Tableau 2. *Longueurs* (Å) *et angles* (°) *de liaison avec leurs écarts-type*

O(1)–C(2)	1,361 (3)	C(13)–C(10)	1,391 (4)
C(2)–C(3)	1,344 (4)	C(12)–C(6)	1,411 (4)
C(3)–C(11)	1,418 (4)	C(6)–C(7)	1,365 (5)
C(11)–C(10)	1,383 (4)	C(7)–C(8)	1,406 (5)
O(1)–C(10)	1,377 (3)	C(8)–C(9)	1,363 (4)
C(4)–C(11)	1,427 (4)	C(9)–C(13)	1,409 (4)
C(4)–C(5)	1,350 (4)	C(2)–N(21)	1,419 (4)
C(5)–C(12)	1,433 (4)	N(21)–O(23)	1,222 (3)
C(12)–C(13)	1,423 (4)	N(21)–O(22)	1,231 (3)
O(1)–C(2)–C(3)	114,0 (2)	C(7)–C(8)–C(9)	119,8 (3)
C(2)–C(3)–C(11)	104,7 (2)	C(8)–C(9)–C(13)	120,4 (2)
C(3)–C(11)–C(10)	106,8 (2)	C(9)–C(13)–C(12)	120,0 (2)
C(11)–C(10)–O(1)	110,1 (2)	C(13)–C(12)–C(6)	117,6 (2)
C(10)–O(1)–C(2)	104,2 (2)	C(5)–C(12)–C(6)	122,2 (2)
C(11)–C(4)–C(5)	118,3 (2)	C(9)–C(13)–C(10)	124,9 (2)
C(4)–C(5)–C(12)	122,6 (2)	O(1)–C(10)–C(13)	124,2 (2)
C(5)–C(12)–C(13)	120,0 (2)	C(3)–C(11)–C(4)	134,6 (2)
C(12)–C(13)–C(10)	114,9 (2)	O(1)–C(2)–N(21)	115,7 (2)
C(13)–C(10)–C(11)	125,5 (2)	C(3)–C(2)–N(21)	130,2 (2)
C(10)–C(11)–C(4)	118,4 (2)	C(2)–N(21)–O(23)	119,1 (2)
C(12)–C(6)–C(7)	121,0 (3)	C(2)–N(21)–O(22)	116,5 (2)
C(6)–C(7)–C(8)	120,8 (3)	O(22)–N(21)–O(23)	124,2 (2)

Aucun atome, y compris ceux du groupe –NO$_2$, ne s'en éloigne de plus de 0,03 Å; l'angle de torsion moyen autour de la liaison C(2)–N(21) est de –0,5°.

La cohésion du cristal est assurée par de multiples interactions de type van der Waals et par des interactions de recouvrement des orbitales π (forces de stacking) de molécules parallèles (centres Ī) et superposées, correspondant à une distance interplanaire de 3,35 Å.

Elle présente une grande analogie structurale (longueurs et angles de liaisons, arrangement moléculaire) avec celles dont la structure cristalline est actuellement connue.

On peut se demander dans ces conditions si son activité biologique ne résulte pas en définitive d'un changement dans la répartition des charges du noyau naphtofuranne induit par la présence de substituants et notamment des groupements méthoxy. En effet des calculs de charges par des méthodes semi-quantiques (Cotrait, Bideau, Buisson & Royer, 1984) semblent bien montrer l'importance de la nature et de la position de ces substituants sur cette distribution.

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# Refinement of the α-Modification of 9,9'-Bifluorenylidene, C$_{26}$H$_{16}$, and Structure Analyses of the β-Modification, the 2:1 Pyrene Complex, 2(C$_{26}$H$_{16}$).C$_{16}$H$_{10}$, and the 2:1 Perylene Complex, 2(C$_{26}$H$_{16}$).C$_{20}$H$_{12}$

