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The Structures of Diisopropyl 9,9′-Bifluorenylidene-1,1′-dicarboxylate and 9,9′-Bifluorenylidene

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Diisopropyl 9,9′-bifluorenylidine-1,1′-dicarboxylate ($C_{34}H_{28}O_4$) crystallizes in space group $I2/c$ with Z = 12, a = 40·385 (5), b = 8·062 (5), c = 23·924 (5) Å, β = 91·54 (1)° and 9,9′-bifluorenylidene ($C_{26}H_{16}$) crystallizes in space group $Pbcn$ with Z = 12, a = 36·71 (1), b = 17·09 (1), c = 8·14 (1) Å. Both structures were solved using data collected by visual estimation from Weissenberg photographs. The final R factors are 0·095 and 0·105. The diffuse reflexions which appear on X-ray photographs of the latter compound are explained by the observed disorder in the crystal structure. Both compounds have the twisted conformation, with approximately planar fluorenylidene fragments. The angle of twist in the substituted compound, which has a *trans* configuration, is approximately 10° greater than that in the unsubstituted compound.

Introduction

Investigation of the conformational behaviour of substituted 9,9′-bifluorenylidenes (Fig. 1) has been undertaken using NMR spectroscopy (Gault, Ollis & Sutherland, 1970; Gault, 1970). A planar 9,9′-bifluorenylidene molecule would exhibit unacceptably short contacts between the H atoms at the 1 and 1′ positions and bulky substituents at these positions would constrain the framework to be non-coplanar. Newman projections of several possible non-planar conformations of 1,1′-substituted 9,9′-bifluorenylidenes are shown in Fig. 2: in the twisted (*t*) conformations the fluorenylidene fragments are each approximately planar, but are mutually twisted about the C(9)—C(9′) bond; in the folded (*f*) conformations each fluorenylidene fragment is non-planar. If R and R' are other than H, a further distinction occurs between *cis* and *trans* isomers for both folded and twisted conformations. No optically active bifluorenylidenes have been isolated, suggesting that rapid interconversion between the various conformations occurs in solution. The temperature-dependent NMR spectra of (I*a*), (I*b*) and (I*c*) (Fig. 1) were consistent with observable populations for the conformations $TRANS_{(f)}$, $TRANS^*_{(f)}$, $CIS_{(f)}$ and $CIS^*_{(f)}$ (Gault, Ollis & Sutherland, 1970). No direct evidence was available to indicate whether the most stable conformations were twisted or folded. Study of the low-temperature PMR spectra of (I*a*), (I*b*) and (I*c*) immediately after solution showed that (I*a*) had a conformation in the solid state which was different from that of the major conformer at equilibrium in solution, whereas the solid-state conformations of (I*b*) and (I*c*) were those of the major conformers in solution. In view of the previously reported structure of 9,9′-bifluorenylidene (Nyburg, 1954), a folded conformation was anticipated and these NMR results were originally interpreted on the reasonable assumption that the major conformer in solution was $TRANS_{(f)}$ for all three compounds; thus, in the solid state, the conformations of (I*b*) and (I*c*) would also be $TRANS_{(f)}$ and (I*a*) could have the conformation $CIS_{(f)}$.

It has been reported that bifluorenylidenes without substituents in the 1 and 1′ positions undergo rapid conformational exchange in solution and that the NMR spectra show no temperature dependence (Gault, 1970). It has also been reported that the 2,2′-disubstituted compounds, the 1,1′-difluoro derivative and bifluorenylidene itself (I*d*) do not undergo *cis–trans* isomerization at temperatures up to 220°C (Agranat, Rabinovitz, Weitzen-Dagan & Gosnay, 1972), and that

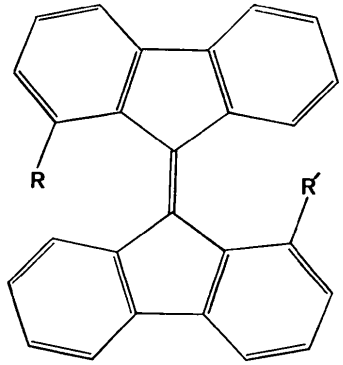

Fig. 1. 1,1′-Disubstituted 9,9′-bifluorenylidenes. (I*a*) $R = R' = CO_2Me$. (I*b*) $R = R' = CO_2{}^iPr$. (I*c*) $R = CO_2Me$, $R' = CO_2{}^iPr$. (I*d*) $R = R' = H$.

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this may be explained by the greater activation energy for *cis–trans* isomerization in these molecules compared with the 1,1′-bis(alkoxycarbonyl) derivatives (I*a*, I*b* and I*c*). In this case the ground state of 9,9′-bifluorenylidene would be expected to be more stable than those of the 1,1′-bis(alkoxycarbonyl) derivatives.

In the earlier crystallographic studies of bifluorenylidene it was assumed that the molecule was approximately planar (Fenimore, 1948), or only slightly distorted from planarity towards the folded conformation (Nyburg, 1954). However, Stegmeyer (1969) explained the anomalously red-shifted band in the electronic spectrum of 9,9′-bifluorenylidene by postulating a twisted model with a dihedral angle of 40°. It was also known that the C(9)—C(9′) bond was highly polarizable and very reactive (Pinck & Hilbert, 1935; Bergmann, 1968), and electrochemical data have been interpreted on the basis that the angle of twist is 60° (Bergmann, 1955).

