axial positions (Fig. 3) (Stoddart, 1971), as expected for the ${}^5H_0$ half-chair conformation. The highly distorted conformation appears to be due to the departure of C(5′) from the plane to avoid steric hindrance between bulky substituents at the contiguous C(4′) and C(5′).

The puckering of the sugar ring required by the ${}^5H_0$ conformation can be described by the values of the C(2′)—C(3′)—C(4′)—C(5′) (−17°) and C(3′)—C(4′)—C(5′)—O(0′) (47·7°) torsion angles (Table 6).

Sundaralingam (1968) has defined the conformation about C(5)—C(6) in pyranosides by the angle φ_{OO} = O(5)—C(5)—C(6)—O(6). In the present structure this angle is described by the squence O(0′)—C(5′)—C(6′)—O(3′) and its value of 175·3° is not in the range common to pyranoside derivatives (±60 ± 30°).

Nucleoside conformation and molecular packing

The orientation of the base relative to the sugar ring described in terms of rotation about the N(7)—C(4′) glycosyl bond for the sequence C(8)—N(7)—C(4′)—C(5′) is *syn* (105·1°) (Sundaralingam, 1975). The conformation about the glycosyl bond with the torsion angle (χ) larger than 90° can also be referred to as *high-anti* (90–130°) (Sundaralingam, 1975). Thus, a comparison of the molecules in the usual *anti* range can be made.

The molecules are joined by N(1′)—H···O(2) (3·09 Å) hydrogen bonds acting between the sugar and base moieties (Fig. 2). Each molecule is connected by two hydrogen bonds with the neighbouring molecule forming infinite chains along **a**.

Base stacking with the shortest interbase distance of 5·003 Å occurs along **b**.

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The Crystal Structures of Two Fluorene Derivatives

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Abstract

The crystal structures of 2,7-dibromo-9-[4-(dimethylamino)benzylidene]fluorene (I) ($C_{22}H_{17}Br_2N$) and 9,9′-(1,4-phenylenedimethylidyne)difluorene (II) ($C_{34}H_{22}$) were determined by X-ray structure analysis. The crystals are monoclinic, space group $P2_1/c$, with a = 8·200 (6), b = 14·536 (7), c = 15·729 (5) Å, β = 103·64 (6)° and Z = 4 for (I), and orthorhombic, space group *Pbca*, with a = 17·640 (6), b = 23·630 (6), c = 10·755 (5) Å and Z = 8 for (II). The structures were solved by Patterson methods for (I) and direct

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phase determination for (II) and then refined by block-matrix least-squares methods to R values of 4·7 and 5·1% for 3027 and 4174 reflexions respectively. The bond distances and the planarity of the fluorene systems are in good agreement with those known from the literature. Steric hindrance of two H atoms causes the benzene rings in both structures not to be coplanar with the rest of the molecule but gives torsion angles of 48·8° and close to 45° respectively.

Introduction

The oligomeric and polymeric vinylenes containing fluorene systems show more or less interesting properties concerning electrical conductivity (Hatscher, 1977). Therefore the conjugated π-electron system of the fluorene was intentionally increased by condensing various aromatic or heteroaromatic systems to the very reactive CH_2 group. Thus a great number of compounds were synthesized by Hatscher (1977); of these, 2,7-dibromo-9-[4-(dimethylamino)benzylidene]-fluorene (I) and 9,9′-(1,4-phenylenedimethylidyne)-difluorene (II) were selected for single-crystal structure analysis.

Experimental

Dark yellow, almost hexagonal-looking crystals of (I) and well formed orange laths of (II) were obtained by recrystallization from ethanol (Hatscher, 1977). Oscillation and Weissenberg photographs revealed the crystals to be monoclinic for (I) and orthorhombic for (II). Systematically absent reflexions uniquely indicated the space groups to be $P2_1/c$ and $Pbca$ respectively. The crystallographic data are given in Table 1. The accurate cell dimensions were obtained from diffractometer measurements as well as intensities, using a $\theta/2\theta$ scan. An automatic diffractometer (Siemens AED) and Ni-filtered Cu $K\alpha$ radiation were used ($3° \leq \theta \leq 70°$). 3027 reflexions were collected for (I) [including 434 'less-thans' with $I < 2\sigma(I)$] and 4173 for (II) (including 1144 'less-thans'). The data for (I) were corrected for absorption, and an anomalous-dispersion correction (f' and f'') for Br was taken from *International Tables for X-ray Crystallography* (1968). The atom form factors for N, S and Br were taken from Cromer & Mann (1968) and for H from Stewart, Davidson & Simpson (1965). All computations were performed on a CDC Cyber 175 computer with XRAY 76 (Stewart, 1976).