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Abstract. Room temperature, Cu $K\alpha$ radiation, $\lambda =$ 1·5418 Å. (i) α-Modification of 9,9'-bifluorenylidene (BFL) {a refinement of that based on photographic data

of Bailey & Hull [*Acta Cryst.* (1978), B34, 3289–3295]}: $M_r = 328\cdot4$, orthorhombic, *Pbcn*, $a =$ 36·68 (1), $b = 17\cdot080$ (5), $c = 8\cdot145$ (6) Å, $V =$ 5103 (4) Å^3, $Z = 12$ molecules per cell, $D_m = 1\cdot28$ (2), $D_x = 1\cdot28$ Mg m^{-3}, μ(Cu $K\alpha$) = 0·56 mm^{-1}, $F(000) =$ 2064, $R_F = 0\cdot074$ for 2560 reflections. (ii) β-

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Modification of BFL: $M_r = 328\cdot4$, orthorhombic, $P2_12_12_1$, $a = 8\cdot991$ (3), $b = 19\cdot350$ (6), $c = 9\cdot715$ (5) Å, $V = 1690$ (1) Å³, $Z = 4$ molecules per cell, $D_m = 1\cdot29$ (2), $D_x = 1\cdot29$ Mg m⁻³, μ(Cu $K\alpha$) = $0\cdot57$ mm⁻¹, $F(000) = 688$, $R_F = 0\cdot050$ for 1393 reflections. (iii) The 2/1 BFL–pyrene complex: $M_r = 859\cdot1$, monoclinic, $C2/c$, $a = 17\cdot846$ (5), $b = 15\cdot449$ (3), $c = 16\cdot270$ (10) Å, $\beta = 95\cdot59$ (3)°, $V = 4464$ (3) Å³, $Z = 4$ formula units per cell, $D_m = 1\cdot28$ (1), $D_x = 1\cdot28$ Mg m⁻³, μ(Cu $K\alpha$) = $0\cdot56$ mm⁻¹, $F(000) = 1800$, $R_F = 0\cdot054$ for 2267 reflections. (iv) The 2/1 BFL–perylene complex: $M_r = 909\cdot2$, monoclinic, $I2/c$, $a = 16\cdot102$ (4), $b = 15\cdot342$ (5), $c = 18\cdot798$ (9) Å, $\beta = 90\cdot39$ (4)°, $V = 4644$ (3) Å³, $Z = 4$ formula units per cell, $D_m = 1\cdot31$ (2), $D_x = 1\cdot30$ Mg m⁻³, μ(Cu $K\alpha$) = $0\cdot57$ mm⁻¹, $F(000) = 1904$, $R_F = 0\cdot050$ for 2100 reflections. In all four structures, the BFL molecules are twisted due to intramolecular conflicts of H atoms. In α-BFL, which is racemic, the disordered structure of Bailey & Hull is confirmed. The $P2_12_12_1$ space group of β-BFL, with $Z = 4$, requires all the molecules to be of the same chirality; hence spontaneous resolution must have occurred. The two BFL complexes are closely related but not strictly isostructural. In both, pairs of BFL molecules and pyrene (or perylene) molecules alternate in columns parallel to the y axis. These columns are packed differently in the two complexes.

Introduction. 9,9'-Bifluorenylidene, BFL, (I), was first reported made by distilling fluorene over lead oxide (De la Harpe & Van Dorp, 1875). Crystals prepared this way were examined by Arzruni (1877) who assigned axial ratios 0·487:1·00:0·527 (cited by Groth, 1906–1919). A crystal specimen of unstated provenance had its unit-cell dimensions measured by X-rays as 36·7 × 34·3 × 8·15 Å by Taylor (1936). Fenimore (1948) obtained the space group and cell dimensions of 17·22 × 36·9 × 8·23 Å, and determined the approximate crystal structure. [Doubling of the b dimension assigned by Taylor (1936) could have been due to the rows of diffuse X-ray reflections which are present.] Harnik, Herbstein, Schmidt & Hirshfeld (1954) reported the existence of a second polymorph. The polymorph examined by Fenimore (1948) they named α, confirming its space group and cell dimensions. The second form they named β; it had space group $P2_12_12_1$ and cell dimensions 19·43 × 9·02 × 9·75 Å.*

In the approximate crystal structure analysis of α-BFL reported by Fenimore (1948) the molecules were said to be nearly flat, but this is highly unlikely due to