Crystallographic investigation of 9,9′-bifluorenylidene and its derivatives was undertaken in order to determine their solid-state conformations and to help in the understanding of their behaviour in solution.

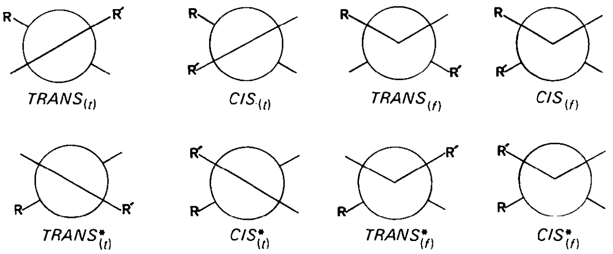

Fig. 2. Newman projections of the possible conformations of 1,1′-disubstituted 9,9′-bifluorenylidenes.

Table 1. *Crystal data*

	(I*b*) (from acetone as red needles)	(I*d*) (from benzene as orange needles)
Crystal dimensions	0·5 × 0·04 × 0·07 mm	1·0 × 0·13 × 0·15 mm
Formula	$C_{34}H_{28}O_4$	$C_{26}H_{16}$
M_r	500·6	328·4
System	monoclinic	orthorhombic
a	40·385 (5) Å	36·71 (1) Å
b	8·062 (5)	17·09 (1)
c	23·924 (5)	8·14 (1)
β	91·54 (1)°	–
	(from Weissenberg and precession photographs)	
U	7790 Å^3	5107 Å^3
D_m	1·30 g cm^{-3}	1·28 g cm^{-3}
Z	12	12
D_c	1·28 g cm^{-3}	1·28 g cm^{-3}
F(000)	3168	2064
Space group	*I*2/*c* [non-standard setting of *C*2/*c* (No. 15)]	*Pbcn* (No. 60)
λ(Cu *Kα*)	1·5418 Å	1·5418 Å
μ(Cu *Kα*)	6 cm^{-1}	6 cm^{-1}

Experimental

Preliminary details of the structure of (I*b*) have previously been reported (Bailey & Hull, 1971). It has not been possible to obtain good single crystals of (I*a*) or (I*c*); their powder patterns do not resemble those of either (I*b*) or (I*d*).

Crystal data for (I*b*) and (I*d*) are given in Table 1. For both structures data were estimated visually from Weissenberg films (layers *h*0*l*–*h*6*l* for I*b*; layers *hk*0–*hk*7 for I*d*) taken with Ni-filtered Cu *Kα* radiation, and were corrected for Lorentz and polarization effects, for the splitting of the $K\alpha_1/K\alpha_2$ doublet and for spot shape expansion on upper levels (Phillips, 1954). No absorption corrections were applied.

For (I*b*) the 3019 independent reflexions were put on a common scale using 619 reflexions previously collected on a Hilger & Watts Y290 four-circle diffractometer but not included in the final refinement. The phases were determined by the symbolic addition method, using the computer program *SYMBAD* (Hitchcock, 1970). The initial *E* map showed 53 out of the 57 heavy atoms in the asymmetric unit; the remaining atoms were located on a difference electron-density map. The positions of the non-methyl H atoms were calculated and the methyl H atoms were placed in the calculated positions which best fitted a difference electron-density synthesis. The structure was refined by block-diagonal least-squares methods to a final *R* factor of 0·095, allowing the heavy atoms anisotropic thermal parameters and constraining the H atoms, for which a single overall isotropic temperature factor was refined, to lie at 1·08 Å from the C atom to which they are bonded. Final positional parameters are listed in Table 2.

The diffuse reflexions which were observed for (I*d*) by Fenimore (1948), and which may have led Taylor (1935) to report a *b* axis twice the length of that reported here, were observed on both Weissenberg and precession photographs, but were ignored in both unit-cell measurement and data collection. No crystals in the alternative crystal form (space group $P2_12_12_1$) reported by Groth (1919) and Harnik, Herbstein, Schmidt & Hirshfeld (1954) were found in the sample.

The 1864 independent reflexions were put on a common scale using 401 reflexions measured from precession photographs (layers *h*0*l*–*h*4*l*) but omitted from the final refinement.

The structure was solved by a combination of direct methods, minimum residual, and difference Fourier techniques. An *E* map calculated using the signs generated by the program *SYMBAD* (Hitchcock, 1970) showed, for each equivalent position, one molecule in a general position; difference electron-density maps at this stage did not reveal the position of the remaining half-molecule, and the model could not be refined by least-squares methods. However, calculation of the residual for 38 low-angle reflexions when various translations were applied to the molecule showed that the true position of the molecule could be obtained by adding 0·33 to the x coordinates. Further difference electron-density syntheses showed that the remainder of the structure was disordered, two overlapping half-population molecules being related by the centre of symmetry at $0\frac{1}{2}0$; this disorder may explain the observed diffuse reflexions (see *Discussion*). Initial refinement of four fluorenylidene fragments with fixed geometry (two half-weight and two whole-weight) and an overall isotropic temperature factor reduced R to 0·19 for the 400 reflexions with the largest $|F_o|$ values. Refinement of individual atomic parameters by block-diagonal least-squares methods using the full data was then started, but no anisotropic temperature factors were refined until the inter-layer scale factors had been optimized. When anisotropic vibrational parameters for the C atoms in the general molecule and isotropic temperature factors for the C atoms in the disordered molecule were refined, R fell to 0·144. A difference electron-density synthesis then showed the positions of the H atoms in both molecules; inclusion of these atoms, at calculated positions, in the structure factor calculations, without refinement of their parameters, reduced R to 0·105. The reflexions 022 and 611 were observed to be much less intense than the calculated values, presumably because of extinction, and were omitted from the later stages of refinement.*

