The Crystal and Molecular Structure of the Photodimer of Biphenylene

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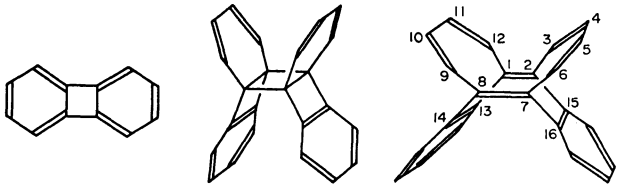
(Received August 25, 1980)

The molecular structure of the photodimer of biphenylene has been determined by X-ray crystal analysis. The crystals are triclinic, with eight molecules in a unit cell with dimensions of $a=15.061$, $b=17.687$, $c=13.091$ Å, $\alpha=108.91$, $\beta=98.52$, and $\gamma=89.71°$; the space group is $P\bar{1}$. 6625 unique intensity data were collected on a four-circle diffractometer with LiF-monochromated Cu $K\alpha$ radiation. The structure was solved by the symbolic-addition method using 8 symbols, and refined by the block-diagonal least-squares method. The final R value was 0.101. The molecular structure thus obtained corresponds to *syn*-13,14 : 15,16-dibenzotricyclo[6.4.2.$2^{2,7}$]hexadeca-1,3,5,7,9,11,13,15-octaene. Of the four crystallographically-independent molecules, two have approximately the C_{2v} symmetry, while the remaining two are somewhat deformed, their symmetry being nearly C_2. The molecules are held together mainly by van der Waals interactions.

In 1968, Goldman and Ruden reported that, on ultraviolet irradiation, biphenylene (**1**) in refluxing hexane affords a dimer to which they assigned the **2** structure.[1] However, an X-ray study of the octahydrodimer[2] showed that this photodimer might correspond to **3**, not **2**. In order to determine the structure unambiguously, we have now undertaken an X-ray crystal analysis of the photodimer itself.



1 **2** **3**

Experimental

The biphenylene dimer (mp 257—267 °C (dec) (lit,[1] mp 255—265 °C (dec))) was prepared by the reported method.[1] The size of the sample used for the X-ray measurement was about $0.5\times0.5\times0.25$ mm³. The crystal data are summarized in Table 1. The cell dimensions and reflection intensities were measured on a Rigaku four-circle diffractometer using Cu $K\alpha$ radiation ($\lambda=1.5418$ Å) monochromated with an LiF crystal. The intensity measurement was made by the θ-2θ continuous-scan technique at a 2θ scan rate of 2° min^{-1}; the background was measured for 20—30 s at each end of the scan range. Three standard reflections, measured at intervals of every 62 reflections, showed no significant decrease in intensity during the course of data collection. The intensities were corrected for the Lorentz and polarization factors, but not for the absorption or the extinction effect. In the range of 2θ values up to 140°, 6625 unique structure factor magnitudes above the $3\sigma(F)$ level were selected for the structure determination.

TABLE 1. THE CRYSTAL DATA

$C_{24}H_{16}$	M.W. 304.39
Triclinic	
Space group	$P\bar{1}$
Cell dimensions	$a=15.061(3)$Å
	$b=17.687(4)$Å
	$c=13.091(4)$Å
	$\alpha=108.91(3)°$
	$\beta=98.52(3)°$
	$\gamma=89.71(3)°$
V	3259.2 Å³
Z	8
D_x	1.241 g cm^{-3}
μ(Cu $K\alpha$)	4.98 cm^{-1}

Structure Determination

The structure was solved by the symbolic-addition method.[3] The space group was assumed to be $P\bar{1}$; this choice was later confirmed by a successful refinement. Of the phases of the 1016 reflections with $|E|$ values above 1.70, 408 were expressed in terms of 8 symbols. Since one of the 2^8 possible combinations of the symbol values led to a phase set showing a low R_K value of 0.240 ($R_K=\sum||E_o|-k|E_c||/\sum|E_o|$) and a nonzero q value[4] of 0.368 ($q=1-\sum_h|E_h|(|\sum_k E_kE_{h-k}|/\sum_k|E_kE_{h-k}|)/\sum_h|E_h|$), this phase set was further extended by the use of 1827 $|E|$ values above 1.40; the R_k and q values thus became 0.288 and 0.496 respectively. An E-map based on 1632 phases afforded two superimposed molecular arrangements which were related to each other by the center of symmetry, and each of which might be taken as centrosymmetric. These molecular arrangements could be easily resolved from a consideration of the molecular packing.