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*Fenimore (1948) inclined to the view that the unit-cell dimensions of the crystal examined by him could not be reconciled with the axial ratios given by Arzruni (1877) despite the fact that 17·22:(36·9/4):8·23 = 1·00:0·536:0·478. Harnik et al. (1954) appear to support this view but it does not appear to be possible to match the cell dimensions of the β-form at all closely with the axial ratios given by Arzruni (1877).

the close conflict of H atoms at positions 1 and 8 [see (I)]. Nyburg (1954), using Fenimore's phased data, calculated electron density sections in the neighborhood of C atoms 1 and 8 and concluded that the molecule was doubly bent, C(A1), C(A8) being on one side of the mean molecular plane, C(B1), C(B8) on the other. This has since been shown by Bailey & Hull, (1978) (B & H hereafter) to be incorrect; the molecule is twisted about C(A9)–C(B9). The structural misidentification is now seen, from the analysis of B & H, to be due to the presence of molecular disorder. (Another contributing factor could have been the quite marked differences in F values given by Fenimore on the one hand and those of B & H and the present work on the other.)

(I)
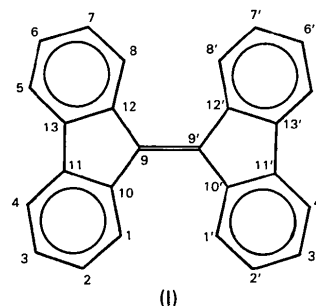
The structure analysis of B & H was based on visually estimated photographic data and thus, not surprisingly, was of limited accuracy. We report here structure analyses of β-BFL, 2/1 BFL complexes with pyrene and with perylene and a refinement of α-BFL based on diffractometer intensity data.

We believe the pyrene and perylene complexes described here have not been characterized before. Although we have not made an extensive search, we have been unable to find any references to complexes with BFL apart from the picrate (De la Harpe & Van Dorp, 1875; Graebe & Von Mantz, 1896).

Experimental. α-BFL was prepared by treating 9-bromo-9,9'-bifluorenyl (Susuki & Fujimoto, 1963) with potassium tert-butoxide (Bethell & Cockerill, 1966). Purified material was recrystallized from carbon tetrachloride/ethanol.

β-BFL was prepared accidentally during our efforts to prepare a BFL–perylene complex (see below). A saturated solution of perylene in acetic acid was added to solid α-BFL and the acetic acid removed by rotary evaporation. A minimum of glacial acetic acid was then added to the remaining solid with warming. Slow evaporation of the acetic acid led to the deposition of crystalline β-BFL.

The 2/1 BFL–pyrene complex was prepared by dissolving BFL (0·82 g, 2·5 mmol) and pyrene (0·05 g, 2·5 mmol) in hot acetic acid (20 ml). The solution was refrigerated overnight. Wine-red crystals suitable for X-ray analysis were separated by filtration.

Table 1. *Experimental data*

	α-BFL	β-BFL	2/1 BFL–pyrene	2/1 BFL–perylene
Crystal dimensions (mm)	0·3 × 0·12 × 0·12	0·22 × 0·19 × 0·4	0·19 × 0·16 × 0·10	0·4 × 0·32 × 0·24
No. of unique reflections	3881	3526	3526	2693
σ(*I*)'s for significance	3	2	2	2
No. of significant reflections	2560	1393	2267	2100
R_F	0·074	0·050	0·054	0·050
wR_F*	0·096	0·068	0·072	0·068
S	1·24	1·25	1·03	1·08
$(\Delta/\sigma)_{mean}$	0·15	0·25	0·26	0·09
$(\Delta/\sigma)_{max}$	0·30	0·41	0·58	0·21

* $w = 1/\sigma^2(F)$.

The 2/1 BFL-perylene complex was prepared by dissolving BFL (0·98 g, 3 mmol) in 30 ml hot acetic acid saturated with perylene. The resultant solution was allowed to evaporate slowly at room temperature. Deep-yellow crystals suitable for X-ray analysis were deposited.