Table 2. *Atomic coordinates* ($\times 10^4$) *for* (I*b*)

	x	y	z
C(*S*1)	361 (2)	4615 (11)	3460 (3)
C(*S*2)	636 (2)	4851 (12)	3821 (4)
C(*S*3)	948 (2)	4222 (13)	3689 (4)
C(*S*4)	996 (2)	3419 (13)	3184 (4)
C(*S*5)	945 (2)	1715 (14)	1963 (4)
C(*S*6)	872 (2)	1147 (14)	1423 (4)
C(*S*7)	545 (2)	1408 (13)	1190 (4)
C(*S*8)	300 (2)	2178 (11)	1506 (4)
C(*S*9)	173 (2)	3343 (11)	2504 (4)
C(*S*10)	400 (2)	3697 (11)	2978 (3)
C(*S*11)	718 (2)	3150 (12)	2828 (4)
C(*S*12)	377 (2)	2748 (12)	2042 (4)
C(*S*13)	707 (2)	2515 (12)	2271 (4)
C(*S*14)	49 (2)	5576 (11)	3588 (4)
C(*S*15)*	−547 (2)	5893 (7)	4418 (1)
C(*S*16)	−240 (2)	6911 (13)	4316 (4)
C(*S*17)*	−99 (1)	7758 (5)	4856 (4)
O(*S*1)	25 (2)	5814 (8)	4141 (3)
O(*S*2)	−137 (1)	6164 (8)	3246 (3)
C(*A*1)	2837 (2)	6046 (12)	1651 (4)
C(*A*2)	2487 (2)	5986 (14)	1573 (4)
C(*A*3)	2331 (2)	6596 (14)	1090 (4)
C(*A*4)	2517 (2)	7177 (14)	654 (4)
C(*A*5)	3073 (2)	8355 (13)	−209 (4)
C(*A*6)	3354 (3)	8654 (14)	−508 (4)
C(*A*7)	3667 (3)	8405 (14)	−261 (4)
C(*A*8)	3710 (2)	7865 (12)	282 (4)
C(*A*9)	3385 (2)	6974 (11)	1162 (3)
C(*A*10)	3022 (2)	6797 (12)	1241 (3)
C(*A*11)	2863 (2)	7292 (12)	724 (4)
C(*A*12)	3427 (2)	7453 (12)	581 (4)
C(*A*13)	3109 (2)	7736 (12)	329 (4)
C(*A*14)	2986 (2)	5049 (13)	2117 (4)
C(*A*15)*	2559 (3)	3771 (2)	3345 (2)
C(*A*16)	2880 (3)	3968 (15)	3031 (4)
C(*A*17)*	3160 (2)	4782 (6)	3387 (3)
O(*A*1)	2794 (2)	5126 (9)	2572 (3)
O(*A*2)	3225 (2)	4212 (9)	2088 (3)
C(*B*1)	4135 (2)	5365 (11)	1135 (4)
C(*B*2)	4480 (2)	5073 (13)	1224 (4)
C(*B*3)	4650 (2)	5617 (13)	1696 (4)
C(*B*4)	4485 (2)	6440 (12)	2110 (4)
C(*B*5)	3983 (2)	8350 (13)	2917 (4)
C(*B*6)	3724 (3)	9150 (15)	3175 (4)
C(*B*7)	3402 (2)	9230 (14)	2913 (4)
C(*B*8)	3344 (2)	8445 (13)	2402 (4)
C(*B*9)	3627 (2)	6883 (11)	1585 (3)
C(*B*10)	3976 (2)	6324 (11)	1532 (4)
C(*B*11)	4143 (2)	6803 (11)	2036 (3)
C(*B*12)	3597 (2)	7565 (12)	2146 (3)
C(*B*13)	3919 (2)	7566 (12)	2412 (4)
C(*B*14)	3983 (2)	4464 (12)	652 (4)
C(*B*15)*	3414 (1)	3765 (6)	−200 (4)
C(*B*16)	3510 (3)	2862 (13)	347 (4)
C(*B*17)*	3211 (2)	2238 (5)	655 (2)
O(*B*1)	3670 (1)	4012 (8)	747 (3)
O(*B*2)	4128 (2)	4108 (11)	230 (3)

* Atom constrained during final refinement.

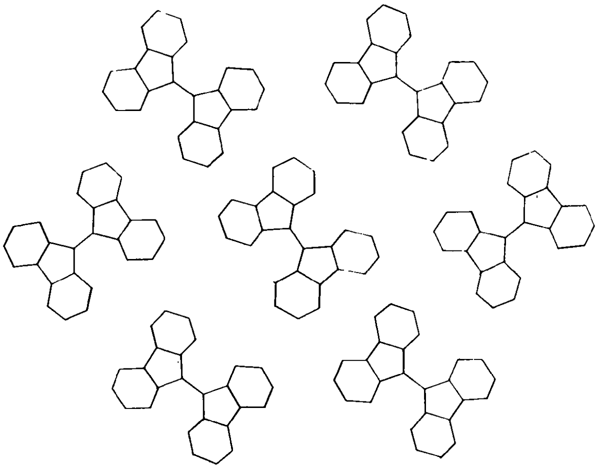

Fig. 3. The structure of (I*d*) projected on to the *ab* plane. One column of 'special' molecules is shown surrounded by six columns of general molecules.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33782 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The disorder of (I*d*)

The final atomic positional parameters for (I*d*) together with their estimated standard deviations are listed in Table 3.

