Crystal and Molecular Structures of (−)-7,7′-Dibromo-3,3,3′,3′,5,5′-hexamethyl-1,1′-spirobi-indane-6,6′-diol and (±)-3,3,3′,3′,5,5′-Hexamethyl-1,1′-spirobi-indane

By **Motoo Shiro,*** **Sanji Hagishita,** and **Kooru Kuriyama,** Shionogi Research Laboratory, Shionogi & Co., Ltd. Fukushimaku, Osaka 553, Japan

The crystal structures of (−)-7,7′-dibromo-3,3,3′,3′,5,5′-hexamethyl-1,1′-spirobi-indane-6,6′-diol (I) and (±)-3,3,3′,3′,5,5′-hexamethyl-1,1′-spirobi-indane (II) have been determined [by the heavy-atom method for (I) and direct methods for (II)] from *X*-ray diffractometer data. Crystals of (I) are orthorhombic, space group $P2_12_12_1$, a = 19.625(2), b = 7.644(1), c = 14.021(2) Å, Z = 4. Crystals of (II) are monoclinic, space group $C2/c$, a = 21.699(2), b = 14.222(1), c = 6.173(1) Å, β = 97.78(1)°, Z = 4 (the molecules lie at the two-fold axes in the crystal). The structures were refined by a block-diagonal least-squares method to R, 0.083 for (I) (1 244 reflections) and 0.066 for (II) (974 reflections). The cyclopentene rings are in the envelope conformation in (I) and (II). The dihedral angle between the two benzene ring planes is 81 (I) and 75.5° (II). The absolute configuration of (I) indicates that the molecule has the (*R*)-configuration.

THE c.d. spectral studies of an extensive series of optically active 3,3,3′,3′-tetramethyl-1,1′-spirobi-indanes and 1,1′-spirobi-indanols have been reported.[1-3] In those spirobi-indanes, the two aromatic chromophores aree linked to a spiro-carbon atom and fixed in a relatively rigid geometry. The absolute configurations of those molecules were determined by the analysis of the c.d. spectrum, taking into consideration that the signs of the Cotton effects associated with the *p*-band region result mainly from the dipole–dipole coupling mechanism.[4] It was shown, by use of an improved theoretical method,[2] that the Cotton effects especially associated with the α-band region were influenced to some extent by homoconjugation between the two benzene chromophores and by the magnetic moment in the direction perpendicular to the benzene plane. Those absolute configurations were confirmed by the results of *X*-ray crystal-structure analysis of (−)-7,7′-dibromo-3,3,3′,3′,5,5′-hexamethyl-1,1′-spirobi-indane-6,6′-diol (I), and later by chemical evidence [5] and Horeau's method.[6]

Although the two bromine atoms were introduced in order that the absolute configuration of (I) could be easily determined, their presence prevented precise determination of molecular dimensions. The crystal structure analysis of (±)-3,3,3′,3′,5,5′-hexamethyl-1,1′-spirobi-indane (II) was therefore carried out to provide the detailed structure of the 1,1′-spirobi-indane skeleton.

EXPERIMENTAL

Samples were prepared by the methods of refs. 1 and 3, and crystals obtained by slow evaporation of ethanol solutions. Preliminary *X*-ray photographs gave space group and unit-cell dimensions. More accurate cell constants were obtained from a least-squares fit of 12 reflections measured by diffractometer. Systematic absences indicated the space group of (II) to be Cc or $C2/c$. The latter centrosymmetric space group was initially assumed since Z was equal to 4 and the crystals were racemic; it was verified by the subsequent successful crystal structure refinement. Crystal data are given in Table 1.

Three-dimensional intensity data were collected on a Hilger and Watts Y 290 diffractometer equipped with scintillation counter and pulse-height analyser. Integrated intensities were measured by the θ—2θ scan technique by use of zirconium-filtered Mo-K_α radiation. Each reflection

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[1] S. Hagishita, K. Kuriyama, M. Hayashi, Y. Nakano, K. Shingu, and M. Nakagawa, *Bull. Chem. Soc. Japan*, 1971, **44**, 496.

[2] S. Hagishita and K. Kuriyama, *Bull. Chem. Soc. Japan*, 1971, **44**, 617.

