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## The Crystal Structure of 4b,9a-Dibromo-9,10-dihydroindeno[1,2-*a*]indene

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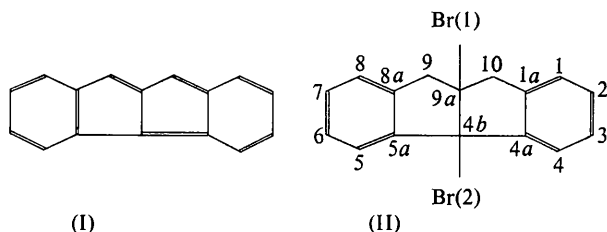
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Crystals of 4b,9a-dibromo-9,10-dihydroindeno[1,2-*a*]indene,  $C_{16}H_{12}Br_2$ , are monoclinic with cell dimensions of  $a=11.430$ ,  $b=7.794$ ,  $c=16.248$  Å,  $\beta=110.68^\circ$ ,  $Z=4$  and space group  $P2_1/c$ . The structure has been determined from three-dimensional X-ray data collected by photographic methods. Positional and thermal parameters were refined by the block-diagonal least-squares method to an  $R$  value of 0.10 for 1864 observed reflexions. The molecule is butterfly-shaped: two indane nuclei are fused with the C(4b)–C(9a) bond in common. It is folded at this C–C bond, the planes of the two indane rings making an angle of  $111^\circ$ . The conformation of the Br–C(4b)–C(9a)–Br group is staggered, and the distance between the two Br atoms is as short as 3.362 Å, indicating that the molecule is overcrowded.

### Introduction

An organic semiconductor, indeno[1,2-*a*]indene (I), originally synthesized by Haga & Miura (1969), is easily hydrogenated to form 9,10-dihydroindeno[1,2-*a*]indene. The double bond at the centre of the molecule is easily brominated to form 4b,9a-dibromo-9,10-dihydroindeno[1,2-*a*]indene (II). Inspection of a molecular model reveals that the *trans* dibromo isomer hardly exists owing to great strain in the molecule, and the *cis* dibromo isomer should be overcrowded because the Br...Br distance is as short as 2.8 Å. Thus, a *gauche* structure is most probable. All attempts to determine the chemical structure of the molecule by means of mass spectroscopy, nuclear magnetic resonance and infrared spectroscopy did not succeed. The crystal-structure analysis of the compound (II) was undertaken to establish the molecular structure and conformation.



### Experimental

The crystals used for X-ray analysis were grown from a carbon tetrachloride solution. They are colourless, transparent, and are stable to X-ray radiation in the air. Cell dimensions were obtained from Weissenberg photographs taken with Cu  $K\alpha$  radiation ( $\lambda=1.5418$  Å). Copper-powder diffraction lines were superposed on the films for calibration purposes.

Crystal data are: 4b,9a-dibromo-9,10-dihydroindeno[1,2-*a*]indene,  $C_{16}H_{12}Br_2$ , M.W. 364.08; monoclinic,  $a=11.430 \pm 0.006$ ,  $b=7.794 \pm 0.003$ ,  $c=16.248 \pm 0.006$  Å,  $\beta=110.68 \pm 0.06^\circ$ ,  $Z=4$ ,  $U=1354$  Å<sup>3</sup>,  $D_x=1.785$ ,  $D_m=1.778$  g.cm<sup>-3</sup>,  $F(000)=712$ ,  $\mu(\text{Cu } K\alpha)=82.4$  cm<sup>-1</sup>, space group  $P2_1/c$  (No. 14,  $C_{2h}^2$ ).

Intensities of reflexions were recorded on multiple-film equi-inclination Weissenberg photographs with Cu  $K\alpha$  radiation. Crystals of maximum dimensions 0.10 mm were used. Six layers,  $h0l \sim h5l$ , were collected around the  $b$  axis and three layers,  $0kl \sim 2kl$ , were collected around the  $a$  axis. Intensities were estimated visually by comparison with a standard scale. A total of 1864 independent reflexions was observed. The intensities covered a range of about 6000:1. Usual Lorentz and polarization corrections, and Phillips spot-shape corrections were made. Relative intensities were placed on an approximately absolute scale by Wilson's method.