The unit cell contains 12 molecules, each with approximate 222 symmetry, eight in general positions and four associated with special positions, which rather than lying across a crystallographic twofold axis are disordered and mutually interpenetrating so that two half-population molecules are related by the centre of symmetry at $0\frac{1}{2}0$. Calculation of contacts between disordered components of these 'special' molecules related by the twofold axis at $0,y,\frac{1}{2}$ and by the *c* glide plane at $y = \frac{1}{2}$ shows that only the latter gives an acceptable packing arrangement parallel to the *c* axis: the former gives overlap of symmetry-related molecules. Thus, adjacent 'special' molecules parallel to the *c* axis are enantiomers and the disorder is necessarily confined to the *ab* plane where, as can be seen from Fig. 3, there is no direct contact between 'special' molecules.

Table 3. *Atomic coordinates* ($\times 10^4$) *and isotropic temperature factors for* (I*d*)

	x	*y*	*z*	*B* (Å^2)
C(*A*1)	6803 (3)	6552 (5)	6721 (12)	
C(*A*2)	6715 (3)	7329 (6)	7103 (15)	
C(*A*3)	6375 (4)	7627 (7)	6670 (16)	
C(*A*4)	6112 (3)	7156 (8)	6011 (15)	
C(*A*5)	5606 (3)	5743 (10)	4655 (15)	
C(*A*6)	5462 (3)	5040 (13)	4177 (15)	
C(*A*7)	5649 (3)	4348 (10)	4108 (16)	
C(*A*8)	6027 (3)	4299 (8)	4607 (13)	
C(*A*9)	6553 (2)	5228 (5)	5619 (11)	
C(*A*10)	6551 (2)	6084 (6)	5956 (11)	
C(*A*11)	6188 (3)	6370 (7)	5666 (11)	
C(*A*12)	6172 (2)	5014 (8)	5190 (11)	
C(*A*13)	5973 (2)	5711 (7)	5147 (12)	
C(*B*1)	7375 (2)	5664 (5)	4511 (11)	
C(*B*2)	7737 (3)	5658 (6)	3946 (12)	
C(*B*3)	7946 (2)	4991 (7)	3969 (12)	
C(*B*4)	7803 (2)	4289 (6)	4475 (11)	
C(*B*5)	7320 (3)	2844 (6)	5905 (14)	
C(*B*6)	7069 (4)	2361 (7)	6602 (14)	
C(*B*7)	6733 (4)	2621 (6)	7101 (13)	
C(*B*8)	6628 (3)	3404 (7)	6764 (12)	
C(*B*9)	6854 (2)	4747 (5)	5576 (11)	
C(*B*10)	6870 (3)	3897 (5)	5951 (10)	
C(*B*11)	7226 (3)	3626 (6)	5606 (10)	
C(*B*12)	7230 (2)	4959 (5)	5092 (10)	
C(*B*13)	7448 (2)	4277 (5)	5038 (10)	
C(*S*1)	717 (4)	4827 (10)	−257 (21)	3·24 (6)
C(*S*2)	1099 (5)	5078 (13)	−97 (25)	4·58 (7)
C(*S*3)	1211 (5)	5790 (11)	−485 (23)	3·75 (6)
C(*S*4)	981 (5)	6368 (12)	−1078 (25)	4·71 (7)
C(*S*5)	268 (5)	7469 (12)	−2016 (24)	4·41 (7)
C(*S*6)	−66 (5)	7787 (9)	−2362 (34)	3·92 (6)
C(*S*7)	−381 (5)	7350 (11)	−2252 (23)	3·65 (6)
C(*S*8)	−369 (4)	6563 (10)	−1672 (20)	2·79 (5)
C(*S*9)	65 (4)	5427 (9)	−967 (20)	2·46 (5)
C(*S*10)	483 (4)	5422 (9)	−866 (20)	2·72 (5)
C(*S*11)	590 (5)	6179 (11)	−1210 (21)	3·28 (6)
C(*S*12)	−41 (5)	6221 (9)	−1339 (20)	3·13 (6)
C(*S*13)	290 (5)	6698 (11)	−1554 (21)	3·39 (6)
C(*T*1)	−742 (4)	5271 (10)	659 (21)	2·92 (5)
C(*T*2)	−1090 (4)	5076 (11)	1157 (21)	3·29 (6)
C(*T*3)	−1214 (5)	4304 (11)	1051 (22)	3·49 (6)
C(*T*4)	−1010 (4)	3746 (9)	170 (19)	2·44 (5)
C(*T*5)	−357 (5)	2719 (11)	−1558 (23)	3·77 (6)
C(*T*6)	−46 (8)	2399 (9)	−2307 (36)	4·61 (6)
C(*T*7)	252 (5)	2846 (10)	−2635 (22)	3·40 (6)
C(*T*8)	247 (5)	3633 (10)	−2135 (22)	3·37 (6)
C(*T*9)	−138 (4)	4770 (9)	−817 (19)	2·42 (5)
C(*T*10)	−536 (4)	4741 (8)	−182 (18)	1·82 (5)
C(*T*11)	−660 (4)	3956 (10)	−378 (20)	2·65 (5)
C(*T*12)	−63 (5)	3957 (10)	−1319 (19)	2·84 (5)
C(*T*13)	−363 (4)	3491 (10)	−1084 (21)	3·14 (6)