[3] S. Hagishita, K. Kuriyama, K. Shingu, and M. Nakagawa, *Bull. Chem. Soc. Japan*, 1971, **44**, 2177.

[4] J. A. Schellman, *Accounts Chem. Res.*, 1968, **1**, 144; J. G. Kirkwood, *J. Chem. Phys.*, 1937, **5**, 479.

[5] R. K. Hill and D. A. Cullison, *J. Amer. Chem. Soc.*, 1973, **95**, 1299.

[6] J. H. Brewster and R. T. Prudence, *J. Amer. Chem. Soc.*, 1973, **95**, 1217.

was integrated in 80 steps at intervals of 0.01° s^{-1}. Backgrounds were counted for 20 s on both sides of each reflection. One standard reflection monitored every 10 reflections showed no significant change in intensity during data collection. All intensities were corrected for Lorentz and polarization factors, but not for absorption effects.

TABLE 1

Crystal data for (I) and (II)

	(I) $C_{23}H_{26}O_2Br_2$	(II) $C_{23}H_{28}$
M	494.3	304.5
a/Å	19.625(2)	21.699(2)
b/Å	7.644(1)	14.222(1)
c/Å	14.021(2)	6.173(1)
β/°		97.78(1)
U/Å^3	2 103.3	1 887.5
D_c/g cm^{-3}	1.56	1.07
D_m(flotation)/g cm^{-3}	1.53	1.06
Z	4	4
Crystal size/mm	0.2 × 0.2 × 0.2	0.3 × 0.3 × 0.3
μ(Mo-K_α)/cm^{-1}	41.4	0.7
Systematic absences	$h00$, h odd; $0k0$ k odd; $00l$, l odd	hkl, $h + k$ odd; $h0l$ l odd
Space group	$P2_12_12_1$	$C2/c$ (or Cc)
Number of reflections measured		
Total no. reflections	1 514	1 406
No. obs.	1 244	974
$\theta_{max.}$/°	22.0	23.5

Intensity data for (II) were collected in two equivalent regions, and corresponding structure factors in these sets then averaged to give the unique reflection data for the monoclinic crystal. The structure factors for which the differences were >3 σ were not used in the structure refinement.

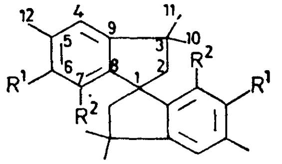
Structure Determination and Refinement.—(I) (−)-7,7′-*Dibromo*-3,3,3′,3′,5,5′-*hexamethyl*-1,1′-*spirobi-indane*-6,6′-*diol*. The structure was solved by conventional heavy-atom method. The electron-density map based on the phases contributed only by the two bromine atoms revealed the positions of all the light atoms except hydrogen. After block-diagonal least-squares refinement a difference electron-density map was calculated, but the positions of the hydrogen atoms, especially those in the methyl groups, could not be distinctly detected. Hence they were excluded from the structure-factor calculation. The absolute configuration of the molecule was determined by the anomalous-dispersion method, differences between the intensities of the Bijvoet pairs hkl and hkl being estimated from c-axis oscillation photographs taken with Cr-K_α radiation. Structure factors were calculated with a scattering factor for Br atom of the form: $f_{Br} + \Delta f'_{Br} + i\Delta f''_{Br}$ where $\Delta f'_{Br} = -0.6$ and $\Delta f''_{Br} = 2.7$. Successive least-squares refinements were carried out on the positional parameters and the thermal parameters which were anisotropic for the two Br atoms and isotropic for the light atoms. $\Delta f'_{Br} = -0.3$ and $\Delta f''_{Br} = 2.6$ for Mo-K_α radiation were used. The final refinement gave R 0.083 for 1 244 reflections.* The absolute configuration was ascertained by use of the counter data (see Supplementary Publication).