Apart from preliminary photographic X-ray examination all diffraction data were collected on an automated four-circle Picker diffractometer using Ni-filtered Cu *K*α radiation and pulse-height discrimination. Experimental data are set out in Table 1. In each case unit-cell dimensions were obtained from a least-squares analysis of 12 centered reflections. Intensity data in θ–2θ scan mode, scan range 2°, $2\theta_{max}$ = 125°. A standard reflection measured every 60 reflections showed all crystals to be quite stable to X-rays. $\sigma(F_o)$ was taken as $\{[Lp\sigma(I)]^2 + 0\cdot02F_o^4\}^{1/2}/2F_o$. No absorption or secondary-extinction corrections.

The atomic coordinates for α-BFL as given by B & H were used as a starting set for refinement. The structures of the other three crystals were solved using *MULTAN* (Germain, Main & Woolfson, 1971). All structures were refined using *XFLS* (Busing, Martin & Levy, 1971) with scattering factors of Cromer & Waber (1965).

α-BFL

The structure has been described by B & H. Eight molecules are in general equivalent positions of space group *Pbcn* and four in special positions (Wyckoff set *b*). These four special positions are space-group centers of symmetry; since the molecules are not centrosymmetric there is disorder at these four sites each being occupied by two molecules of occupancy 0·5. The crystal is racemic (unlike the β-modification, see below), four pairs of molecules of opposite chirality occupying the general equivalent positions and four pairs half-occupying the special positions. The structure is shown in *z* projection in Fig. 3 of B & H. For molecules in general equivalent positions we have used the same atomic numbering scheme, (I), as used by B & H.* The two fragments of the disordered molecules at the special

positions were labeled S and T by B & H but with a different symmetry of numbering of the constituent atoms. We have used the S and T notation also but have preserved the numbering symmetry shown in (I).

There are short distances (0·3–0·6 Å) between several atomic images at the disordered sites, namely those involving atoms C(S1), C(S3), C(S6), C(T1) and C(T3). Accordingly, in the last cycle of refinement, their positions were calculated by matching the well resolved S and T atomic positions to those of the BFL–pyrene complex using the rigid-body matching program *BMFIT* (Nyburg, 1974). Accordingly, no positional e.s.d.'s or bond lengths and angles involving these atoms are given. The positions of H atoms (from ΔF map) were refined with fixed isotropic temperature factors $B = 5\cdot0$ Å^2. C-atom positional parameters are listed in Table 2.*

Geometric details derived from the atomic coordinates are deferred to the *Discussion* where comparisons between the four crystal structures are made. A discussion of the nature of the disorder present has been given by B & H.

β-BFL

Crystal data are given in Table 1 and details of the data collection are the same as for the α-modification above. C-atom positional parameters are given in Table 3. Because the space group is $P2_12_12_1$ the crystal, unlike that of the α-modification, is not racemic and the method of preparation must have brought about spontaneous resolution. The method of molecular packing available to the α-form in which molecules of alternating chirality are stacked one upon the other is not available to the β-form. The packing, which is not easily described, is shown in perspective (Fig. 1) and in projection (Fig. 2).

The 2/1 BFL–pyrene and BFL–perylene complexes

The method of structure analysis is given above. Crystal data are set out in Table 1, C-atom coordinates

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* The table of coordinates of B & H (their Table 3) has atoms C(B10) through C(B13) wrongly labeled. They should be C(B12), C(B13), C(B10) and C(B11) respectively.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters for all four compounds and tables of bond lengths and angles in the BFL molecules have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39903 (58 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional atomic coordinates* $(\times 10^4)$ *and* B_{eq} *values* (Å^2) *with e.s.d.'s for* C *atoms of* α-BFL

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j \beta_{ij}\mathbf{a}_i \cdot \mathbf{a}_j.$$

