0.434$. The ethylenic bond of the molecule at the origin (projected on the x, y plane) makes an angle of 39° with the y axis, that of the other molecule an angle of 45° . Both molecules are tilted 35.5° about axes parallel to the x axis. The numbering of atoms follows the scheme shown.

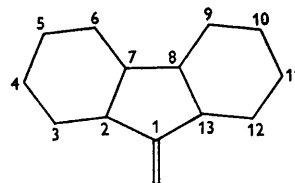


Table 2. Comparison of observed and calculated structure amplitudes

<i>hkl</i>	<i>F</i> _{obs.}	<i>F</i> _{calc.}	<i>hkl</i>	<i>F</i> _{obs.}	<i>F</i> _{calc.}	<i>hkl</i>	<i>F</i> _{obs.}	<i>F</i> _{calc.}
002	8.0	6.0	524	4.4	4.4	840	1.2	0.0
004	1.0	-0.8	620	1.6	-1.7	841	1.7	-0.5
200	16.0	17.1	621	<i>vw</i>	-0.5	842	2.0	1.4
201	3.6	-4.8	622	1.7	1.3	843	2.0	1.5
202	9.7	-12.0	623	1.3	0.8	10.4.0	1.0	0.4
203	1.0	-1.1	624	3.0	-3.7	052	32.0	-30.3
204	1.3	0.5	721	<i>vw</i>	-0.3	054	2.8	-1.7
400	13.0	15.0	722	3.3	-3.9	150	0.8	-0.4
401	<i>vw</i>	0.1	723	1.0	2.8	151	3.0	-2.5
402	3.6	5.1	820	1.2	0.1	152	3.5	-4.8
403	<i>vw</i>	-0.4	821	1.3	-0.7	153	<i>vw</i>	1.7
404	1.2	-0.8	822	<i>vw</i>	1.1	154	1.0	1.5
600	5.0	-4.5	823	2.0	-1.2	251	1.8	-2.3
601	1.4	0.5	10.2.0	2.6	2.7	252	2.5	-2.7
602	4.4	6.4	032	2.3	-0.5	253	2.3	-2.3
603	1.0	1.8	034	2.3	-1.2	254	1.5	1.6
604	2.1	-2.5	130	23.0	28.4	350	1.4	0.8
800	7.0	6.1	231	5.0	-0.6	351	2.2	-1.8
801	0.6	-0.4	232	1.0	-0.5	352	0.8	0.8
802	1.8	1.8	233	1.3	1.3	353	2.0	-0.4
803	<i>vw</i>	0.5	234	<i>vw</i>	-0.2	354	2.8	3.6
10.0.0	3.0	-4.1	330	9.9	-8.1	451	0.8	-0.9
012	5.0	3.1	331	1.2	-0.5	452	2.0	-4.0
014	0.8	-0.8	332	2.0	-1.5	453	1.5	-1.0
211	2.0	-2.0	333	<i>vw</i>	-1.0	454	2.4	-1.7
212	6.5	-6.4	334	3.0	0.0	550	2.0	1.1
213	1.7	-0.2	431	<i>vw</i>	0.0	551	1.7	-0.7
214	1.0	0.5	432	<i>vw</i>	-0.1	552	2.0	-2.0
310	1.0	-1.3	433	2.0	-1.4	553	2.0	-1.2
311	2.5	2.4	434	1.5	-1.0	554	1.2	-0.9
312	2.0	-2.0	530	1.0	0.7	651	0.6	1.2
313	1.0	0.2	531	<i>vw</i>	-1.1	652	2.1	2.7
314	<i>vw</i>	0.6	532	0.8	-0.1	653	1.8	-1.7
411	<i>vw</i>	-0.4	533	2.6	-1.6	750	2.0	0.8
412	1.4	2.2	534	1.0	-0.4	751	<i>vw</i>	1.5
413	2.5	-3.2	631	0.6	1.0	752	2.4	-1.3
414	2.8	-2.4	632	<i>vw</i>	-0.1	753	1.1	-0.9
510	2.0	-2.2	633	<i>vw</i>	0.3	851	0.4	-0.2
511	1.0	-0.2	634	<i>vw</i>	-1.0	852	3.0	-3.2
512	1.1	0.7	730	7.8	8.0	853	<i>vw</i>	-1.7
513	1.2	0.2	731	1.2	1.7	951	0.7	-0.3
514	<i>vw</i>	-1.7	732	4.0	5.6	060	2.0	6.4
611	1.0	0.2	733	<i>vw</i>	1.0	062	40.0	28.5
612	1.7	2.2	831	1.0	0.8	064	4.5	3.0
613	2.0	-2.1	832	<i>vw</i>	0.6	161	4.0	2.2
614	5.0	-4.9	833	0.4	-0.9	162	2.9	2.2
710	2.0	-2.0	931	1.7	1.9	163	4.4	4.2
711	1.4	-1.4	042	7.0	8.9	164	2.6	2.6
712	1.8	2.0	044	2.0	4.0	260	22.4	-23.4
713	3.0	2.9	240	0.6	0.4	261	0.8	1.3
714	<i>vw</i>	-1.1	241	3.0	-0.5	263	1.2	0.0
811	<i>vw</i>	-0.1	242	1.0	-0.6	264	2.3	-0.6
812	5.0	-5.1	243	3.0	-1.5	361	2.4	2.0
813	1.0	-2.8	244	2.6	-2.9	362	<i>vw</i>	-0.5
910	<i>vw</i>	0.6	341	3.0	3.0	363	1.3	-1.3
022	4.0	-2.4	342	2.6	2.5	364	<i>vw</i>	2.0
024	4.5	-2.9	343	1.6	-1.6	460	3.0	3.6
220	0.5	-0.3	344	2.5	2.0	461	1.6	-2.5
221	2.6	-2.4	440	0.5	-0.1	462	1.9	2.0
222	1.3	1.1	441	0.9	-0.4	463	<i>vw</i>	-2.6
223	3.0	2.8	442	<i>vw</i>	1.2	561	1.6	2.0
224	1.0	-0.2	443	2.0	0.2	562	<i>vw</i>	1.3
321	0.5	0.4	444	2.0	2.0	563	2.6	-0.9
322	5.9	5.2	541	2.0	-1.7	660	5.4	6.2
323	1.0	1.0	542	<i>vw</i>	-2.3	661	<i>vw</i>	-2.4
324	2.0	-2.4	543	<i>vw</i>	0.4	662	5.6	-7.1
420	1.0	-1.7	544	<i>vw</i>	-1.9	663	2.0	1.5
421	0.8	0.7	640	0.5	0.3	761	1.0	3.0
422	<i>vw</i>	1.0	641	1.6	0.0	762	<i>vw</i>	-3.7
423	<i>vw</i>	-2.4	642	1.4	-0.9	763	0.5	-0.5
424	1.6	-2.2	643	<i>vw</i>	0.6	860	12.3	12.5
521	0.4	-0.6	741	<i>vw</i>	-0.6	861	2.0	-3.9
522	1.5	-0.3	742	1.6	1.8	862	1.2	0.6
523	2.1	2.3	743	<i>vw</i>	1.7	863	<i>vw</i>	-0.2
						10.6.0	0.4	0.2