(II) (±)-3,3,3′,3′,5,5′-*Hexamethyl*-1,1′-*spirobi-indane*. The structure was solved by use of the program MULTAN [7] with local modifications on a FACOM 270 30 computer. In the E map based on the solution of the highest figure-of-merit, the molecules lying at the two-fold axes were located. 203 E values ($E \geq 1.6$) were used for the calculation of the E map. After the co-ordinates and isotropic temperature factors were refined by block-diagonal least-squares method, a difference electron-density map was calculated, in which all the hydrogen atoms were located in positions not far from those expected on chemical grounds. They were given the isotropic temperature factors of the carbon atoms to which they were attached. The positional and thermal parameters of the hydrogen atoms were fixed in the subsequent refinement. Anisotropic refinement on the carbon atoms reduced R 0.066 for 974 reflections.

The standard deviation of each reflection was taken as $\sigma(F_o) = [\sigma_1{}^2(F_o) + c^2|F_o|^2]^{1/2}$, where $\sigma_1(F_o)$ is the estimated standard deviation depending on the counting error.[8] Values of c^2 were 0.002 11 for (I) and 0.001 26 for (II). The weighting scheme used for $\sqrt{w} = 1/\sigma(F_o)$ for $|F_c| \geq \sigma(F_o)$ and $\sqrt{w} = 0$ for $|F_c| < \sigma(F_o)$ or $|\Delta F| > 3\sigma(F_o)$. The function minimized in the refinement is $\Sigma(w|\Delta F|^2)$. The value $[\Sigma(w|\Delta F|^2)/(m - n)]^{1/2}$, where m is the number of structure factors in the summation and n is the number of variables, was 1.127 for (I) and 1.195 for (II). The parameter shifts in the final cycle were sufficiently small compared with their σ. Scattering factors were taken from ref. 9.

RESULTS AND DISCUSSION

The formulae show the atom-numbering system used for each molecule. The two halves of molecule (II) are related by a two-fold axis, so that symmetry related atoms in one of a pair are primed in the other. The atoms in (I) are numbered similarly.



Atom-numbering system used for (I) and (II). (I): $R^1 = OH$, $R^2 = Br$. (II): $R^1 = R^2 = H$

For (I), positional and thermal parameters, with their estimated standard deviations, are listed in Table 2. The molecular structure in a right-handed co-ordinate system indicates the absolute configuration. It can be concluded that molecule (I) has the (R)-configuration. Corresponding information for (II) is given in Table 3. The molecular dimensions of (I) are of low precision because of the rather large estimated standard deviations of the positional parameters.

Bond distances and angles for (I) and (II), involving only heavy atoms, are shown in Tables 4 and 5. Bond lengths in (I) and (II) are all as expected. Bond angles around C(1) in (I) are compatible with the corresponding

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* Observed and calculated structure amplitudes for both compounds, and details of Bijvoet pairs for (I), are listed in Supplementary Publication No. SUP 21762 (8 pp.). For details see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

[7] P. Main, G. Germain, and M. M. Woolfson, 'MULTAN: A System of Computer Programs for the Automatic Solution of Noncentrosymmetric Crystal Structure,' University of York.

[8] D. F. Grant, R. C. G. Killean, and J. L. Lawrence, *Acta Cryst.*, 1969, **B25**, 374.

[9] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

TABLE 2

Fractional co-ordinates for non-hydrogen atoms ($\times 10^4$ for Br, others $\times 10^3$), and isotropic thermal parameters, with estimated standard deviations in parentheses, for (I). Values for primed atoms are on the right-hand side

	x	y	z	$B/\text{Å}^2$	x	y	z	$B/\text{Å}^2$
Br	2 442(1)	7 402(3)	−202(1)	*	1 694(1)	7 561(3)	2 694(1)	*
C(1)	211(1)	408(2)	134(1)	2.4(3)				
C(2)	169(1)	298(2)	203(1)	3.3(3)	256(1)	298(2)	66(1)	3.7(3)
C(3)	96(1)	278(2)	168(1)	2.4(3)	328(1)	290(2)	106(1)	3.1(3)
C(4)	33(1)	507(2)	62(1)	2.7(3)	383(1)	515(2)	218(1)	3.7(4)
C(5)	38(1)	643(2)	−3(1)	3.2(3)	378(1)	657(2)	283(1)	3.7(3)
C(6)	100(1)	702(2)	−29(1)	3.7(3)	311(1)	729(2)	294(1)	2.6(3)
C(7)	160(1)	642(2)	17(1)	2.4(3)	257(1)	652(2)	245(1)	2.4(3)
C(8)	157(1)	505(2)	80(1)	2.3(3)	263(1)	514(2)	184(1)	2.3(3)
C(9)	91(1)	442(2)	103(1)	2.7(3)	329(1)	444(2)	175(1)	2.4(3)
C(10)	46(1)	289(2)	251(1)	4.7(4)	383(1)	300(2)	31(1)	4.1(4)
C(11)	83(1)	117(2)	107(1)	4.5(4)	339(1)	118(2)	164(1)	4.0(4)
C(12)	−25(1)	730(3)	−47(1)	6.1(5)	435(1)	736(2)	333(1)	4.6(4)
O	104(1)	844(2)	−94(1)	5.0(3)	303(1)	865(2)	355(1)	3.7(2)