|	x	y	z	B_{eq}
C(A1)	6804 (1)	6559 (2)	6719 (5)	5·3 (1)
C(A2)	6705 (1)	7332 (3)	7063 (6)	7·4 (2)
C(A3)	6366 (2)	7614 (3)	6669 (7)	8·9 (2)
C(A4)	6103 (1)	7140 (4)	5983 (6)	8·7 (2)
C(A5)	5608 (1)	5700 (4)	4620 (6)	9·8 (3)
C(A6)	5448 (1)	5017 (6)	4142 (7)	13·7 (4)
C(A7)	5658 (1)	4357 (4)	4104 (6)	10·5 (3)
C(A8)	6023 (1)	4329 (3)	4589 (5)	7·7 (2)
C(A9)	6556 (1)	5230 (2)	5614 (4)	4·6 (1)
C(A10)	6546 (1)	6078 (2)	5952 (4)	4·9 (1)
C(A11)	6197 (1)	6363 (3)	5659 (5)	6·1 (1)
C(A12)	6177 (1)	5020 (3)	5173 (4)	5·8 (1)
C(A13)	5970 (1)	5710 (3)	5124 (4)	7·0 (2)
C(B1)	7377 (1)	5654 (2)	4496 (4)	4·6 (1)
C(B2)	7737 (1)	5653 (2)	3939 (5)	5·7 (1)
C(B3)	7946 (1)	4985 (3)	3945 (5)	5·9 (1)
C(B4)	7803 (1)	4290 (3)	4481 (5)	5·8 (1)
C(B5)	7315 (1)	2849 (2)	5899 (5)	6·7 (1)
C(B6)	7057 (2)	2369 (2)	6609 (6)	8·3 (2)
C(B7)	6723 (2)	2653 (3)	7077 (5)	8·1 (2)
C(B8)	6617 (1)	3428 (2)	6746 (5)	6·6 (1)
C(B9)	6856 (1)	4755 (2)	5582 (4)	4·1 (1)
C(B10)	7228 (1)	4957 (2)	5096 (4)	3·9 (1)
C(B11)	7443 (1)	4275 (2)	5039 (4)	4·4 (1)
C(B12)	6870 (1)	3906 (2)	5943 (4)	4·7 (1)
C(B13)	7220 (1)	3628 (2)	5606 (4)	5·0 (1)
C(S1)	726	4863	-337	5·8
C(S2)	1091 (2)	5068 (6)	-172 (13)	6·9 (3)
C(S3)	1209	5817	-548	7·2
C(S4)	967 (2)	6371 (6)	-1092 (12)	7·1 (3)
C(S5)	272 (3)	7449 (5)	-2102 (11)	6·3 (3)
C(S6)	-61	7777	-2433	6·8
C(S7)	-378 (2)	7344 (5)	-2269 (11)	5·7 (3)
C(S8)	-368 (2)	6565 (4)	-1744 (8)	4·5 (2)
C(S9)	74 (2)	5418 (4)	-1001 (8)	3·8 (2)
C(S10)	475 (2)	5419 (4)	-855 (9)	4·4 (2)
C(S11)	600 (2)	6189 (4)	-1210 (9)	4·5 (2)
C(S12)	33 (2)	6226 (4)	-1370 (8)	4·2 (2)
C(S13)	287 (2)	6685 (4)	-1598 (9)	4·8 (2)
C(T1)	243	3646	-2152	4·5
C(T2)	244 (2)	2871 (4)	-2640 (9)	4·5 (3)
C(T3)	-60	2407	-2329	5·3
C(T4)	-367 (2)	2710 (4)	-1575 (10)	4·4 (2)
C(T5)	-992 (2)	3747 (4)	161 (9)	4·3 (2)
C(T6)	-1206 (3)	4319 (7)	937 (12)	4·9 (2)
C(T7)	-1085 (2)	5074 (4)	1131 (10)	4·9 (2)
C(T8)	-744 (3)	5288 (6)	546 (14)	4·4 (2)
C(T9)	148 (2)	4769 (4)	-836 (7)	3·6 (2)
C(T10)	54 (2)	3959 (4)	-1331 (8)	3·7 (2)
C(T11)	-364 (2)	3484 (4)	-1105 (8)	4·0 (2)
C(T12)	-525 (2)	4743 (4)	-249 (8)	3·7 (2)
C(T13)	-655 (2)	3964 (4)	-399 (8)	4·1 (2)

Table 3. *Fractional atomic coordinates* $(\times 10^4)$ *and* B_{eq} *values* (Å^2) *with e.s.d.'s for* C *atoms of* β-BFL