Table 2 (cont.)

<i>hkl</i>	$F_{\text{obs.}}$	$F_{\text{calc.}}$	<i>hkl</i>	$F_{\text{obs.}}$	$F_{\text{calc.}}$	<i>hkl</i>	$F_{\text{obs.}}$	$F_{\text{calc.}}$
072	3.0	-4.3	391	0.8	-1.4	1.12.1	2.0	-2.3
074	5.6	5.0	392	1.0	-0.4	1.12.2	1.3	0.0
170	<i>vw</i>	-0.4	393	1.2	-1.2	1.12.3	1.0	-0.9
171	3.0	2.0	491	3.6	1.3	2.12.0	1.5	1.5
172	2.8	2.6	492	<i>vw</i>	0.8	2.12.1	2.7	2.7
173	4.4	-3.5	493	1.6	-1.0	2.12.2	<i>vw</i>	-1.9
174	<i>vw</i>	-1.3	590	4.0	-3.5	3.12.1	0.5	0.6
271	2.0	-1.5	591	1.0	-1.4	3.12.2	1.8	-2.7
272	<i>vw</i>	-0.2	592	3.0	-3.9	3.12.3	0.5	0.0
273	0.8	1.0	593	<i>vw</i>	-1.1	4.12.0	5.0	-4.9
274	3.0	3.3	691	1.4	1.4	4.12.1	1.5	-2.1
370	1.4	1.3	692	1.1	0.8	4.12.2	3.0	2.5
371	1.0	-0.2	693	<i>vw</i>	-0.1	4.12.3	2.0	-2.3
372	0.9	0.3	790	3.4	8.7	5.12.1	1.0	-1.3
373	1.3	-0.9	791	2.0	-1.9	5.12.2	<i>vw</i>	1.5
374	<i>vw</i>	-5.8	792	0.8	-0.5	6.12.0	8.0	-10.1
471	2.0	-2.8	891	<i>vw</i>	0.4	6.12.1	2.4	3.2
472	3.2	-3.3	990	1.4	-1.1	6.12.2	1.9	0.6
473	2.4	-4.3				8.12.0	2.8	-3.2
570	3.0	2.4	0.10.0	1.0	-0.8			
571	1.6	1.8	0.10.2	3.1	5.0	0.13.2	6.7	6.0
572	<i>vw</i>	2.7	1.10.1	1.4	-1.0	1.13.0	0.8	0.5
573	2.0	-1.4	1.10.2	1.6	-1.9	1.13.1	<i>vw</i>	0.6
671	0.6	0.2	1.10.3	2.8	3.0	1.13.2	<i>vw</i>	-2.3
672	3.7	-5.0	1.10.4	4.6	4.5	1.13.3	1.6	1.5
673	<i>vw</i>	3.0	2.10.0	0.8	0.7	2.13.1	1.0	1.0
770	1.4	1.6	2.10.1	2.1	1.5	2.13.2	1.8	-2.1
771	<i>vw</i>	2.7	2.10.2	3.0	-4.0	3.13.0	2.4	-1.6
772	<i>vw</i>	2.7	2.10.3	0.9	-0.9	3.13.1	1.0	-0.5
773	1.3	-0.5	3.10.1	2.0	-2.4	3.13.2	3.4	-5.2
871	1.0	-1.7	3.10.2	2.0	2.4	3.13.3	2.0	0.6
970	1.6	1.1	3.10.3	1.5	-1.5	4.13.1	2.0	-4.5
			4.10.0	1.0	1.0	4.13.2	<i>vw</i>	2.1
080	1.4	-1.7	4.10.1	1.8	1.0	5.13.0	2.9	2.6
082	7.1	-7.5	4.10.2	<i>vw</i>	1.4	5.13.1	2.5	-1.4
084	2.3	2.6	4.10.3	1.2	0.8	5.13.2	2.2	2.5