* The anisotropic temperature factor of the form: $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$, with parameters ($\times 10^4$):

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	26(1)	217(4)	68(1)	−49(3)	9(1)	92(5)
Br′	24(1)	205(3)	59(1)	35(3)	8(1)	−44(5)

TABLE 3

(*a*) Fractional co-ordinates and thermal parameters for non-hydrogen atoms of (II), all $\times 10^4$. The form of the anisotropic temperature factor is defined in Table 2

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	0(0)	2 559(3)	7 500(0)	23(1)	54(2)	300(14)	0(0)	25(6)	0(0)
C(2)	393(2)	3 148(2)	9 317(5)	29(1)	64(2)	320(10)	−10(2)	47(5)	−44(8)
C(3)	1 063(1)	3 207(2)	8 719(5)	25(1)	59(2)	338(10)	−7(2)	32(5)	−20(7)
C(4)	1 608(1)	1 947(2)	6 578(5)	22(1)	71(2)	355(11)	−6(2)	34(5)	10(8)
C(5)	1 539(1)	1 177(2)	5 174(5)	27(1)	69(2)	314(10)	4(2)	52(5)	14(8)
C(6)	953(2)	822(2)	4 539(5)	31(1)	59(2)	320(11)	1(2)	47(5)	−29(7)
C(7)	430(1)	1 217(2)	5 239(5)	26(1)	64(2)	295(10)	1(2)	23(5)	−24(7)
C(8)	502(1)	1 989(2)	6 615(5)	24(1)	49(2)	257(8)	1(2)	30(4)	21(6)
C(9)	1 091(1)	2 349(2)	7 287(5)	23(1)	55(2)	248(9)	−2(2)	18(4)	11(6)
C(10)	1 552(2)	3 193(3)	10 753(6)	37(1)	95(3)	414(13)	3(3)	−25(6)	−107(10)
C(11)	1 154(2)	4 091(2)	7 386(7)	38(1)	63(2)	533(15)	−15(3)	95(7)	−30(9)
C(12)	2 105(2)	752(3)	4 347(6)	38(1)	91(3)	478(15)	14(3)	116(7)	−23(11)

(*b*) Hydrogen atom parameters for (II)

	x	y	z	$B/\text{Å}^2$		x	y	z	$B/\text{Å}^2$
H[C(2)]	0.021	0.385	0.932	5.0	H″[C(10)]	0.197	0.310	1.023	6.7
H′[C(2)]	0.036	0.270	1.086	5.0	H[C(11)]	0.115	0.468	0.836	6.1
H[C(4)]	0.200	0.220	0.696	5.0	H′[C(11)]	0.082	0.410	0.600	6.1
H[C(6)]	0.091	0.025	0.368	5.0	H″[C(11)]	0.162	0.415	0.668	6.1
H[C(7)]	0.003	0.105	0.473	4.8	H[C(12)]	0.250	0.115	0.500	6.8
H[C(10)]	0.149	0.369	1.177	6.7	H′[C(12)]	0.206	0.010	0.432	6.8
H′[C(10)]	0.155	0.260	1.155	6.7	H″[C(12)]	0.212	0.100	0.273	6.8

TABLE 4

Bond lengths (Å) for (I) and (II), with estimated standard deviations in parentheses. For (I), values for primed atoms follow