Cheng & Nyburg (1975) investigated the disorder of 1,1,3,3,8,8,10,10-octamethyl-2,9-dioxa-6,12,13-trithiadispiro[4.1.4.2]tridecane-4,11-dione and concluded that the structure consisted of ordered molecular layers of two types, related to each other by mirror symmetry. The layers could have been stacked randomly but, because of the absence of diffuse scattering, it was concluded that in fact the crystal contained substantial domains consisting of layers of one type only. For (I*d*) the situation is complicated by the presence of the general molecules and the possibility of disorder in two directions, and, since the diffuse reflexions appear between the Bragg reflexions in such a way as to apparently double the *b* axis, it is possible that there is some ordering of the 'special' molecules in this plane which could be transmitted either through weak interactions between the 'special' molecules or through the general molecules, which would themselves have to be slightly disordered.

Table 4. *Bond lengths* (Å) *for* (I*b*)

C(*S*9)–C(*S*9′)	1·395 (11)	C(*A*9)–C(*B*9)	1·391 (11)
	Fragment *S*	Fragment *A*	Fragment *B*
C(9)–C(10)	1·467 (11)	1·489 (11)	1·488 (11)
C(9)–C(12)	1·476 (12)	1·458 (12)	1·458 (12)
C(10)–C(11)	1·416 (11)	1·433 (12)	1·419 (11)
C(12)–C(13)	1·438 (12)	1·420 (12)	1·436 (11)
C(11)–C(13)	1·427 (13)	1·435 (12)	1·431 (12)
C(1)–C(10)	1·383 (12)	1·387 (12)	1·395 (12)
C(8)–C(12)	1·391 (12)	1·404 (13)	1·398 (12)
C(1)–C(2)	1·404 (12)	1·422 (13)	1·424 (12)
C(7)–C(8)	1·405 (13)	1·376 (13)	1·390 (14)
C(2)–C(3)	1·401 (12)	1·390 (14)	1·375 (14)
C(6)–C(7)	1·434 (14)	1·393 (14)	1·431 (14)
C(3)–C(4)	1·389 (13)	1·383 (14)	1·377 (13)
C(5)–C(6)	1·394 (15)	1·380 (14)	1·388 (14)
C(4)–C(11)	1·408 (12)	1·408 (12)	1·420 (12)
C(5)–C(13)	1·387 (13)	1·384 (13)	1·381 (13)
C(1)–C(14)	1·515 (12)	1·488 (13)	1·483 (13)
C(14)–O(1)	1·343 (11)	1·355 (11)	1·344 (11)
C(14)–O(2)	1·193 (11)	1·181 (11)	1·215 (11)
O(1)–C(16)	1·459 (11)	1·477 (13)	1·469 (12)
C(16)–C(15)	1·513 (12)	1·521 (15)	1·537 (13)
C(16)–C(17)	1·554 (12)	1·544 (13)	1·519 (13)

Calculations using the computer program *EENY* (Motherwell, 1976) showed that there are weak interactions between the columns of 'special' molecules related by translations parallel to *b*, but no interaction at all between columns related by translations in the *a* direction. These calculations are consistent with the explanation that the diffuse reflexions arise from a partial ordering of the 'special' molecules in the direction parallel to the *b* axis in such a way that an arrangement in which adjacent columns are of different types is favoured, and the repeat unit is doubled. As there are no diffuse reflexions leading to doubling of the *a* axis, it seems likely that the order of the columns of 'special' molecules related by translations along *a* is completely random.

Any disorder of the general molecules has not been investigated and is not expected to be significant, although the large anisotropic thermal parameters for several atoms of fragment *A* of the general molecule [C(*A*2), C(*A*3), C(*A*4), C(*A*5), C(*A*6) and C(*A*7)] could be an indication of some slight disorder.

As a consequence of the disorder the positional estimated standard deviations are rather high, particularly for atoms in the disordered 'special' molecule.

Discussion

The bond lengths and angles with their estimated standard deviations are listed in Tables 4 to 7; the molecules are illustrated in Figs. 4 and 5, and the torsion angles are shown in Figs. 6 and 7 which also show the atomic numbering schemes.

The geometries of the bifluorenylidene frameworks in the two compounds are similar and may be described as twisted (*t*). The unit cell of (I*b*) contains eight general molecules and four molecules lying across twofold axes; both types of molecule have the *trans* configuration. The angles between the mean planes of the fluorenylidene fragments in (I*b*) are 50 and 54° for the general and special molecules respectively; the corresponding angles in (I*d*) are 43 and 41°. The differing

Table 5. *Bond angles* (°) *for* (I*b*)

C(*S*9′)–C(*S*9)–C(*S*10)	127·9 (8)
C(*B*9)–C(*A*9)–C(*A*10)	125·4 (7)
C(*A*9)–C(*B*9)–C(*B*10)	127·1 (8)
C(*S*9′)–C(*S*9)–C(*S*12)	124·7 (8)
C(*B*9)–C(*A*9)–C(*A*12)	127·6 (8)
C(*A*9)–C(*B*9)–C(*B*12)	125·0 (8)