The structure thus obtained was refined by the block-diagonal-matrix least-squares method. After all the 64 hydrogen atoms had been located in a difference Fourier map, a further least-squares refinement was done including the hydrogen atoms with isotropic temperature factors. The weighting scheme used was as follows: $w=1/\{\sigma(F)^2\exp(AX^2+BY^2+CXY+DX+EY)\}$, where $X=|F_o|$ and $Y=\sin\theta/\lambda$. The A, B, C, D, and E coefficients are constants which were determined from the $(\Delta F)^2$ values; $A=0.2254\times10^{-4}$, $B=8.219$, $C=0.05559$, $D=-0.01387$, and $E=-7.770$. The final R value was 0.101. The final atomic parameters are listed in Table 2. The tables of the anisotropic temperature factors and hydrogen parameters, and those of the observed and calculated structure factors, are kept at the Chemical Society of Japan (Document No. 8126).

The calculations were performed on a FACOM 230-75 computer at the Hokkaido University Computing

Table 2. The final atomic parameters and estimated standard deviations
The coordinates are multiplied by 10^4.

Atom	x	y	z	B_{eq}[a)]/Å^2	Atom	x	y	z	B_{eq}[a)]/Å^2
C(A1)	− 870(4)	2142(3)	1241(5)	5.14	C(C1)	5937(4)	2930(3)	1602(5)	4.59
C(A2)	− 625(4)	2940(3)	1821(6)	5.30	C(C2)	6750(4)	3017(4)	2259(6)	5.37
C(A3)	− 579(4)	3227(3)	2917(6)	4.84	C(C3)	6787(4)	3300(3)	3374(6)	5.32
C(A4)	− 761(4)	2734(3)	3503(5)	4.17	C(C4)	6009(4)	3481(3)	3829(5)	4.42
C(A4a)	−1022(4)	1938(3)	2948(5)	3.65	C(C4a)	5191(3)	3366(3)	3178(5)	3.44
C(A5)	−1290(4)	1332(3)	3460(5)	3.60	C(C5)	4308(3)	3529(3)	3587(4)	3.40
C(A6)	− 738(3)	788(3)	3577(4)	3.33	C(C6)	3752(3)	2921(3)	3490(5)	3.60
C(A6a)	162(4)	749(3)	3213(5)	3.78	C(C6a)	4008(3)	2069(3)	2976(5)	3.56
C(A7)	968(4)	984(3)	3880(5)	4.38	C(C7)	4257(4)	1556(3)	3582(5)	4.77
C(A8)	1755(4)	965(3)	3464(6)	5.39	C(C8)	4457(4)	765(4)	2994(6)	6.05
C(A9)	1723(4)	687(3)	2330(6)	5.66	C(C9)	4382(4)	513(3)	1896(6)	6.01
C(A10)	924(4)	427(3)	1660(5)	4.90	C(C10)	4130(4)	1016(3)	1281(5)	4.52
C(A10a)	131(4)	460(3)	2062(5)	3.78	C(C10a)	3956(3)	1808(3)	1856(5)	3.44
C(A11)	− 791(4)	214(3)	1420(5)	3.78	C(C11)	3651(3)	2412(3)	1309(5)	3.60
C(A12)	−1355(4)	754(3)	1302(5)	4.32	C(C12)	4223(4)	3019(3)	1409(5)	3.60
C(A12a)	−1055(4)	1629(3)	1818(5)	4.03	C(C12a)	5141(3)	3085(3)	2026(5)	3.70
C(A13)	−2346(4)	591(3)	927(6)	5.36	C(C13)	3908(4)	3764(3)	1148(5)	4.30