	(I)		(II)
Br–C(7)	1.89(1)	1.93(1)	
C(1)–C(2)	1.53(2)	1.55(2)	1.558(4)
C(2)–C(3)	1.51(2)	1.52(2)	1.551(5)
C(1)–C(8)	1.49(2)	1.48(2)	1.518(4)
C(3)–C(9)	1.55(2)	1.52(2)	1.512(4)
C(4)–C(5)	1.38(2)	1.41(2)	1.393(5)
C(5)–C(6)	1.35(2)	1.43(2)	1.375(4)
C(6)–C(7)	1.42(2)	1.38(2)	1.387(5)
C(7)–C(8)	1.38(2)	1.36(2)	1.385(4)
C(8)–C(9)	1.41(2)	1.40(2)	1.387(4)
C(4)–C(9)	1.39(2)	1.33(2)	1.383(4)
C(3)–C(10)	1.52(2)	1.52(2)	1.529(5)
C(3)–C(11)	1.52(2)	1.56(2)	1.531(5)
C(5)–C(12)	1.53(3)	1.46(2)	1.518(5)
C(6)–O	1.42(2)	1.36(2)	

ones in (II). In (I), however, the angle C(8)–C(1)–C(8′) seems to be larger than C(2)–C(1)–C(2′), though in (II) these are almost the same. The difference is probably due to steric effects of the two bromine atoms.

The least-squares planes through the four atoms C(1), C(3), C(8), C(9) in the five-membered ring and the six atoms in the benzene ring are given in Table 6. The dihedral angles between both benzene ring planes are 81 and 75.5° in (I) and (II), respectively.

Torsion angles in the cyclopentene are shown in Table 7. The displacements of C(2) [or C(2′)] atom from the plane of the other four atoms in the five-membered ring are 0.34 and 0.34 in (I), and 0.390 Å in (II). The rings are thus in the envelope conformation just like those in (−)-(*S*)-spiro[4,4]nonane-1,6-dione,[10] 3,3′-spiro-

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[10] C. Altona, R. A. G. de Graaff, C. H. Leeuwestein, and C. Romers, *Chem. Comm.*, 1971, 1305.

TABLE 5

Bond angles (°) for (I) and (II), with estimated standard deviations in parentheses. For (I) values for primed atoms follow

	(I)	(II)
C(2)–C(1)–C(8)	102(1)	101.4(2)
C(2′)–C(1)–C(8′)	101(1)	101.4(2)
C(2)–C(1)–C(8′)	112(1)	112.1(2)
C(2′)–C(1)–C(8)	112(1)	112.1(2)
C(2)–C(1)–C(2′)	114(1)	115.0(2)
C(8)–C(1)–C(8′)	117(1)	115.4(2)

	(I)		(II)
C(1)–C(2)–C(3)	111(1)	109(1)	107.3(2)
C(2)–C(3)–C(9)	100(1)	102(1)	102.0(2)
C(2)–C(3)–C(10)	111(1)	113(1)	111.9(2)
C(2)–C(3)–C(11)	115(1)	111(1)	111.5(2)
C(9)–C(3)–C(10)	111(1)	113(1)	113.0(2)
C(9)–C(3)–C(11)	108(1)	109(1)	109.3(2)
C(10)–C(3)–C(11)	111(1)	108(1)	109.1(3)
C(5)–C(4)–C(9)	119(1)	123(1)	119.9(3)
C(4)–C(5)–C(6)	120(1)	115(1)	119.0(3)
C(4)–C(5)–C(12)	122(1)	125(1)	119.9(3)
C(6)–C(5)–C(12)	118(1)	120(1)	121.1(3)
C(5)–C(6)–C(7)	121(1)	119(1)	121.8(3)
C(5)–C(6)–O	119(1)	118(1)	
C(7)–C(7)–O	120(1)	124(1)	
Br–C(7)–C(6)	118(1)	114(1)	
Br–C(7)–C(8)	121(1)	121(1)	
C(6)–C(7)–C(8)	121(1)	125(1)	118.9(3)
C(1)–C(8)–C(9)	111(1)	113(1)	111.8(2)
C(1)–C(8)–C(7)	132(1)	131(1)	128.2(2)
C(7)–C(8)–C(9)	116(1)	116(1)	120.0(3)
C(3)–C(9)–C(8)	111(1)	110(1)	111.4(2)
C(3)–C(9)–C(4)	126(1)	128(1)	128.1(3)
C(4)–C(9)–C(8)	122(1)	122(1)	120.5(2)