	Fragment *S*	Fragment *A*	Fragment *B*
C(10)–C(9)–C(12)	106·9 (7)	106·6 (7)	107·3 (7)
C(1)–C(10)–C(9)	131·7 (7)	132·8 (8)	132·9 (8)
C(1)–C(10)–C(11)	120·2 (7)	119·7 (7)	120·9 (7)
C(9)–C(10)–C(11)	107·3 (7)	106·5 (7)	105·9 (7)
C(8)–C(12)–C(9)	133·0 (8)	131·7 (8)	132·6 (8)
C(8)–C(12)–C(13)	119·3 (8)	118·9 (8)	118·0 (8)
C(9)–C(12)–C(13)	106·8 (7)	108·7 (7)	108·1 (7)
C(2)–C(1)–C(10)	118·6 (7)	118·3 (8)	117·1 (8)
C(2)–C(1)–C(14)	117·1 (8)	117·4 (8)	114·8 (8)
C(10)–C(1)–C(14)	123·8 (7)	123·5 (8)	127·8 (8)
C(7)–C(8)–C(12)	120·9 (8)	118·2 (8)	120·7 (8)
C(1)–C(2)–C(3)	121·0 (8)	121·6 (9)	122·3 (9)
C(2)–C(3)–C(4)	120·8 (8)	120·3 (8)	120·3 (8)
C(3)–C(4)–C(11)	118·0 (8)	119·3 (9)	119·8 (8)
C(6)–C(7)–C(8)	120·7 (9)	122·2 (9)	119·6 (9)
C(5)–C(6)–C(7)	118·8 (9)	120·4 (9)	121·0 (9)
C(6)–C(5)–C(13)	120·8 (9)	118·5 (9)	118·5 (8)
C(4)–C(11)–C(10)	120·9 (8)	120·3 (8)	119·2 (8)
C(4)–C(11)–C(13)	128·8 (8)	129·9 (8)	129·7 (8)
C(10)–C(11)–C(13)	110·0 (7)	109·6 (7)	111·0 (7)
C(5)–C(13)–C(12)	120·5 (8)	121·6 (8)	122·3 (8)
C(5)–C(13)–C(11)	131·1 (8)	130·1 (8)	129·9 (8)
C(11)–C(13)–C(12)	108·3 (7)	108·3 (7)	107·5 (7)
C(1)–C(14)–O(1)	110·8 (7)	110·4 (8)	112·0 (7)
C(1)–C(14)–O(2)	125·1 (9)	125·4 (9)	124·3 (9)
O(1)–C(14)–O(2)	123·9 (8)	124·0 (9)	123·6 (9)
C(14)–O(1)–C(16)	116·3 (7)	116·2 (8)	117·4 (7)
C(15)–C(16)–O(1)	109·2 (7)	104·4 (8)	110·6 (7)
C(17)–C(16)–O(1)	104·5 (6)	107·2 (8)	103·5 (7)
C(15)–C(16)–C(17)	112·8 (7)	113·1 (7)	112·5 (7)

Table 6. *Bond lengths* (Å) *for* (I*d*)

C(*A*9)–C(*B*9)	1·377 (12)	C(*S*9)–C(*T*9)	1·353 (21)

	Fragment *A*	Fragment *B*	Fragment *S*	Fragment *T*
C(9)–C(10)	1·489 (14)	1·487 (12)	1·537 (22)	1·550 (20)
C(9)–C(12)	1·487 (12)	1·480 (11)	1·443 (22)	1·475 (22)
C(10)–C(11)	1·439 (13)	1·417 (13)	1·382 (24)	1·426 (22)
C(12)–C(13)	1·399 (17)	1·416 (12)	1·474 (25)	1·372 (23)
C(11)–C(13)	1·437 (16)	1·454 (13)	1·442 (25)	1·467 (23)
C(1)–C(10)	1·372 (13)	1·390 (14)	1·419 (23)	1·364 (22)
C(8)–C(12)	1·415 (18)	1·399 (12)	1·365 (23)	1·428 (24)
C(1)–C(2)	1·401 (14)	1·419 (16)	1·475 (24)	1·383 (23)
C(7)–C(8)	1·447 (15)	1·407 (12)	1·426 (25)	1·405 (25)
C(2)–C(3)	1·395 (18)	1·375 (19)	1·321 (29)	1·398 (26)
C(6)–C(7)	1·368 (26)	1·373 (15)	1·379 (25)	1·360 (30)
C(3)–C(4)	1·367 (18)	1·359 (17)	1·388 (27)	1·409 (24)
C(5)–C(6)	1·369 (26)	1·373 (16)	1·372 (27)	1·406 (33)
C(4)–C(11)	1·401 (17)	1·401 (14)	1·475 (26)	1·405 (22)
C(5)–C(13)	1·407 (14)	1·381 (12)	1·373 (27)	1·376 (25)

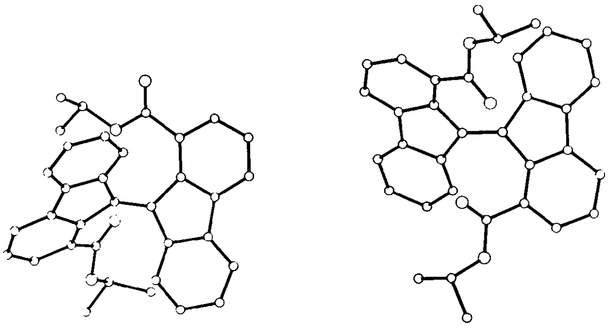

(*a*) (*b*)

Fig. 4. (*a*) The general molecule of (I*b*). (*b*) The special molecule of (I*b*).

distortion in the two compounds is also shown by the magnitudes of the torsion angles across the C(9)—C(9′) bonds. The lengths of the C(9)—C(9′) bonds in (I*b*) are 1·40 and 1·39 Å, indicating a partial diradical character for the bond; the corresponding lengths in (I*d*) are not significantly different (1·38 and 1·35 Å).