## Structure determination

A three-dimensional Patterson synthesis was carried out. The Harker section at  $y=\frac{1}{2}$  contained no non-Harker peaks, so the Patterson peaks were straightforwardly interpreted, and the positions of the bromine atoms were deduced. These coordinates were used to calculate structure factors. A three-dimensional electron density map was then plotted with all the terms the signs of which were calculated on the basis of the bromine atoms. The resulting map showed all the carbon atoms in the molecule. Positional and thermal parameters were refined by the least-squares method with block-diagonal program *HBL5 IV* written by Dr Ashida.

A weighting scheme,  $w=(F_{\max}/F_o)^2$  (if  $F_o \geq F_{\max}$ , and  $w=1$  otherwise), was employed and scattering factors used were those listed in *International Tables for X-ray*

Table 1 (cont.)

Table 1. Observed and calculated structure factors

L	F0	FC	L	F0	FC	L	F0	FC	L	F0	FC	L	F0	FC	L	F0	FC	L	F0	FC	L	F0	FC
1	10	10	1	10	10	1	10	10	1	10	10	1	10	10	1	10	10	1	10	10	1	10	10
2	10	10	2	10	10	2	10	10	2	10	10	2	10	10	2	10	10	2	10	10	2	10	10
3	10	10	3	10	10	3	10	10	3	10	10	3	10	10	3	10	10	3	10	10	3	10	10
4	10	10	4	10	10	4	10	10	4	10	10	4	10	10	4	10	10	4	10	10	4	10	10
5	10	10	5	10	10	5	10	10	5	10	10	5	10	10	5	10	10	5	10	10	5	10	10
6	10	10	6	10	10	6	10	10	6	10	10	6	10	10	6	10	10	6	10	10	6	10	10
7	10	10	7	10	10	7	10	10	7	10	10	7	10	10	7	10	10	7	10	10	7	10	10
8	10	10	8	10	10	8	10	10	8	10	10	8	10	10	8	10	10	8	10	10	8	10	10
9	10	10	9	10	10	9	10	10	9	10	10	9	10	10	9	10	10	9	10	10	9	10	10
10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
11	10	10	11	10	10	11	10	10	11	10	10	11	10	10	11	10	10	11	10	10	11	10	10
12	10	10	12	10	10	12	10	10	12	10	10	12	10	10	12	10	10	12	10	10	12	10	10
13	10	10	13	10	10	13	10	10	13	10	10	13	10	10	13	10	10	13	10	10	13	10	10
14	10	10	14	10	10	14	10	10	14	10	10	14	10	10	14	10	10	14	10	10	14	10	10
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16	10	10	16	10	10	16	10	10	16	10	10	16	10	10	16	10	10	16	10	10	16	10	10
17	10	10	17	10	10	17	10	10	17	10	10	17	10	10	17	10	10	17	10	10	17	10	10
18	10	10	18	10	10	18	10	10	18	10	10	18	10	10	18	10	10	18	10	10	18	10	10
19	10	10	19	10	10	19	10	10	19	10	10	19	10	10	19	10	10	19	10	10	19	10	10
20	10	10	20	10	10	20	10	10	20	10	10	20	10	10	20	10	10	20	10	10	20	10	10
21	10	10	21	10	10	21	10	10	21	10	10	21	10	10	21	10	10	21	10	10	21	10	10
22	10	10	22	10	10	22	10	10	22	10	10	22	10	10	22	10	10	22	10	10	22	10	10
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42	10	10	42	10	10	42	10	10	42	10	10	42	10	10	42	10	10	42	10	10	42	10	10
43	10	10	43	10	10	43	10	10	43	10	10	43	10	10	43	10	10	43	10	10	43	10	10
44	10	10	44	10	10	44	10	10	44	10	10	44	10	10	44	10	10	44	10	10	44	10	10
45	10	10	45	10	10	45	10	10	45	10	10	45	10	10	45	10	10	45	10	10	45	10	10
46	10	10	46	10	10	46	10	10	46	10	10	46	10	10	46	10	10	46	10	10	46	10	10
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50	10	10	50	10	10	50	10	10	50	10	10	50	10	10	50	10	10	50	10	10	50	10	10
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55	10	10	55	10	10	55	10	10	55	10	10	55	10	10	55	10	10	55	10	10	55	10	10
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61	10	10	61	10	10	61	10	10	61	10	10	61	10	10	61	10	10	61	10	10	61	10	10
62	10	10	62	10	10	62	10	10	62	10	10	62	10	10	62	10	10	62	10	10	62	10	10
63	10	10	63	10	10	63	10	10	63	10	10	63	10	10	63	10	10	63	10	10	63	10	10
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65	10	10	65	10	10	65	10	10	65	10	10	65	10	10	65	10	10	65	10	10	65	10	10
66	10	10	66	10	10	66	10	10	66	10	10	66	10	10	66	10	10	66	10	10	66	10	10
67	10	10	67	10	10	67	10	10	67	10	10	67	10	10	67	10	10	67	10	10	67	10	10
68	10	10	68	10	10	68	10	10	68	10	10	68	10	10	68	10	10	68	10	10	68	10	10
69	10	10	69	1																			