C(A14)	−2986(4)	771(4)	1546(6)	6.27	C(C14)	3786(4)	4469(3)	1917(6)	5.58
C(A15)	−2963(4)	1103(3)	2730(6)	5.45	C(C15)	3851(4)	4733(3)	3089(6)	5.06
C(A16)	−2280(4)	1312(3)	3534(6)	5.08	C(C16)	4024(4)	4366(3)	3817(5)	4.24
C(A17)	−1005(4)	71(3)	3864(5)	4.05	C(C17)	2774(4)	3006(3)	3598(5)	4.71
C(A18)	−1171(4)	− 663(3)	3118(5)	4.44	C(C18)	2092(4)	2832(3)	2814(6)	5.38
C(A19)	−1198(4)	− 973(3)	1957(6)	4.94	C(C19)	2038(4)	2557(4)	1611(6)	5.83
C(A20)	−1071(4)	− 648(3)	1188(5)	4.72	C(C20)	2662(4)	2401(3)	960(5)	4.85
C(B1)	− 552(4)	5174(3)	8480(5)	4.81	C(D1)	5526(4)	−1497(3)	1498(5)	4.73
C(B2)	−1305(4)	5345(3)	7885(6)	5.72	C(D2)	6293(4)	−1044(3)	2104(6)	5.13
C(B3)	−1471(4)	5055(4)	6778(6)	5.46	C(D3)	6452(4)	− 810(3)	3206(6)	5.15
C(B4)	− 862(4)	4556(3)	6210(5)	4.36	C(D4)	5830(4)	−1029(3)	3771(5)	4.60
C(B4a)	− 105(3)	4364(3)	6790(5)	3.41	C(D4a)	5068(3)	−1487(3)	3183(5)	3.39
C(B5)	634(3)	3881(3)	6281(5)	3.28	C(D5)	4334(4)	−1736(3)	3681(5)	3.60
C(B6)	798(3)	3170(3)	6400(4)	2.98	C(D6)	4178(3)	−2508(3)	3574(5)	3.56
C(B6a)	236(3)	2797(3)	6954(4)	2.86	C(D6a)	4752(3)	−3149(3)	2983(5)	3.36
C(B7)	− 384(3)	2162(3)	6419(5)	3.82	C(D7)	5365(4)	−3543(3)	3495(5)	4.27
C(B8)	− 870(4)	1848(3)	7026(6)	5.02	C(D8)	5838(4)	−4141(4)	2857(6)	5.56
C(B9)	− 752(4)	2151(4)	8122(6)	5.26	C(D9)	5692(4)	−4362(3)	1743(6)	5.50
C(B10)	− 122(4)	2778(3)	8679(5)	4.62	C(D10)	5072(4)	−3981(3)	1222(5)	4.62
C(B10a)	352(3)	3116(3)	8104(5)	3.29	C(D10a)	4597(3)	−3362(3)	1853(5)	3.34
C(B11)	1069(3)	3759(3)	8579(4)	3.42	C(D11)	3881(4)	−2917(3)	1394(5)	3.85
C(B12)	949(4)	4478(3)	8467(5)	3.58	C(D12)	4019(4)	−2149(3)	1488(5)	3.88
C(B12a)	74(4)	4674(3)	7927(5)	3.65	C(D12a)	4909(3)	−1717(3)	2046(5)	3.63
C(B13)	1732(4)	5053(3)	8609(6)	5.50	C(D13)	3265(4)	−1631(3)	1327(6)	5.32
C(B14)	2056(4)	5223(3)	7824(6)	5.65	C(D14)	2931(4)	−1095(3)	2134(6)	5.62
C(B15)	1860(4)	4926(3)	6644(6)	5.34	C(D15)	3107(4)	− 852(3)	3312(6)	5.50
C(B16)	1292(4)	4347(3)	5941(6)	4.82	C(D16)	3659(4)	−1106(3)	4004(5)	4.91
C(B17)	1679(4)	2788(3)	6192(5)	4.14	C(D17)	3316(4)	−2800(3)	3772(6)	4.88
C(B18)	2340(4)	2730(3)	6960(6)	4.85	C(D18)	2643(4)	−3214(3)	2994(6)	6.04
C(B19)	2467(4)	3017(3)	8146(6)	5.22	C(D19)	2500(4)	−3444(3)	1820(6)	5.90
C(B20)	1970(4)	3474(3)	8870(5)	5.14	C(D20)	2965(4)	−3313(3)	1129(6)	5.63

a) $B_{eq}=8\pi^2(u_1^2+u_2^2+u_3^2)/3$, where u_i is the root-mean-square deviation in the i-th principal axis of the thermal ellipsoid.