TABLE 6

Equations of the least-squares plane and deviations (Å) of the atoms from the plane

The equation of plane is of the form $AX + BY + CZ = D$, where A, B, and C are the direction cosines referred to respective crystal axes, and X, Y, and Z are in Å. Values for primed atoms in (I) follow those for unprimed atoms

	(I)		(II)
Plane: C(1), C(3), C(8), C(9)			
A	−0.082 2	0.120 7	−0.029 1
B	0.609 9	0.600 3	−0.585 2
C	0.788 2	−0.790 6	0.806 8
D	3.021 5	0.909 6	1.606 2
C(1)	0.02	−0.02	−0.001
C(3)	−0.02	0.02	0.001
C(8)	−0.03	0.03	0.001
C(9)	0.03	−0.03	−0.001
C(2)	0.34	0.34	0.390
C(5)	−0.12	−0.14	−0.106
C(6)	−0.23	−0.09	−0.090
Plane: C(4)—(9)			
A	−0.077 9	0.158 4	−0.004 6
B	0.674 1	0.623 2	−0.612 0
C	0.734 6	−0.765 8	0.784 2
D	3.202 4	1.278 9	1.470 0
C(4)	0.00	0.02	0.003
C(5)	0.02	−0.01	−0.005
C(6)	−0.04	0.01	0.002
C(7)	0.03	−0.01	0.003
C(8)	−0.01	0.01	−0.005
C(9)	0.00	−0.02	0.001
C(1)	−0.04	−0.11	−0.067
C(2)	0.16	0.23	0.296
C(3)	−0.18	−0.02	−0.051
C(12)	0.11	0.01	−0.042
O	0.02	−0.02	
Br	0.02	−0.02	

bis(bicyclo[3.1.0]hexane)-2,2′-dione,[11] and (±)-2,2′-spirobi-indane-1,1′-dione.[12]

TABLE 7

Torsion angles (°) in the five-membered ring. The angle about the bond C(1)–C(2) is the dihedral angle between plane C(8)–C(1)–C(2) and plane C(1)–C(2)–C(3). Its value is positive if the normal of the latter plane takes a clockwise rotation referred to that of the former when viewed in the direction from C(1) to C(2). Values for primed atoms of (I) follow those for unprimed atoms

	(I)		(II)
C(8)–C(1)–C(2)–C(3)	20	23	23.7
C(1)–C(2)–C(3)–C(9)	−23	−20	−23.7
C(2)–C(3)–C(9)–C(8)	18	9	14.7
C(3)–C(9)–C(8)–C(1)	−6	6	0.2
C(9)–C(8)–C(1)–C(2)	−8	−18	−14.9

In the molecule of trindan[13] three five-membered rings are fused symmetrically around a benzene ring. Two of the three apical carbon atoms which correspond to C(2) [or C(2′)] in (I) and (II) are displaced by *ca.* 0.2 Å from the mean plane of the rest of the molecule; the other lies in the plane. The cyclopentene rings in this crystal structure adopt an envelope or a planar conformation. It was concluded that there are little changes in potential energy, as a function of the dis-

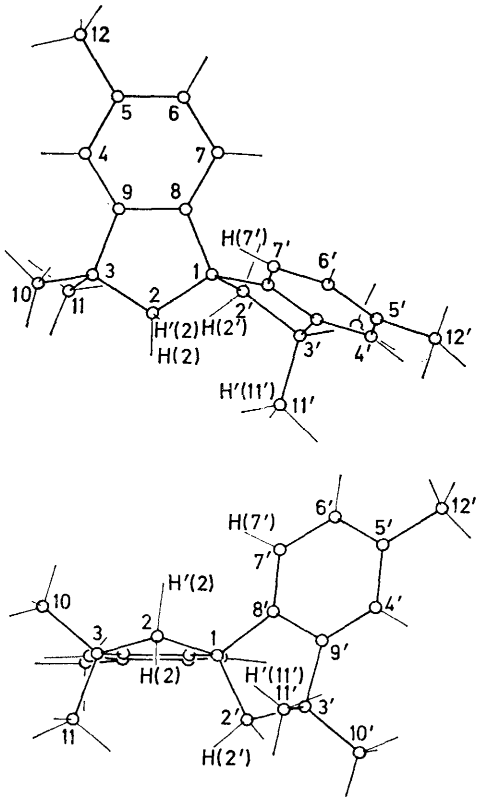

FIGURE 1 Perspective views of the molecule of (II)