The five- and six-membered rings in both compounds are approximately planar: in (I*b*) the r.m.s. deviations range from 0·008 to 0·036 Å and in (I*d*) they range from 0·008 to 0·036 Å. All the fluorenylidene fragments are approximately planar [r.m.s. deviations in (I*b*) are 0·082, 0·068 and 0·046 Å; in (I*d*) they are 0·064, 0·061, 0·063 and 0·044 Å]. However, examination of the torsion angles (Fig. 6) shows that all the fragments have a similar asymmetric distortion such that the angles C(4)—C(11)—C(13)—C(5) are significantly different from zero, and the angles C(9′)—C(9)—C(10)—C(1) vary from 20 to 25° in (I*b*) and from 16 to 20° in (I*d*), whereas the largest C(9′)—C(9)—C(12)—C(8) angle in either compound is 5°.

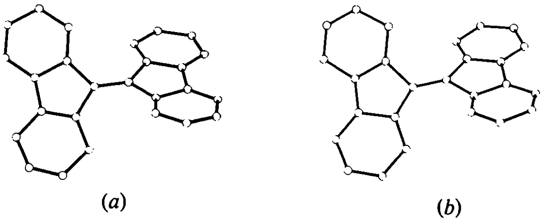

(*a*) (*b*)

Fig. 5. (*a*) The general molecule of (I*d*). (*b*) The 'special' molecule of (I*d*).

Bond lengths within the six-membered rings of (I*b*) (mean 1·402 Å) are similar to those found in benzene (1·397 Å), however, the bonds common to the five- and six-membered rings are slightly longer (mean 1·427 Å) than the remaining bonds (mean 1·397 Å). The average length of the C(11)—C(13) bonds in (I*b*) is 1·431 Å, rather shorter than those found in other fluorene derivatives, *e.g.* 1·47 Å in fluorene (Burns & Iball, 1955) and 1·52 Å in 2,4,7-trinitrofluorenone (Dorset, Hybl & Ammon, 1972). However, in the complex bis(biphenylidene)butadienehexacarbonyldiiron the corresponding distances are 1·42 and 1·39 Å (Bright & Mills, 1972), suggesting that the electronic structure of the fluorenylidene fragment is altered when it forms part of a more extensive conjugated system. The remaining bonds in the five-membered rings are formally single bonds and their average length is 1·473

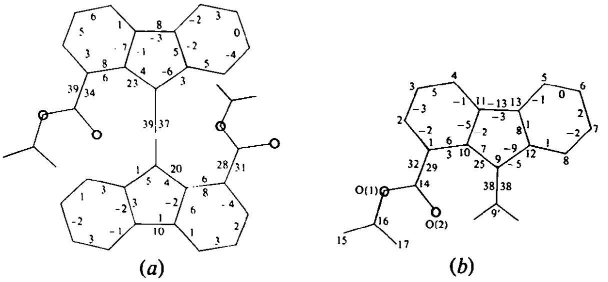
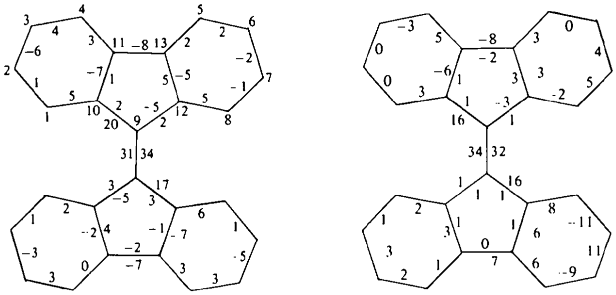


Fig. 6. Torsion angles (°) for (I*b*). (*a*) The general molecule – fragments *A* (top) and *B*. (*b*) The special molecule – fragment *S*, showing the atomic numbering scheme.

Table 7. *Bond angles* (°) *for* (I*d*)

C(*B*9)–C(*A*9)–C(*A*10)	126·6 (8)	C(*B*9)–C(*A*9)–C(*A*12)	127·0 (9)
C(*A*9)–C(*B*9)–C(*B*10)	127·5 (8)	C(*A*9)–C(*B*9)–C(*B*12)	127·5 (8)
C(*T*9)–C(*S*9)–C(*S*10)	122·6 (14)	C(*T*9)–C(*S*9)–C(*S*12)	130·7 (15)
C(*S*9)–C(*T*9)–C(*T*10)	125·1 (14)	C(*S*9)–C(*T*9)–C(*T*10)	130·8 (14)