Center, using our own programs. The atomic scattering factors were taken from the International Tables.[5)]

Results and Discussion

The molecular framework thus obtained is shown in Fig. 1. The bond distances and angles are listed in Table 3, while the torsion angles are given in Fig. 2. From these results, it is concluded that the biphenylene dimer has the **3** structure. As may be seen in Fig. 2, of the four crystallographically-independent molecules, the A and C molecules have approximately the C_{2v} symmetry, while the B and D molecules are somewhat deformed, their symmetry being nearly C_2. The mean

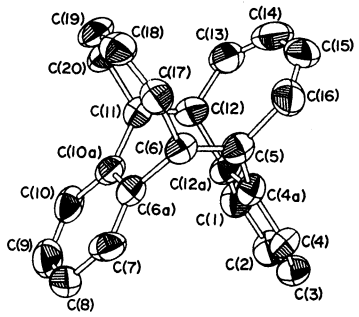


Fig. 1. A perspective view of the A molecule, and the numbering system of atoms. Carbon atoms are represented as thermal ellipsoids enclosing 50% probabilities. For the sake of clarity, hydrogen atoms are omitted.

values of the equivalent bond distances and angles for the four molecules are given in the last column of Table 3, the C_{2v} symmetry being assumed for all these molecules.

The mean lengths for the C(4a)–C(5) and C(5)–C(16) bonds, 1.499 and 1.500 Å, show that there is no appreciable conjugation between the C(5)=C(6) double bond and the benzene ring or the C(13)=C(14)–C(15)=C(16) diene part.[6] This can be explained by the fact that the mean magnitudes for the C(12a)–C(4a)–C(5)–C(6) and C(6)–C(5)–C(16)–C(15) torsion angles are 74 and 101° respectively. On the other hand, the mean length for C(14)–C(15), 1.450 Å, indicates that the C(13)=C(14) and C(15)=C(16) double bonds are thoroughly conjugated.

The central cyclooctatetraene ring takes a tub form. The bridging by the conjugated diene systems causes a close approach between the C(5)=C(6) and C(11)=C(12) double bonds; the average distance between the midpoints of these bonds is 2.67 Å, while the corresponding average for the C(4a)–C(12a) and C(6a)–C(10a) bonds is 2.85 Å. Because of this approach, the C(5)–C(4a)–C(12a) bond angle is somewhat shrunk, its mean value being 115.2°. The conjugated diene system further brings about a remarkable out-of-plane bending deformation[7] of the C(5)=C(6) and C(11)=C(12)

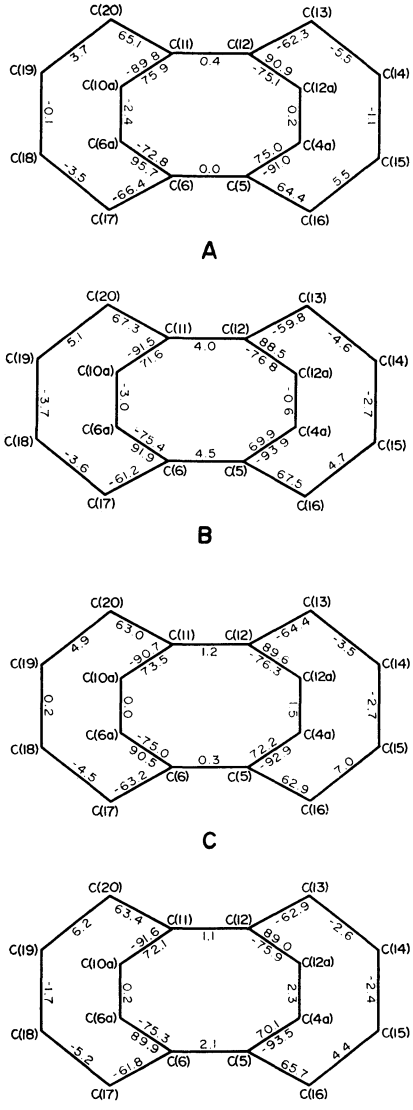


Fig. 2. The torsion angles (ϕ/°) for the tricyclo [6.4.-2.2^{2,7}]hexadeca-1,3,5,7,9,11,13,15-octaene skeletons. Only the torsion angles relevant to atoms which form the same ring are given in the ring.

Table 3. The bond distances (l/Å) and angles (ϕ/°), with their standard deviations
The standard deviations given in parentheses refer to the last decimal position.