Table 1. *Crystal data*

	(I) 2,7-Dibromo-9-[4-(dimethylamino)benzylidene]fluorene	(II) 9,9′-(1,4-Phenylenedimethylidyne)-difluorene
Formula	$C_{22}H_{17}Br_2N$	$C_{34}H_{22}$
M_r	455·21	430·55
Space group	$P2_1/c$	$Pbca$
a	8·200 (6) Å	17·640 (6) Å
b	14·536 (7)	23·630 (6)
c	15·729 (5)	10·755 (5)
β	103·64 (6)°	–
V	1821·95 Å^3	4483·04 Å^3
Z	4	8
$F(000)$	860	1808
D_m	1·62 Mg m^{-3}	1·23 Mg m^{-3}
D_x	1·667	1·280
μ(Cu $K\alpha$ radiation)	5·90 mm^{-1}	0·559 mm^{-1}
Crystal size	0·13 × 0·54 × 0·60 mm (dark-yellow platelets)	0·12 × 0·31 × 0·42 mm (orange-red platelets)

Structure determination and refinement

2,7-Dibromo-9-[4-(dimethylamino)benzylidene]-fluorene (I)

The structure of this compound was solved by the heavy-atom method using a three-dimensional Patterson function. A Fourier synthesis based on the Br-atom positions was then calculated in which the positions of all non-hydrogen atoms could be located. Block-diagonal least-squares refinement was carried out with all nonhydrogen atoms anisotropic, converging to an R value of 15·8% ($R = \sum||F_o| - |F_c||/\sum |F_o|$). On the

Table 2. *Positional parameters* ($\times 10^4$) *of* 2,7-*dibromo*-9-[4-(*dimethylamino*)*benzylidene*] *fluorene with e.s.d.'s*

	x	y	z
Br(1)	9572 (1)	7205 (1)	2656 (1)
Br(2)	1107 (1)	5530 (1)	6542 (1)
N(1)	2667 (9)	5476 (5)	−431 (4)
C(1)	6712 (7)	6666 (4)	3246 (4)
C(2)	8307 (8)	7040 (4)	3500 (4)
C(3)	9024 (8)	7294 (5)	4360 (4)
C(4)	8141 (8)	7141 (5)	4999 (4)
C(5)	5591 (8)	6581 (4)	6215 (4)
C(6)	4300 (9)	6280 (4)	6579 (4)
C(7)	2887 (8)	5906 (4)	6031 (4)
C(8)	2705 (9)	5814 (4)	5141 (4)
C(9)	4169 (7)	6089 (4)	3865 (3)
C(10)	5821 (7)	6525 (4)	3894 (4)
C(11)	6566 (8)	6763 (4)	4771 (4)
C(12)	5443 (8)	6498 (4)	5319 (4)
C(13)	3997 (7)	6101 (4)	4783 (3)
C(14)	3054 (7)	5667 (4)	3221 (4)
C(15)	2938 (7)	5635 (4)	2278 (3)
C(16)	2396 (8)	4841 (4)	1801 (4)
C(17)	2301 (9)	4788 (5)	916 (4)
C(18)	2713 (8)	5536 (5)	445 (4)
C(19)	3158 (8)	6363 (5)	911 (4)
C(20)	3259 (8)	6406 (4)	1809 (4)
C(21)	3350 (10)	6198 (6)	−882 (5)
C(22)	2240 (10)	4618 (7)	−895 (5)

application of an absorption correction and the introduction of an isotropic extinction parameter (Larson, 1967), the R value dropped to 6·0%. Nine of the 17 H atoms could then be located in a difference electron density map. The positions of the two H atoms bonded at C(1) and C(20), respectively, could not be found unambiguously and were calculated. The six H atoms of the two methyl groups could not be located and no attempt was made to include their theoretical positions in the refinement, because of relatively high thermal vibrations. Further refinements with isotropic temperature factors for the H atoms and a dispersion correction for the Br atoms (*International Tables for X-ray Crystallography*, 1968) converged to a final R value of 4·7% with an extinction parameter of $0{\cdot}76\,(2) \times 10^{-4}$. The final positional parameters are listed in Table 2.*

Fig. 1 shows a plot of the molecule viewed normal to the fluorene plane, while Fig. 2 is a line diagram of the molecule giving the atom numbering (numbered circles, unless otherwise indicated, represent C atoms) and bond lengths and angles (including e.s.d.'s).