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[11] F. H. Herbstein and H. Regev, *J. Chem. Soc.* (*B*), 1971, 1696.
[12] K. B. Petersen and J. Danielsen, *Acta Cryst.*, 1974, **B30**, 338.
[13] E. R. Boyko and P. A. Vaughan, *Acta Cryst.*, 1964, **17**, 152.

placements, in the vicinity of the plane, and that the packing effects operate partly on the actual form of each ring. Beckett *et al.*[14] argued that the potential energy is unchanged by displacements up to 0.3 Å in cyclopentene itself. In (I) and (II), however, the molecules with cyclopentene planar would not be stable owing to the respulsive interaction between H(2) and H(2′). If the cyclopentene with atoms with unprimed numbers takes the envelope form, with C(10) and C(8′) occupying quasi-axial positions, the other one takes a similar form, with C(10′) and C(8) at the quasi-axial positions, in order to reduce the repulsion between H(2) and H(2′). Molecules having such two rings would be also unfavourable because of the increase of repulsion between the C(10) [or C(10′)] methyl group and R^2 atoms. Thus, the two cyclopentenes appear to be fixed in the envelope form as shown in Figures 1 and 2. The distances H(2) $\cdots$ H′(11′), H(2) $\cdots$ H(2′), and H′(2) $\cdots$ H(7′) in (II) are 2.25, 2.31, and 2.51 Å, respectively.

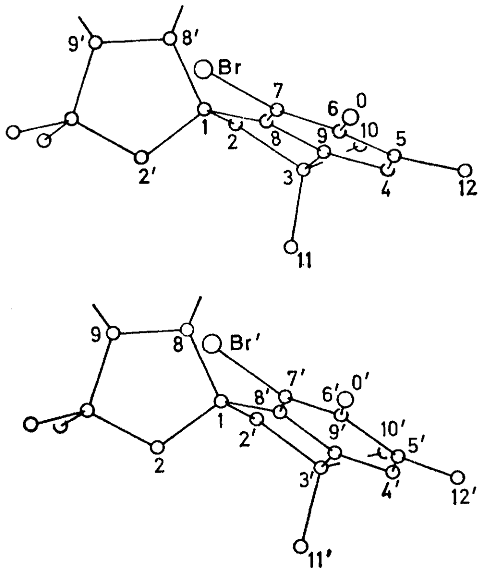

FIGURE 2 Projections viewed vertical to the plane of C(1), C(3), C(8), C(9) for (I)