	Mol. A	Mol. B	Mol. C	Mol. D	Mean[a]
C(1)–C(2)	1.391(7)	1.369(9)	1.366(8)	1.391(7)	
C(3)–C(4)	1.387(10)	1.394(8)	1.381(9)	1.402(10)	
C(7)–C(8)	1.371(9)	1.391(10)	1.416(8)	1.386(8)	
C(9)–C(10)	1.364(8)	1.393(8)	1.399(10)	1.376(9)	1.386(5)
C(1)–C(12a)	1.408(10)	1.405(8)	1.384(8)	1.382(9)	
C(4)–C(4a)	1.387(7)	1.378(8)	1.366(7)	1.383(7)	
C(6a)–C(7)	1.366(7)	1.390(6)	1.404(10)	1.379(8)	
C(10)–C(10a)	1.368(9)	1.373(10)	1.402(7)	1.406(7)	1.386(4)
C(2)–C(3)	1.349(10)	1.355(10)	1.373(10)	1.351(10)	
C(8)–C(9)	1.398(11)	1.344(10)	1.347(11)	1.364(11)	1.360(7)
C(4a)–C(12a)	1.394(8)	1.394(8)	1.417(8)	1.393(8)	
C(6a)–C(10a)	1.419(8)	1.411(8)	1.377(8)	1.385(8)	1.399(5)
C(4a)–C(5)	1.521(9)	1.501(7)	1.497(8)	1.498(9)	
C(6)–C(6a)	1.496(8)	1.474(8)	1.512(7)	1.500(7)	
C(10a)–C(11)	1.499(7)	1.485(7)	1.504(9)	1.500(8)	

Table 3. (Continued)

	Mol. A	Mol. B	Mol. C	Mol. D	Mean[a]
C(12)–C(12a)	1.515(7)	1.494(8)	1.479(7)	1.508(7)	1.499(3)
C(5)–C(6)	1.300(8)	1.334(8)	1.328(8)	1.343(8)	
C(11)–C(12)	1.306(8)	1.334(8)	1.340(8)	1.336(8)	1.328(6)
C(5)–C(16)	1.510(8)	1.495(9)	1.486(7)	1.506(8)	
C(6)–C(17)	1.506(9)	1.506(7)	1.503(8)	1.488(9)	
C(11)–C(20)	1.505(8)	1.485(8)	1.490(8)	1.493(8)	
C(12)–C(13)	1.499(8)	1.512(8)	1.522(9)	1.489(8)	1.500(3)
C(13)–C(14)	1.323(10)	1.316(11)	1.357(8)	1.331(9)	
C(15)–C(16)	1.316(8)	1.339(7)	1.312(10)	1.322(10)	
C(17)–C(18)	1.345(7)	1.335(9)	1.299(8)	1.349(8)	
C(19)–C(20)	1.346(11)	1.349(9)	1.329(10)	1.299(11)	1.329(4)
C(14)–C(15)	1.464(11)	1.446(10)	1.440(11)	1.443(11)	
C(18)–C(19)	1.434(9)	1.451(10)	1.480(11)	1.440(11)	1.450(5)
C(2)–C(1)–C(12a)	118.9(6)	118.9(6)	121.9(6)	118.7(6)	
C(3)–C(4)–C(4a)	119.3(6)	119.0(6)	120.6(6)	119.1(6)	
C(6a)–C(7)–C(8)	121.5(6)	119.6(5)	117.2(6)	118.6(6)	
C(9)–C(10)–C(10a)	121.8(6)	120.0(6)	117.1(6)	119.0(6)	119.5(4)
C(1)–C(2)–C(3)	121.0(7)	122.7(6)	119.3(6)	122.1(7)	
C(2)–C(3)–C(4)	121.2(5)	119.5(6)	120.5(5)	119.7(5)	
C(7)–C(8)–C(9)	118.7(5)	121.1(5)	121.1(7)	121.8(6)	