9,9′-(1,4-*Phenylenedimethylidyne*)*difluorene* (II)

This structure was solved by direct methods using the *MULTAN* 77 procedure (Main, Lessinger, Woolfson, Germain & Declercq, 1977). Three reflexions in the starting set were taken for phase variation and 400 reflexions with $E > 1{\cdot}63$ were used for calculation. The phase subset with the highest figure of merit of 3·00 was taken for the electron density map calculation, in which all 34 C atoms could be located unambiguously. After one cycle of isotropic crystallographic least-squares refinement (XRAY 76 system, Stewart, 1976), the R value was already 13·5% and converged after three cycles to 12·8%.

A block-matrix refinement including anisotropic temperature parameters then converged to an R value of 9·4%. A difference electron density map clearly showed the positions of all 22 H atoms. Two reflexions which probably suffered from extinction (because of large negative ΔF values) were excluded from the refinement. No absorption correction was made because of the small value of μ and the crystal dimensions (see Table 1). On inclusion of the positional and isotropic temperature parameters for the H atoms further refinements converged to a final R value of 5·1%. A final difference electron density map only showed a residual electron density of between +0·17 and −0·17 e Å^{-3}. Fig. 3 shows a plot of the molecule viewed normal to the plane of the fluorene system [C(1)–C(13)] with the C-atom numbering, while Fig. 4 gives the bond lengths and angles. The average of the estimated standard deviations is 0·0038 Å for C—C and 0·028 Å for C—H bond lengths, and 0·24° for the C—C—C angles. Table

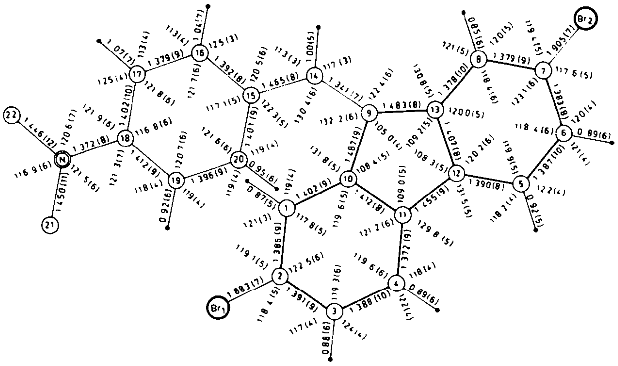

Fig. 2. Bond lengths (Å) and angles (°) of (I) (with e.s.d.'s).

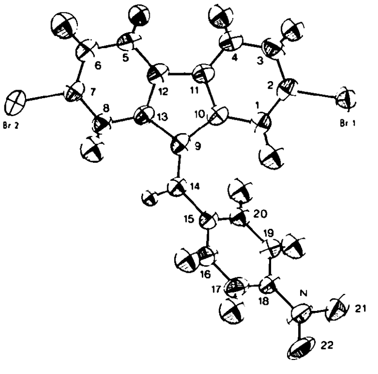

Fig. 1. *ORTEP* projection of (I) on the fluorene plane. Thermal ellipsoids are at 50% probability (Johnson, 1965). H-atom labels are omitted.

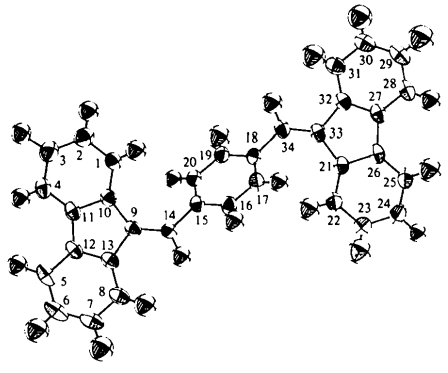

Fig. 3. *ORTEP* projection of (II) on the plane of fluorene C(1)–C(13). Thermal ellipsoids are at 50% probability (Johnson, 1965). H-atom labels are omitted.