181	3.0	-3.2	5.10.1	<i>vw</i>	-0.5	7.13.0	2.0	-2.1
182	0.9	-1.7	5.10.2	<i>vw</i>	-3.1			
183	3.0	1.5	5.10.3	1.2	-1.0	0.14.0	5.0	1.5
184	<i>vw</i>	-0.6	6.10.0	1.4	1.0	0.14.2	<i>vw</i>	-0.2
280	1.4	1.3	6.10.1	0.8	0.8	1.14.1	1.0	0.8
281	<i>vw</i>	-0.9	6.10.2	1.4	1.2	1.14.2	3.3	3.0
282	1.2	-0.8	6.10.3	1.3	-0.4	1.14.3	1.9	-1.7
283	3.5	2.9	7.10.1	1.0	1.8	2.14.0	1.8	-1.5
284	5.2	6.8	7.10.2	<i>vw</i>	-2.0	2.14.1	<i>vw</i>	0.3
381	<i>vw</i>	-0.7	8.10.0	0.6	0.3	2.14.2	3.2	4.9
382	2.2	-1.5	8.10.1	1.3	1.2	3.14.1	3.0	-2.7
383	0.9	-0.2	10.10.0	2.4	-2.4	3.14.2	<i>vw</i>	1.1
384	1.4	-0.4				4.14.0	1.0	1.1
480	1.6	2.0	0.11.2	<i>vw</i>	-6.0	4.14.1	2.4	-2.9
481	1.4	-1.1	1.11.0	1.0	-0.1	4.14.2	<i>vw</i>	0.4
482	2.0	-2.7	1.11.1	1.2	1.0	5.14.1	2.5	-2.1
483	3.0	-2.7	1.11.2	1.0	0.4	6.14.0	1.2	0.5
581	1.5	-0.9	1.11.3	1.4	1.9	8.14.0	<i>vw</i>	1.0
582	<i>vw</i>	0.2	2.11.1	1.0	-0.4			
583	2.0	-2.1	2.11.2	4.0	6.9	0.15.2	2.0	5.0
680	3.2	3.3	2.11.3	1.5	-1.7	1.15.0	6.0	-4.0
681	1.9	2.5	3.11.0	1.2	-0.6	1.15.1	3.5	3.6
682	1.7	-2.1	3.11.1	<i>vw</i>	-0.5	1.15.2	4.9	4.2
683	<i>vw</i>	0.7	3.11.2	3.4	2.8	1.15.3	1.6	1.8
781	2.0	1.3	3.11.3	1.5	-2.1	2.15.1	<i>vw</i>	-0.1
782	1.3	-1.6	4.11.1	4.0	-4.2	2.15.2	2.0	-2.1
880	1.7	1.0	4.11.2	1.0	-0.9	3.15.0	5.5	2.3
881	1.0	2.0	4.11.3	0.5	2.0	3.15.1	0.6	-0.3
10.8.0	1.0	-2.0	5.11.0	2.6	2.8	3.15.2	2.0	2.9
			5.11.1	<i>vw</i>	-0.9	4.15.1	1.2	0.8
092	2.5	2.7	5.11.2	1.0	-0.3	5.15.0	4.0	-8.7
190	4.0	2.6	5.11.3	1.7	-1.4	5.15.1	1.2	0.4
191	4.0	3.3	6.11.1	0.8	-0.8	7.15.0	4.0	-4.0
192	6.1	7.1	6.11.2	1.0	-0.6			
193	3.5	3.7	6.11.3	1.3	1.2	0.16.0	2.6	2.3
194	4.7	2.4	7.11.0	6.6	-2.0	0.16.2	2.0	4.0
291	1.0	-0.7	7.11.1	1.2	-0.3	1.16.1	2.0	2.1
292	<i>vw</i>	-0.9				1.16.2	3.1	3.9
293	1.0	-1.0	0.12.0	5.0	4.4	1.16.3	1.6	-1.1
390	1.8	1.6	0.12.2	1.7	1.0	2.16.0	2.7	-2.4