C(8)–C(9)–C(10)	120.1(6)	120.4(7)	122.3(5)	120.2(6)	120.7(3)
C(4)–C(4a)–C(12a)	120.1(6)	121.5(5)	119.7(5)	120.6(6)	
C(7)–C(6a)–C(10a)	119.8(6)	119.0(5)	121.0(5)	120.6(5)	
C(6a)–C(10a)–C(10)	118.0(5)	119.8(4)	121.2(6)	119.9(5)	
C(1)–C(12a)–C(4a)	119.5(5)	118.4(5)	118.0(5)	119.8(5)	119.8(3)
C(4)–C(4a)–C(5)	125.9(5)	124.5(5)	124.9(5)	124.6(5)	
C(6)–C(6a)–C(7)	125.9(5)	124.4(5)	123.0(5)	123.9(5)	
C(10)–C(10a)–C(11)	127.3(5)	126.2(5)	123.4(5)	124.7(5)	
C(1)–C(12a)–C(12)	125.1(5)	124.6(5)	127.3(6)	123.6(5)	125.0(3)
C(5)–C(4a)–C(12a)	114.0(4)	113.8(5)	115.5(4)	114.7(4)	
C(6)–C(6a)–C(10a)	114.3(4)	116.5(4)	115.9(5)	115.5(5)	
C(6a)–C(10a)–C(11)	114.7(5)	113.8(5)	115.3(4)	115.4(4)	
C(4a)–C(12a)–C(12)	115.3(6)	116.9(5)	114.7(5)	116.4(5)	115.2(2)
C(4a)–C(5)–C(6)	119.8(5)	120.3(6)	119.5(4)	121.3(5)	
C(5)–C(6)–C(6a)	120.9(6)	122.6(5)	120.4(5)	121.2(5)	
C(10a)–C(11)–C(12)	120.4(5)	120.5(5)	118.5(5)	121.1(5)	
C(11)–C(12)–C(12a)	118.7(5)	121.2(5)	120.9(6)	120.3(5)	120.5(3)
C(4a)–C(5)–C(16)	113.3(5)	114.2(5)	115.5(5)	113.4(5)	
C(6a)–C(6)–C(17)	114.5(4)	115.4(5)	114.2(4)	115.1(4)	
C(10a)–C(11)–C(20)	114.7(5)	114.4(5)	115.0(5)	114.2(5)	
C(12a)–C(12)–C(13)	115.3(5)	115.4(5)	115.6(4)	115.7(4)	114.7(2)
C(6)–C(5)–C(16)	125.2(6)	123.4(5)	123.2(5)	123.1(5)	
C(5)–C(6)–C(17)	123.5(5)	120.8(5)	123.7(5)	122.0(5)	
C(12)–C(11)–C(20)	123.2(5)	122.9(5)	124.4(5)	122.6(5)	
C(11)–C(12)–C(13)	124.4(5)	121.7(5)	121.9(5)	122.1(5)	123.0(3)
C(12)–C(13)–C(14)	126.7(6)	126.3(5)	123.9(6)	124.5(6)	
C(5)–C(16)–C(15)	128.3(7)	123.8(7)	125.3(5)	124.8(6)	
C(6)–C(17)–C(18)	122.8(6)	125.5(6)	127.3(6)	125.8(7)	
C(11)–C(20)–C(19)	124.5(5)	124.9(6)	126.4(6)	126.3(6)	125.4(3)
C(13)–C(14)–C(15)	132.6(6)	134.2(5)	134.3(7)	134.8(6)	
C(14)–C(15)–C(16)	130.8(6)	132.5(7)	133.0(5)	132.9(6)	
C(17)–C(18)–C(19)	133.6(7)	133.3(5)	131.8(6)	132.8(7)	
C(18)–C(19)–C(20)	134.4(5)	132.5(6)	132.6(5)	132.9(5)	133.1(3)
C–H[b]	1.04(1)				
C–C–H(Benzene)[b]	120(1)				
C=C–H (Octaene)[b]	119(1)				
C–C–H (Octaene)[b]	112(1)				