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* Lists of structure factors, thermal parameters and H-atom parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34206 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

3 contains the final positional parameters of the C atoms.*

Results and discussion

The bond distances of the fluorene systems of the title compounds are in good agreement with each other. The average of all bond lengths of the benzene rings of structure (II) is 1·393 ± 0·002 Å, which agrees with the accepted value of 1·394 Å (Sutton, 1965). Apart from C(10)—C(11) and the corresponding C(21)—C(26), all other bond distances are within ±3σ of the average. Neglecting these exceptions the geometry of the fluorene systems is in good agreement with those of fluorene itself (Burns & Iball, 1955), 9-fluorenone (Luss & Smith, 1972) and the fluorene which is connected by a double bond to the dimer from 1-phenyl-3,3-biphenylene-allene (Dreissig, Luger & Rewicki, 1974). The same situation has been found with structure (I), where the corresponding C(10)—C(11) bond is longer than all the others of the benzene rings which lie within ±3σ of the average, in this case 1·390 ± 0·003 Å.

The benzene systems C(15)—C(20) of both structures show the typical decrease from 120° of about 2° for the bond angles at the substituted atom (Domenicano, Vaciago & Coulson, 1975).

Since there is a severe steric hindrance of atoms H(1)–H(20) for both structures and the corresponding H(17)–H(22) for structure (II) the C(15)—C(20) benzene-system rings are no longer coplanar with the rest of the molecule concerned, as can be assumed for similar compounds in accordance with theory and observation. Torsion angles of between 43 and 49°

Table 3. *Positional parameters* (×10⁴) *for 9,9'-(1,4-phenylenedimethylidyne)difluorene with e.s.d.'s*

	x	y	z
C(1)	9226 (1)	−508 (1)	853 (2)
C(2)	9330 (2)	−841 (1)	−196 (3)
C(3)	8783 (2)	−1231 (1)	−564 (3)
C(4)	8108 (2)	−1279 (1)	97 (3)
C(5)	6657 (2)	−1197 (1)	1995 (3)
C(6)	6139 (1)	−1066 (1)	2926 (3)
C(7)	6293 (1)	−653 (1)	3801 (3)
C(8)	6973 (1)	−356 (1)	3786 (3)
C(9)	8270 (1)	−257 (1)	2651 (2)
C(10)	8560 (1)	−557 (1)	1543 (2)
C(11)	7997 (1)	−943 (1)	1133 (2)
C(12)	7341 (1)	−898 (1)	1973 (2)
C(13)	7496 (1)	−481 (1)	2851 (2)
C(14)	8573 (1)	145 (1)	3399 (2)
C(15)	9350 (1)	368 (1)	3482 (2)
C(16)	9461 (1)	939 (1)	3774 (2)
C(17)	10179 (1)	1161 (1)	3923 (3)
C(18)	10820 (1)	815 (1)	3834 (2)
C(19)	10710 (1)	245 (1)	3547 (2)
C(20)	9991 (1)	24 (1)	3374 (2)
C(21)	11546 (1)	1728 (1)	5802 (2)
C(22)	10864 (1)	1664 (1)	6449 (2)
C(23)	10720 (2)	1996 (1)	7485 (3)
C(24)	11247 (2)	2389 (1)	7897 (3)
C(25)	11932 (2)	2451 (1)	7288 (3)
C(26)	12080 (1)	2124 (1)	6250 (2)
C(27)	12770 (1)	2083 (1)	5496 (2)
C(28)	13559 (2)	2384 (1)	5558 (3)
C(29)	14020 (2)	2247 (1)	4729 (3)
C(30)	13926 (2)	1818 (1)	3867 (3)
C(31)	13246 (1)	1516 (1)	3797 (3)
C(32)	12667 (1)	1652 (1)	4616 (2)
C(33)	11884 (1)	1425 (1)	4730 (2)
C(34)	11601 (1)	1030 (1)	3960 (2)

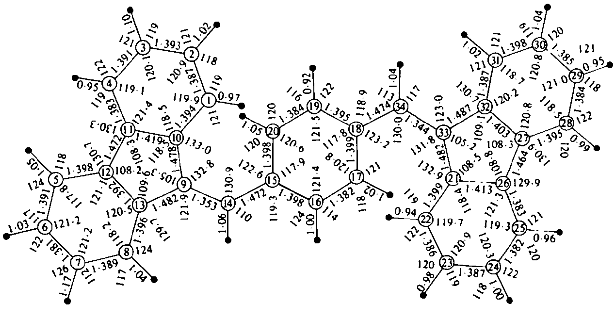

Fig. 4. Bond lengths (Å) and angles (°) of (II) (average e.s.d.'s in bond lengths: 0·004 Å for C—C, 0·03 Å for C—H; for C—C—C angles: 0·2°).