Table 2 (cont.)

<i>hkl</i>	<i>F</i> _{obs.}	<i>F</i> _{calc.}	<i>hkl</i>	<i>F</i> _{obs.}	<i>F</i> _{calc.}	<i>hkl</i>	<i>F</i> _{obs.}	<i>F</i> _{calc.}
2.16.1	1.0	-1.1	6.18.0	0.8	0.2	5.21.0	<i>vw</i>	-1.0
2.16.2	1.0	-2.1	8.18.0	1.2	-1.4	7.21.0	2.0	-2.4
3.16.1	2.0	-2.3						
3.16.2	2.0	1.9	1.19.0	1.6	1.8	0.22.0	<i>vw</i>	2.4
4.16.0	<i>vw</i>	0.0	3.19.0	3.0	-4.4	2.22.0	1.2	-1.0
6.16.0	1.0	0.4	5.19.0	2.0	1.8	4.22.0	<i>vw</i>	-1.1
8.16.0	1.0	1.0	7.19.0	1.0	-1.5	6.22.0	1.0	-0.1
1.17.0	3.0	1.2	0.20.0	2.0	3.0	1.23.0	2.0	1.2
3.17.0	5.5	-4.8	2.20.0	2.0	-2.5	3.23.0	1.6	-2.2
5.17.0	3.0	2.6	4.20.0	1.5	-1.6	5.23.0	2.3	2.0
7.17.0	1.4	-1.5	6.20.0	0.5	-0.1	7.23.0	2.0	-1.7
0.18.0	8.0	4.0	1.21.0	4.0	8.1	0.24.0	2.0	0.5
2.18.0	8.0	9.4	3.21.0	4.0	6.7	2.24.0	0.6	-0.2
4.18.0	3.0	6.9						