a) The mean value calculated for the four molecules on the assumption that they all have the C_{2v} symmetry. The standard deviation was estimated from the formula: $\sigma^2=\Sigma(x_i-\bar{x})^2/n(n-1)$. b) The mean value for the four molecules.

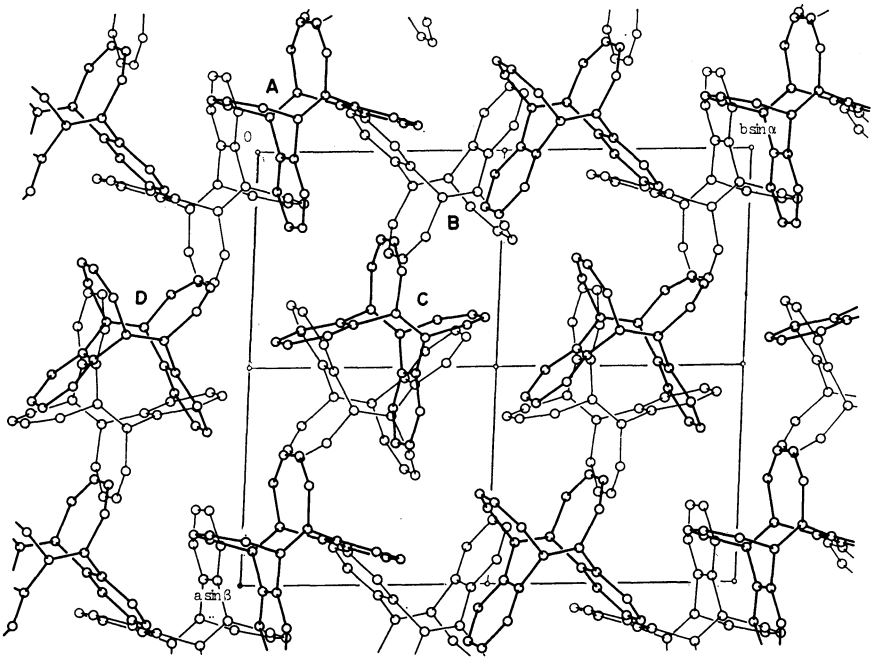


Fig. 3. The crystal structure viewed along the c axis.

Table 4. The projections (ϕ/°) of the bond angles along the C(5)=C(6) or C(11)=C(12) bond

	A	B	C	D
(1) Along C(5)=C(6)				
C(4a)–C(5)–C(16)	164.2	162.2	163.9	161.9
C(6a)–C(6)–C(17)	167.5	166.6	164.0	164.3
(2) Along C(11)=C(12)				
C(10a)–C(11)–C(20)	164.4	161.6	162.6	162.3
C(12a)–C(12)–C(13)	164.6	164.4	165.1	163.9

ethylenic groups (see Table 4); the average for the projected angle of C(4a)–C(5)–C(16) along the C(5)=C(6) double bond is 164°.

On the other hand, the restricted approach between the C(5)=C(6) and C(11)=C(12) double bonds results in an enlargement of the C(12)–C(13)=C(14) and C(13)=C(14)–C(15) bond angles; the averages for these bond angles are 125.4 and 133.1° respectively. Such a way of deformation of the two bond angles can be reproduced by the following simple calculation. If one assumes that the C(12)–C(13)=C(14)–C(15)=C(16)–C(5) moiety has the C_{2v} symmetry, the C(5)···C(12) distance, l, is expressed by:

$$l = l_1 - 2l_2 \cos\theta_1 + 2l_3 \cos(\theta_1+\theta_2), \quad (1)$$

where l_1, l_2, and l_3 are the C(14)–C(15), C(13)=C(14), and C(12)–C(13) distances respectively, and where θ_1 and θ_2 are the C(13)=C(14)–C(15) and C(12)–C(13)=C(14) angles respectively. If, as a first approximation, the change in the bond distortion of the C(5) and C(12) terminal atoms is neglected, the variable part of the strain energy due to the bond-angle deformation, ΔE, is given by:

$$\Delta E = k\{(\theta_1-\theta_0)^2 + (\theta_2-\theta_0)^2\}, \quad (2)$$

where k is the force constant for the deformation of the C=C–C bond angle and where θ_0 is the strainless C=C–C bond angle, for which 120° is assumed in the present calculation. When the average observed values of 1.450, 1.329, 1.500, and 2.675 Å are used for l_1, l_2, l_3, and l respectively, ΔE is minimized at $\theta_1=132°$ and $\theta_2=127°$ under the conditions of Eq. 1. These θ_1 and θ_2 values are in good agreement with their respective observed values. For $\theta_1=\theta_2=120°$, $(\partial l/\partial\theta_1)$ is greater than $(\partial l/\partial\theta_2)$ by a factor of 1.886, while $(\partial\Delta E/\partial\theta_1)$ is equal to $(\partial\Delta E/\partial\theta_2)$; that is, the enlargement of θ_1 can separate the C(5) and C(12) atoms more effectively than that of θ_2. This explains why, in both the observed and calculated geometries, θ_1 is greater than θ_2.

In all four molecules, the C(14) and C(15) atoms deviate slightly from the least-squares plane for the C(5), C(12), C(13), and C(16) atoms onto the side of the benzene ring (C(1), C(2), C(3), C(4), C(4a), and C(12a)); the average for the dihedral angle between this plane and the least-squares plane of the C(13)=C(14)–C(15)=C(16) part is 3.9°.

The crystal structure viewed along the c axis is shown in Fig. 3. The orientations of the four independent molecules are somewhat different from one another. All the intermolecular contacts correspond to the normal van der Waals interactions.

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