Table 4. *Distances of atoms from least-squares planes defined by the atoms belonging to the corresponding fluorene systems*

Values are in Å and have been multiplied by 10³.

	Structure (I)	Structure (II) Fluorene C(1) − C(13)	Fluorene C(21) − C(33)	
Br(1)	−160	–	–	
Br(2)	20	–	–	
C(1)	−6*	−2†	−20‡	C(22)
C(2)	−48	31	−71	C(23)
C(3)	−11	11	−50	C(24)
C(4)	17	0	5	C(25)
C(5)	3	15	45	C(28)
C(6)	17	−11	−3	C(29)
C(7)	−11	11	−69	C(30)
C(8)	−1	25	−66	C(31)
C(9)	−4	−29	63	C(33)
C(10)	40	−38	66	C(21)
C(11)	42	−15	63	C(26)
C(12)	8	2	44	C(27)
C(13)	−8	30	−6	C(32)
C(14)	−150	−52	115	C(34)
C(15)	−77	−292	363	C(18)
C(18)	15	−830	836	C(15)
N(1)	22	–	–	
C(34)	–	−1114	1039	C(14)

* E.s.d. of atoms defining plane: 22 × 10⁻³ Å.
† E.s.d. of atoms defining plane: 21 × 10⁻³ Å.
‡ E.s.d. of atoms defining plane: 53 × 10⁻³ Å.

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* See previous footnote.

were observed. With this assumption of a system of conjugated double bonds, a discontinuity in free π-electron movement is exhibited, since the overlap integral for π-electron orbitals has a maximum in the parallel position (0°) and decreases rapidly with increasing torsion angle (Heilbronner & Bock, 1970). Electronic spectra have also shown that the electron resonance does not cover the entire molecule in both cases (Kossmehl, 1978). This steric hindrance causes a fairly large increase in the angles of the type C(10)—C(9)—C(14) which ought to be near 126° (Dreissig, Luger & Rewicki, 1974; Griffiths & Hine, 1970*a*; Luss & Smith, 1972; Tulip, Corfield & Ibers, 1978). In the same way the angles of the type C(9)—C(14)—C(15) are enlarged from the regular 120° to about 130°.

The fluorene systems themselves are planar, as judged by the average deviations of the atoms from their least-squares planes. Average values of 0·018 Å for compound (I), 0·017 Å in the fluorene system C(1)—C(13) and 0·044 Å in C(21)—C(33) for compound (II) were found (see Table 4).

An angle of 48·80° between the benzene C(15)—C(20) and the fluorene system, each represented by a least-squares plane, for structure (I) was found, while the corresponding angles for structure (II) were $\angle$C(15)—C(20), C(1)—C(13) = 45·77° and $\angle$C(15)—C(20), C(21)—C(33) = 43·12°. The angle between the two fluorene systems for structure (II) was found to be 2·19°. This is in good agreement with the data for 2-bromofluorenone (2-bromoketofluorene) and 9-diazo-2-bromofluorene (Griffiths & Hine, 1970*a,b*) and also with the idea that the fluorene system is a conjugated π-electron system.

The average bond length of 1·483 (3) Å, taken over six bond lengths of the type C(9)—C(10), is much larger than the values of 1·43 (2) Å for fluorene (Burns & Iball, 1955) and 1·443 (5) Å for 9-diazofluorene (Tulip, Corfield & Ibers, 1978), indicating less interaction of C(9) with the benzenoid fragments. Thus it can be supposed that the above-mentioned discontinuity of conjugated double bonds causes a more or less significant disturbance of the predicted molecular aromaticities of the title compounds.

No intermolecular distances less than the sums of the van der Waals radii were found.

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