Discussion

It has been established that dibiphenylene-ethylene is centrosymmetric and approximately planar. A fair agreement between observed and calculated structure amplitudes has been obtained with the planar model of Fig. 7, although it cannot be claimed that any of the distances or angles are known with precision. The deviation, calculated by the formula,

$$\frac{\sum ||F_{hkl}(\text{obs.})| - |F_{hkl}(\text{calc.})||}{\sum |F_{hkl}(\text{obs.})|},$$

is 0.31 for the *h**h*0 reflections alone and 0.36 for all reflections. The molecular centers lie at $x=y=z=0$ and at $x=\frac{1}{2}$, $y=\frac{1}{2}$, $z=0.434$. The ethylenic bond of the molecule in the special position (projected on the x, y plane) makes an angle of 39° with the y axis, that of the molecule in the general position an angle of 45° . Both molecules are tilted approximately 35.5° about axes parallel to the x axis, and the perpendicular distance between the molecular planes is 3.4 Å.

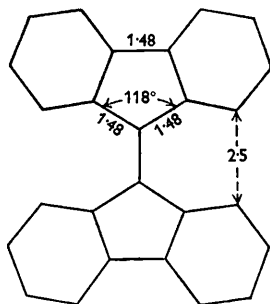
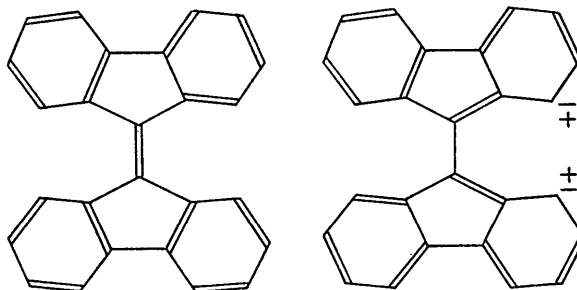


Fig. 7. Planar molecular model of dibiphenylene-ethylene. All C-C benzene distances are 1.40 Å. Ethylenic C-C distance is 1.33 Å.

The retention of at least approximate planarity in dibiphenylene-ethylene despite the close approach of non-bonded carbons (2.5 Å.) must introduce considerable strain energy into the molecule which would be released on disruption of the double bond, and the reactivity cited in the introduction is an obvious consequence of this strain. It is more difficult to understand why the molecule absorbs at a longer wave-

length than does its butadiene analog; that is, why the energy separation of the ground state and an excited level should be smaller than would ordinarily be expected. It might be supposed that both the ground and the excited levels of a hypothetical strain-free molecule would be raised on going over to the actual strained molecule. However, the excited form possesses a charge separation which is largely denied the ground state (Rodebush, 1947), and it may be pointed out that the geometry of dibiphenylene-ethylene is such that the charge separation could confer what might be considered as an ionic intramolecular attraction, thus diminishing the strain energy of the excited level relative to the energy increase of the ground level.



Such an effect would be inappreciable in the butadiene analog.

Even the details of the long wave-length absorption bands may be qualitatively explicable by the planarity of dibiphenylene-ethylene. The separation of the two maxima in the spectrum of the butadiene compound corresponds to the reasonable vibration frequency $4 \times 10^{13} \text{ sec}^{-1}$. It may be pointed out that if the same two maxima were to exist in a hypothetical strain-free ethylenic compound, then on going over to the actual strained molecule the vibrational structure might be smeared by an intramolecular pressure-broadening and be completely unresolved.