conformation of the Br-C(5)-C(13)-Br group is staggered with a dihedral angle of  $34^\circ$  as seen in the Newman projection along the bond C(13)-C(5) (Fig. 4). This rather large twist is probably due to repulsion between the Br atoms. The Br...Br distance in the molecule is as short as 3.36 Å, indicating that the molecule is overcrowded. The angles Br(1)-C(5)-C(13) and Br(2)-C(13)-C(5) are  $113^\circ$  and  $116^\circ$ , respectively. The C(5)-C(13) bond of 1.58 Å is slightly longer than the normal value of 1.54 Å. These large

bond angles and the long distance also seem to result from the repulsion between the Br atoms.

Table 3 shows the deviations of the atoms from the best plane through the benzene rings. Both half-molecules are planar within the deviation 0.04 Å, except C(5); this carbon atom is displaced 0.48 and 0.46 Å from planes I and II, respectively. The carbon atom is on the same side of plane I as Br(1) is, whereas C(5) and Br(1) are displaced on the opposite side of plane II. The five-membered rings are both in the eclipsed

Table 2. Final atomic parameters and *e.s.d.*'s (all quantities  $\times 10^4$ )

Temperature factors are of the form:  $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + hkB_{12} + hlB_{13} + klB_{23})]$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>11</sub>	<i>B</i> <sub>22</sub>	<i>B</i> <sub>33</sub>	<i>B</i> <sub>12</sub>	<i>B</i> <sub>13</sub>	<i>B</i> <sub>23</sub>
Br(1)	8049 (1)	5440 (2)	5469 (1)	126 (1)	137 (3)	48 (1)	-44 (3)	69 (2)	-36 (2)
Br(2)	5579 (1)	2776 (2)	4940 (1)	69 (1)	190 (3)	37 (0)	25 (2)	36 (1)	4 (2)
C(1)	6388 (12)	-32 (20)	2255 (8)	80 (11)	248 (34)	31 (5)	-16 (28)	19 (12)	-43 (19)
C(2)	6903 (11)	1593 (20)	2512 (7)	75 (11)	272 (36)	26 (4)	39 (27)	20 (11)	18 (17)
C(3)	7123 (10)	2131 (14)	3364 (6)	75 (9)	86 (24)	28 (4)	-1 (20)	22 (10)	7 (13)
C(4)	7670 (11)	3861 (18)	3771 (7)	90 (11)	186 (31)	33 (5)	-41 (26)	37 (12)	4 (17)
C(5)	8075 (10)	3420 (16)	4782 (7)	81 (10)	126 (26)	33 (4)	-28 (22)	57 (11)	-26 (15)
C(6)	9363 (10)	2529 (15)	5160 (7)	64 (8)	126 (27)	36 (5)	8 (21)	42 (10)	6 (15)
C(7)	9156 (9)	1289 (15)	5799 (6)	69 (8)	105 (26)	29 (4)	4 (21)	23 (9)	-34 (13)
C(8)	10076 (12)	485 (16)	6504 (8)	91 (11)	153 (31)	33 (5)	35 (25)	-4 (12)	-46 (17)
C(9)	9703 (13)	-674 (17)	7020 (8)	122 (14)	125 (29)	36 (5)	63 (28)	24 (13)	29 (16)
C(10)	8470 (12)	-1053 (17)	6849 (7)	104 (12)	147 (30)	33 (5)	33 (28)	6 (12)	4 (17)
C(11)	7549 (11)	-228 (16)	6154 (6)	85 (10)	142 (27)	27 (4)	-27 (23)	26 (11)	18 (15)
C(12)	7897 (9)	905 (14)	5634 (6)	56 (8)	98 (23)	19 (3)	6 (19)	3 (8)	-19 (12)
C(13)	7135 (9)	1971 (14)	4839 (6)	71 (8)	98 (23)	18 (3)	-30 (20)	22 (8)	9 (12)
C(14)	6847 (9)	1071 (14)	3966 (6)	70 (8)	70 (23)	26 (4)	-10 (19)	24 (9)	-11 (12)
C(15)	6330 (10)	-534 (15)	3712 (7)	73 (10)	149 (30)	29 (4)	-18 (22)	25 (11)	-9 (14)
C(16)	6101 (11)	-1135 (20)	2859 (8)	78 (11)	226 (34)	37 (5)	-50 (27)	18 (12)	-42 (19)