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j \beta_{ij}\mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B_{eq}
C(A1)	-5030 (4)	1308 (2)	5321 (4)	4·2 (1)
C(A2)	-6422 (5)	1595 (2)	5107 (5)	4·9 (1)
C(A3)	-6637 (5)	2097 (2)	4084 (5)	5·5 (1)
C(A4)	-5500 (5)	2287 (2)	3238 (5)	4·9 (1)
C(A5)	-2374 (6)	2555 (2)	1604 (4)	4·7 (1)
C(A6)	-950 (7)	2566 (3)	1099 (5)	5·4 (1)
C(A7)	131 (6)	2152 (2)	1664 (4)	4·7 (1)
C(A8)	-188 (5)	1695 (2)	2728 (4)	3·9 (1)
C(A9)	-2280 (4)	1295 (2)	4442 (4)	3·3 (1)
C(A10)	-3834 (4)	1538 (2)	4513 (4)	3·6 (1)
C(A11)	-4094 (4)	2010 (2)	3430 (4)	3·9 (1)
C(A12)	-1637 (4)	1649 (2)	3214 (3)	3·5 (1)
C(A13)	-2728 (5)	2099 (2)	2667 (4)	3·8 (1)
C(B1)	-2718 (5)	1221 (2)	7747 (4)	4·0 (1)
C(B2)	-2603 (6)	1126 (2)	9158 (4)	4·7 (1)
C(B3)	-1589 (6)	671 (3)	9709 (4)	5·3 (1)
C(B4)	-639 (6)	302 (3)	8866 (5)	5·1 (1)
C(B5)	1193 (5)	-431 (2)	6363 (5)	5·1 (1)
C(B6)	1838 (5)	-627 (2)	5151 (6)	5·6 (1)
C(B7)	1382 (5)	-361 (2)	3902 (6)	5·2 (1)
C(B8)	293 (5)	157 (2)	3855 (5)	4·1 (1)
C(B9)	-1551 (4)	881 (2)	5357 (4)	3·2 (1)
C(B10)	-1823 (4)	833 (2)	6873 (4)	3·6 (1)
C(B11)	-763 (5)	391 (2)	7441 (4)	3·8 (1)
C(B12)	-307 (4)	406 (2)	5084 (4)	3·4 (1)
C(B13)	132 (4)	95 (2)	6340 (4)	4·0 (1)
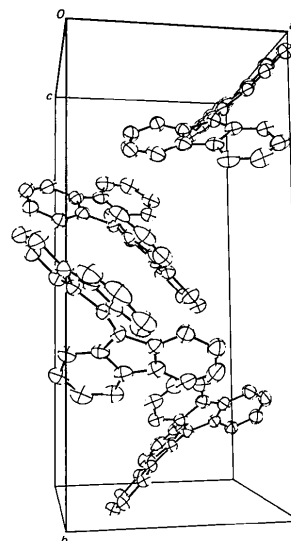
Fig. 1. Molecular packing in β-BFL.

in Tables 4 and 5. The positional and isotropic thermal parameters of H atoms were refined. In both complexes the eight BFL molecules per cell lie in general equivalent positions of the space groups. The four pyrene or perylene molecules per cell lie in special positions and are required to have diad axes through their centers normal to their mean molecular planes.

Both complexes are made up of similar columns parallel to the y axis with diad axes along their cores (see y projections, Figs. 3, 4). In any one column, pairs of BFL molecules and single pyrene (or perylene) molecules, normal to y, alternate in the y direction. In each column adjacent BFL pairs of molecules have the same chirality (because of the diad which relates them) with their central double bonds almost parallel to the y axis. Hence the almost identical b cell dimensions of the two complexes.
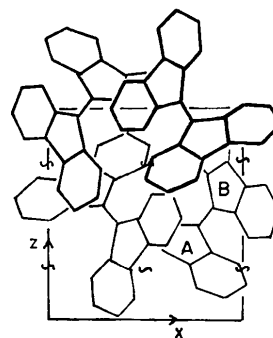
Fig. 2. β-BFL in y projection. A, B are at $(1+x, y, z)$ of Table 3.