Experimental

Dibiphenylene-ethylene crystals were obtained from Dr McLain; dibiphenylene-butadiene was prepared

according to Wislicenus (1915). The absorption spectra of these compounds in benzene solution were determined with a Beckman spectrophotometer. The spectral examination of the pleochroism of the solid was carried out on a Bausch and Lomb high-dispersion grating spectrograph and involved a comparison, by the rotating-sector method, of the transmission of plane polarized light through a single crystal held in different orientations. Light was polarized by transmission through polaroid. The crystal was prepared by melting dibiphenylene-ethylene on a microscope slide, pushing a cover down on to the melt to obtain a thin section, allowing the melt to crystallize, and painting with black paint over all but a small area of a single acicular crystal. The pleochroism of the crystal allowed orienting the *c* axis in the desired manner.

Cu radiation filtered through nickel was used for all X-ray work. Intensities were estimated by visual comparison with a prepared scale running from 1 to 4000 in arbitrary units. Intensities were corrected by Lorentz and polarization factors. The empirical scattering power of carbon in hydrocarbons (Robertson, 1935) was used in calculating the structure amplitudes and the Fourier series were summed by the method of Patterson & Tunell (1942).

The author wishes to express his deep gratitude to Prof. J. D. H. Donnay for proposing this problem and

for the many suggestions and conversations that accompanied the work on it.

References

- BROOKER, L. G. S. (1942). *Rev. Mod. Phys.* **14**, 275.
 BUNN, C. W. (1945). *Chemical Crystallography*. Oxford: Clarendon Press.
 DONNAY, J. D. H. & HARKER, D. (1937). *Amer. Min.* **22**, 446.
 FUSON, R. C. & PORTER, H. D. (1948). *J. Amer. Chem. Soc.* **70**, 895.
 GROTH, P. (1906–19). *Chemische Krystallographie*. Leipzig: Engelmann.
 HARKER, D. (1936). *J. Chem. Phys.* **4**, 381.
 LONSDALE, K. (1929). *Proc. Roy. Soc. A*, **123**, 494.
 McLAIN, J. H. (1946). Thesis, The Johns Hopkins University.
 PATTERSON, A. L. & TUNELL, G. (1942). *Amer. Min.* **27**, 655.
 ROBERTSON, J. M. (1935). *Proc. Roy. Soc. A*, **150**, 110.
 ROBERTSON, J. M. & WHITE, J. G. (1945). *J. Chem. Soc.* p. 607.
 RODEBUSH, W. H. (1947). *Chem. Rev.* **41**, 318.
 SCHIEBE, G., HARTWIG, S. & MÜLLER, R. (1943). *Z. Elektrochem.* **49**, 372.
 WAWZONEK, S. & FAN, J. W. (1946). *J. Amer. Chem. Soc.* **68**, 2541.
 WELLS, A. F. (1946). *Phil. Mag.* **37**, 221.
 WISLICENUS, W. (1915). *Ber. deutsch. chem. Ges.* **48**, 617.

Acta Cryst. (1948). **1**, 303

Secondary Extinction and Neutron Crystallography

By G. E. BACON AND R. D. LOWDE

Ministry of Supply, Atomic Energy Research Establishment, Harwell, Didcot, Berks., England

(Received 21 August 1948 and in revised form 5 October 1948)

A detailed study of the effects of secondary extinction is made, with particular stress on the behaviour of the virtually non-absorbing crystals introduced by the advent of neutron diffraction. The penetration of a beam into a mosaic crystal of this kind will always be complete, and the relative importance of absorption and extinction is the reverse of that familiar in X-ray techniques. It is found that with increasing thickness the integrated reflexion of mosaic crystals falls away from proportionality to F^2 and, for normal thicknesses, has values of the order of the mosaic spread of the crystal expressed in radians. There is a useful range where the integrated reflexion is proportional to F , as with the perfect crystal. The discussion leads to an illuminating comparison between primary and secondary extinction. Criteria for 'thin', 'thick', 'non-absorbing' and 'absorbing' crystals are given. The importance of these results for neutron crystallography is discussed; if a technique similar to X-ray goniometry is to be developed, then crystals even smaller than those conventional with X-ray technique will be required. For this work the best crystals are those of the greatest mosaic spread.

1. INTRODUCTION

In a recent paper, Bacon & Thewlis (in the Press) discuss neutron diffraction from the point of view of the crystallographer. They point out that the very low

value of true absorption coefficient for neutrons which most substances present entirely alters the problem of measuring structure factors, and leads to different results for the integrated reflexions measured in