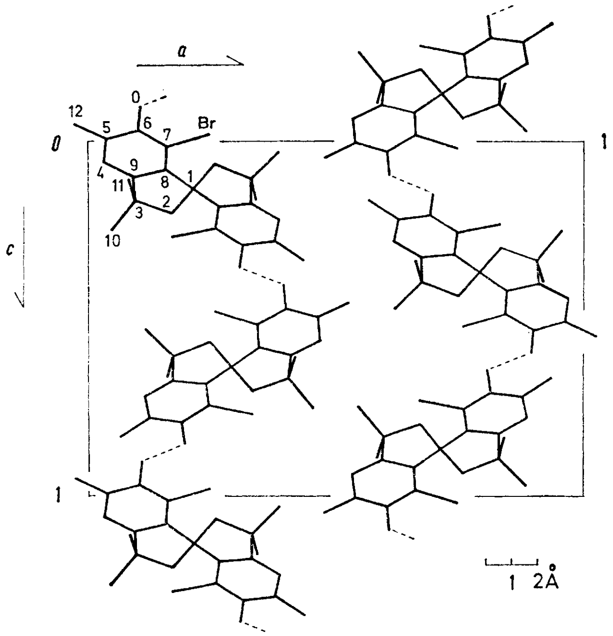

FIGURE 3 Crystal structure of (I), viewed down the *b* axis

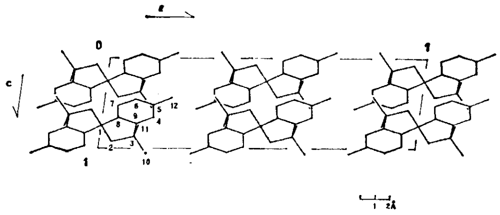

FIGURE 4 Crystal structure of (II), viewed down the *b* axis

The Br and Br′ atoms in (I) are brought close to C(8′) and C(8), respectively (Figure 2). These distances (3.37 and 3.28 Å) are within the van der Waals distances for C and Br or between the benzene plane and Br. This fact seems to support the argument [1] that exchange of electrons through overlap between the carbon π and the bromine lone-pair orbitals would be one reason for the absence of a coupling pattern in the Cotton effect in the *p*-band region.

TABLE 8

Short intermolecular distances (Å) in (I)

$\mathrm{C}(6') \cdots \mathrm{C}(11'^{\mathrm{I}})$	3.53	$\mathrm{Br} \cdots \mathrm{O}'^{\mathrm{IV}}$	3.61
$\mathrm{C}(11) \cdots \mathrm{O}^{\mathrm{II}}$	3.53	$\mathrm{O} \cdots \mathrm{C}(12'^{\mathrm{IV}})$	3.46
$\mathrm{C}(11') \cdots {}^{\mathrm{II}}$	3.38	$\mathrm{O} \cdots \mathrm{O}'^{\mathrm{IV}}$	2.96
$\mathrm{O} \cdots \mathrm{C}(11'^{\mathrm{III}})$	3.59	$\mathrm{C}(12) \cdots \mathrm{C}(4'^{\mathrm{V}})$	3.59
$\mathrm{C}(2') \cdots \mathrm{O}'^{\mathrm{III}}$	3.42		

Roman numeral superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I $x, 1 + y, z$
II $x, -1 + y, z$
III $\frac{1}{2} - x, 1 - y, -\frac{1}{2} + z$
IV $\frac{1}{2} - x, 2 - y, -\frac{1}{2} + z$
V $-\frac{1}{2} + x, \frac{3}{2} - y, -z$

TABLE 9

Short intermolecular distances (Å) in (II). There were no C $\cdots$ C distances <3.7 Å. Short contacts between methyl groups are listed with the shortest H $\cdots$ H distances in parentheses

$\mathrm{C}(10) \cdots \mathrm{C}(12^{\mathrm{I}})$	4.206(2.7)	$\mathrm{C}(10) \cdots \mathrm{C}(11^{\mathrm{IV}})$	4.114(2.7)
$\mathrm{C}(12) \cdots \mathrm{C}(12^{\mathrm{II}})$	3.755(2.6)	$\mathrm{C}(11) \cdots \mathrm{C}(12^{\mathrm{V}})$	4.070(2.3)
$\mathrm{C}(11) \cdots \mathrm{C}(11^{\mathrm{III}})$	4.026(2.6)	$\mathrm{C}(10) \cdots \mathrm{C}(12^{\mathrm{VI}})$	4.186(2.8)

Roman numeral superscripts refer to the following equivalent position relative to the reference molecule at x, y, z:

I $x, y, 1 + z$
II $x, -y, -\frac{1}{2} + z$
III $x, 1 - y, -\frac{1}{2} + z$
IV $x, 1 - y, \frac{1}{2} + z$
V $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$
VI $\frac{1}{2} - x, \frac{1}{2} - y, 2 - z$

Figures 3 and 4 indicate the crystal structures of (I) and (II). The molecules of (II) lie at two-fold axes in the crystal, with the C(1) atoms at those positions, so

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[14] C. W. Beckett, N. K. Freeman, and K. S. Pitzer, *J. Amer. Chem. Soc.*, 1948, **70**, 4227.

that the molecules have C_2 molecular symmetry. The molecules of (I) are arranged with their imaginary two-fold axes, supposedly like the true ones in (II), approximately parallel to the *b* axis. They are linked by hydrogen bonds (O · · · O 2.96 Å) to form a spiral chain around the 2_1 axis in the *c* direction. Short intermolecular distances are listed in Tables 8 and 9.

[6/046 *Received, 8th January,* 1976]