The two complexes are not, however, isostructural. The relation between their crystal structures can be seen from schematic depictions of their y projections, Figs. 5 and 6. Pyrene (or perylene) molecules lie on the twofold axes, the large crosses indicating the (twisted) BFL molecules. In the pyrene complex (Fig. 5) columns within a given yz plane are related by **c** glides at $y = 0$,

Table 4. *Fractional atomic coordinates* ($\times 10^4$) *and* B_{eq} *values* (Å^2) *with e.s.d.'s for* C *atoms of* 2/1 *BFL–pyrene complex*

$$B_{eq} = \tfrac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j.$$

	x	y	x	B_{eq}
C(A1)	3539 (2)	2552 (2)	8862 (2)	4·3 (1)
C(A2)	3029 (2)	3213 (2)	8950 (2)	4·9 (1)
C(A3)	3243 (2)	4069 (2)	8897 (2)	5·4 (1)
C(A4)	3971 (2)	4282 (2)	8768 (2)	5·3 (1)
C(A5)	5740 (2)	4388 (2)	8474 (2)	5·4 (1)
C(A6)	6489 (2)	4261 (2)	8394 (2)	5·7 (1)
C(A7)	6789 (2)	3438 (2)	8412 (2)	5·0 (1)
C(A8)	6347 (2)	2726 (2)	8530 (2)	4·3 (1)
C(A9)	4961 (1)	2220 (2)	8698 (2)	3·9 (1)
C(A10)	4270 (1)	2754 (2)	8702 (2)	3·9 (1)
C(A11)	4481 (2)	3626 (2)	8671 (2)	4·0 (1)
C(A12)	5590 (1)	2838 (2)	8643 (2)	3·7 (1)
C(A13)	5291 (2)	3676 (2)	8595 (2)	4·2 (1)
C(B1)	3783 (2)	796 (2)	7891 (2)	4·8 (1)
C(B2)	3404 (2)	69 (2)	7580 (2)	5·7 (1)
C(B3)	3686 (2)	−743 (2)	7769 (2)	6·4 (1)
C(B4)	4356 (2)	−854 (2)	8260 (2)	5·9 (1)
C(B5)	5939 (2)	−683 (2)	9433 (2)	5·9 (1)
C(B6)	6588 (2)	−436 (3)	9886 (2)	6·3 (1)
C(B7)	6757 (2)	425 (3)	10012 (2)	5·9 (1)
C(B8)	6290 (2)	1069 (2)	9660 (2)	4·7 (1)
C(B9)	5011 (2)	1344 (2)	8752 (2)	4·1 (1)
C(B10)	4443 (2)	703 (2)	8414 (2)	4·1 (1)
C(B11)	4731 (2)	−129 (2)	8577 (2)	4·6 (1)
C(B12)	5648 (1)	829 (2)	9150 (2)	4·0 (1)
C(B13)	5470 (2)	−54 (2)	9064 (2)	4·5 (1)
C(P1)	4223 (3)	3281 (2)	4100 (3)	8·6 (2)
C(P2)	3503 (3)	3277 (3)	3707 (4)	9·6 (2)
C(P3)	3355 (3)	3278 (3)	2885 (4)	8·8 (2)
C(P4)	3822 (3)	3267 (2)	1503 (3)	7·7 (2)
C(P5)	4400 (3)	3268 (2)	1037 (3)	7·9 (2)
C(P6)	4845 (2)	3272 (2)	3622 (2)	6·4 (1)
C(P7)	4697 (2)	3271 (2)	2755 (2)	4·6 (1)
C(P8)	3945 (2)	3271 (2)	2390 (2)	6·0 (1)

Table 5. *Fractional atomic coordinates* ($\times 10^4$) *and* B_{eq} *values* (Å^2) *with e.s.d.'s for* C *atoms of* 2/1 *BFL–perylene complex*