	Fragment *A*	Fragment *B*	Fragment *S*	Fragment *T*
C(10)–C(9)–C(12)	106·2 (8)	105·0 (7)	106·6 (13)	103·8 (12)
C(1)–C(10)–C(9)	130·7 (9)	131·7 (9)	128·8 (14)	131·9 (14)
C(1)--C(10)–C(11)	120·1 (9)	119·1 (9)	124·7 (15)	120·3 (13)
C(9)–C(10)–C(11)	108·0 (8)	108·3 (8)	105·6 (13)	107·1 (12)
C(8)–C(12)–C(9)	130·2 (9)	130·9 (7)	133·0 (16)	130·1 (15)
C(8)–C(12)–C(13)	122·0 (8)	118·9 (7)	117·7 (15)	118·6 (15)
C(9)–C(12)–C(13)	106·7 (10)	109·5 (7)	108·9 (15)	110·9 (14)
C(2)–C(1)–C(10)	119·9 (9)	119·4 (10)	113·1 (16)	120·0 (15)
C(7)–C(8)–C(12)	113·9 (11)	117·6 (8)	119·9 (15)	121·1 (15)
C(1)–C(2)–C(3)	119·7 (10)	119·4 (11)	122·9 (18)	120·6 (16)
C(2)–C(3)–C(4)	121·1 (11)	122·4 (11)	123·3 (17)	119·9 (15)
C(3)–C(4)–C(11)	120·2 (11)	119·1 (10)	117·5 (17)	118·3 (15)
C(6)–C(7)–C(8)	121·3 (13)	121·9 (9)	120·4 (16)	118·0 (17)
C(5)–C(6)–C(7)	125·2 (11)	121·1 (8)	121·4 (16)	121·4 (16)
C(6)–C(5)–C(13)	114·6 (13)	118·2 (9)	119·3 (17)	120·4 (17)
C(4)–C(11)–C(10)	118·5 (10)	120·2 (9)	117·9 (16)	119·8 (14)
C(4)–C(11)–C(13)	134·5 (10)	130·4 (9)	128·5 (17)	131·7 (15)
C(10)–C(11)–C(13)	106·9 (9)	109·3 (8)	113·4 (15)	108·3 (13)
C(5)–C(13)–C(12)	122·7 (11)	122·1 (8)	121·1 (16)	120·3 (16)
C(5)–C(13)–C(11)	125·4 (12)	130·2 (9)	133·5 (17)	129·8 (15)
C(11)–C(13)–C(12)	112·0 (8)	107·7 (7)	105·5 (15)	109·8 (15)



(*a*) (*b*)

Fig. 7. Torsion angles (°) for (I*d*). (*a*) The general molecule – fragments *A* (top) and *B*, showing the atomic numbering scheme. (*b*) The 'special' molecule – fragments *S* (top) and *T*.

Å, similar to those found in the other compounds referred to above. The bond lengths in (I*d*) have been determined with less accuracy: the average lengths within the six-membered rings are 1·395 and 1·399 Å for the general and 'special' molecules respectively. The C(11)–C(13) bonds are longer than in (I*b*), but the standard errors are too large to enable any conclusions to be drawn.

The C(1)–C(8′) intramolecular contacts are only slightly longer in (I*b*) (mean distance 3·31 Å) than in (I*d*) (mean distance 3·17 Å), showing that the presence of the bulky isopropoxycarbonyl groups in (I*b*) has no large effect on the conformation of the bifluorenylidene framework; the shortest non-bonded contacts between the two halves of the molecules of (I*b*) are between C(8) and C(14′) (mean distance 3·11 Å). The C(1)–C(8′) contacts in both compounds are rather longer than those in bixanthenylidene and bianthronylidene, for which the corresponding distances are 2·99 Å (Mills & Nyburg, 1963) and 2·9 Å (Harnik & Schmidt, 1954) respectively. It appears that the ground states of (I*b*) and (I*d*) are strained to a very similar extent, and that the difference in ground-state energy is not sufficient to explain the NMR results of Agranat *et al.* (1972).

In (I*b*) the major difference between the general and special molecules is in the orientation of the substituent isopropoxycarbonyl groups: in the special molecule both groups are oriented in the same way [with the carbonyl O atom the closer of the two O atoms to the C(9)–C(9′) bond], whereas in the general molecule the positions of the O atoms belonging to one of the isopropoxycarbonyl groups are reversed; these differences are clearly shown in Fig. 4. These different orientations are probably due to crystal packing effects and may explain the slight differences in the angles between the fluorenylidene planes in the two molecules. The bond lengths and angles within the isopropoxycarbonyl fragments are close to those found in similar compounds, with the exception of the C(14)–O(1) single bonds, for which the average length is 1·35 Å, rather more than for equivalent bonds in propargyl 2-bromo-3-nitrobenzoate (1·31 Å) (Calabrese, McPhail & Sim, 1966) and isozygosporin A *p*-bromobenzoate (1·32 Å) (Tsukuda & Koyama, 1972), but less than that in 9,10-anthrohydroquinone dibenzoate (1·39 Å) (Iball & Mackay, 1962).

The only intermolecular contacts less than the sum of the van der Waals radii are C(*S*3)–C(*B*14) ($\frac{1}{2}-x$, $\frac{1}{2}-y$, $\frac{1}{2}-z$) (3·37 Å) and C(*S*14)–C(*B*3) ($\frac{1}{2}-x$, $1\frac{1}{2}-y$, $\frac{1}{2}-z$) (3·38 Å) in (I*b*), and C(*B*7)–C(*B*13) (x, $1-y$, $-\frac{1}{2}+z$) (3·36 Å), C(*S*8)–C(*T*11) (x, $1-y$, $-\frac{1}{2}+z$) (3·32 Å) and C(*S*13)–C(*T*7) (x, $1-y$, $\frac{1}{2}+z$) (3·29 Å) in (I*d*).

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