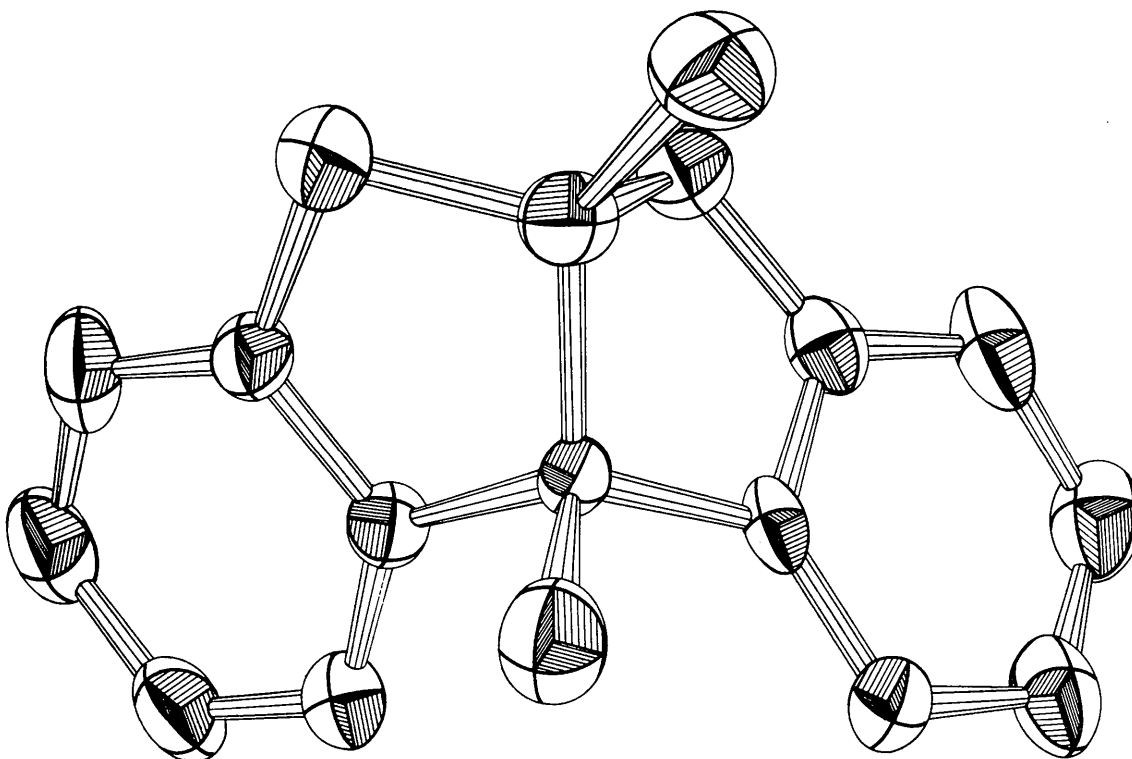


Fig. 1. Perspective drawing of the molecule showing ellipsoids of thermal motion with a 50% probability.



Table 4. *Interatomic distances (between the molecules) of less than 4 Å*

				Superscripts designate:			
'	$x$	$1+y$	$z$	vii	$x$	$\frac{1}{2}-y$	$-\frac{1}{2}+z$
''	$1-x$	$-y$	$1-z$	viii	$x$	$\frac{3}{2}-y$	$\frac{1}{2}+z$
'''	$1-x$	$1-y$	$1-z$	ix	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
iv	$2-x$	$-y$	$1-z$	x	$1-x$	$-\frac{3}{2}+y$	$\frac{1}{2}-z$
v	$2-x$	$1-y$	$1-z$	xi	$2-x$	$\frac{1}{2}+y$	$\frac{3}{2}-z$
vi	$x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$	xii	$2-x$	$-\frac{1}{2}+y$	$\frac{3}{2}-z$
	Br(1)···C(6 <sup>v</sup> )	3·800 (12)	C(2)····C(16 <sup>ix</sup> )	3·718 (19)			
	Br(1)···C(9 <sup>'</sup> )	3·966 (12)	C(3)····C(16 <sup>x</sup> )	3·766 (15)			
	Br(1)···C(10 <sup>'</sup> )	3·459 (13)	C(8)····C(1 <sup>iv</sup> )	3·843 (17)			
	Br(1)···C(11 <sup>'</sup> )	3·663 (13)	C(8)····C(2 <sup>iv</sup> )	3·633 (17)			
	Br(2)···Br(2 <sup>'''</sup> )	3·741 (2)	C(8)····C(3 <sup>iv</sup> )	3·737 (18)			
	Br(2)···C(1 <sup>vi</sup> )	3·954 (13)	C(8)····C(6 <sup>iv</sup> )	3·804 (18)			
	Br(2)···C(1 <sup>ix</sup> )	3·877 (12)	C(9)····C(2 <sup>iv</sup> )	3·749 (19)			
	Br(2)···C(2 <sup>vi</sup> )	3·941 (11)	C(9)····C(8 <sup>xi</sup> )	3·788 (18)			
	Br(2)···C(11 <sup>''</sup> )	3·924 (11)	C(10)····C(4 <sup>viii</sup> )	3·940 (19)			
	Br(2)···C(15 <sup>'</sup> )	3·998 (13)	C(10)····C(8 <sup>xii</sup> )	3·749 (17)			
	C(2)····C(11 <sup>vii</sup> )	3·920 (19)					

mately connected with one another. Atom Br(2) contacts (at the van der Waals distance) atom Br(2), related by a centre of symmetry, and carbon atoms of neighbouring molecules (Fig. 2). Also, the two indane rings are surrounded by neighbouring molecules at the van der Waals distances.

All calculations were carried out on an IBM S360-75 computer at the Mitsubishi Computer Centre.

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## La Liaison Intermoléculaire Oxygène–Halogène en Série Quinonique

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Crystallography and infrared absorption spectroscopy have made possible a description of the bonding between the oxygen and halogen atoms of quinonic molecules. Its nature, essentially charge-transfer, and its linear geometry are similar to those of hydrogen bonding; a hypothesis is proposed to explain the geometry of these ( $n-\sigma$ ) self-complexes. The bonding strength increases with acceptor strength from Cl through Br to I; fluorine was not considered. The bonding always exists in solution; in the solid state it is not compatible with all molecular conformations or in some cases with strong hydrogen bonds.

### Introduction

L'analyse radiocristallographique de nombreux composés quinoniques a montré que les molécules de naphtho- ou anthraquinone se disposent toujours dans des plans parallèles, pour former des piles dont la direction moyenne est celle de la croissance du cristal.

Parmi les distances intermoléculaires latérales, des distances anormalement courtes ont été souvent obser-

vées entre atomes d'oxygène et d'halogène ainsi qu'une disposition très particulière des groupements C=O et C-X.

Les auteurs, dans la description qu'ils ont donnée des structures cristallines correspondantes, ont proposé l'hypothèse d'une liaison intermoléculaire dont la nature serait un 'transfert de charge', au sens de Mulliken & Person (1969). La synthèse que nous présentons met en évidence l'existence d'une telle liaison et con-