Equivalent positions of $I2/c$: $(0,0,0;\ \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}) + x,y,z;\ \bar{x},\bar{y},\bar{z};\ \bar{x},y,\tfrac{1}{2}-z;\ x,\bar{y},\tfrac{1}{2}+z.$

$$B_{eq} = \tfrac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j.$$

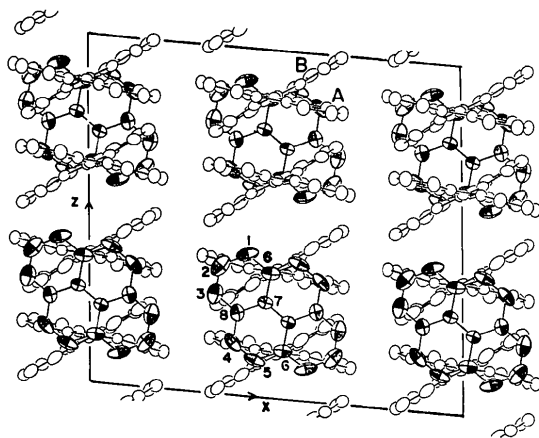|	x	y	z	B_{eq}
C(A1)	7858 (2)	3460 (2)	−3882 (1)	4·4 (1)
C(A2)	7539 (2)	2804 (2)	−4308 (2)	5·1 (1)
C(A3)	7663 (2)	1938 (2)	−4133 (2)	5·5 (1)
C(A4)	8061 (2)	1715 (2)	−3515 (2)	5·1 (1)
C(A5)	9094 (2)	1605 (2)	−2017 (2)	5·2 (1)
C(A6)	9561 (2)	1737 (2)	−1410 (2)	5·6 (1)
C(A7)	9756 (2)	2569 (2)	−1185 (1)	4·9 (1)
C(A8)	9478 (2)	3296 (2)	−1560 (1)	3·9 (1)
C(A9)	8684 (1)	3794 (2)	−2709 (1)	3·4 (1)
C(A10)	8311 (1)	3246 (2)	−3277 (1)	3·5 (1)
C(A11)	8381 (2)	2371 (2)	−3077 (1)	3·9 (1)
C(A12)	8980 (2)	3175 (2)	−2159 (1)	3·6 (1)
C(A13)	8806 (2)	2321 (2)	−2397 (1)	4·0 (1)
C(B1)	9034 (2)	5091 (2)	−4041 (1)	4·0 (1)
C(B2)	9165 (2)	5776 (2)	−4508 (1)	4·8 (1)
C(B3)	9140 (2)	6624 (2)	−4281 (2)	6·1 (1)
C(B4)	9018 (2)	6809 (2)	−3574 (2)	6·3 (1)
C(B5)	8718 (2)	6830 (2)	−1857 (2)	6·6 (1)
C(B6)	8585 (2)	6662 (2)	−1152 (2)	6·5 (1)
C(B7)	8509 (2)	5823 (2)	−911 (2)	5·0 (1)
C(B8)	8570 (2)	5125 (2)	−1372 (1)	4·1 (1)
C(B9)	8760 (1)	4685 (2)	−2708 (1)	3·4 (1)
C(B10)	8858 (2)	5266 (2)	−3332 (1)	3·6 (1)
C(B11)	8888 (2)	6132 (2)	−3098 (2)	4·5 (1)
C(B12)	8742 (2)	5273 (2)	−2084 (1)	3·7 (1)
C(B13)	8796 (2)	6135 (2)	−2326 (2)	4·6 (1)
C(P1)	714 (2)	783 (1)	2969 (1)	4·1 (1)
C(P2)	1376 (2)	760 (2)	3437 (2)	5·3 (1)
C(P3)	1268 (2)	784 (2)	4170 (2)	6·2 (1)
C(P4)	496 (2)	828 (2)	4447 (2)	5·9 (1)
C(P5)	−1020 (2)	875 (2)	4283 (2)	5·6 (1)
C(P6)	−1696 (2)	859 (2)	3851 (2)	5·8 (1)
C(P7)	−1597 (2)	814 (2)	3121 (2)	5·0 (1)
C(P8)	825 (2)	794 (1)	2807 (1)	4·0 (1)
C(P9)	−106 (2)	802 (1)	3256 (1)	4·0 (1)
C(P10)	−212 (2)	836 (2)	4006 (1)	4·7 (1)

Fig. 3. 2/1 BFL–pyrene complex in y projection showing pyrene atomic numbering. These atoms and those of BFL fragments A and B are (x, y, z) of Table 4.
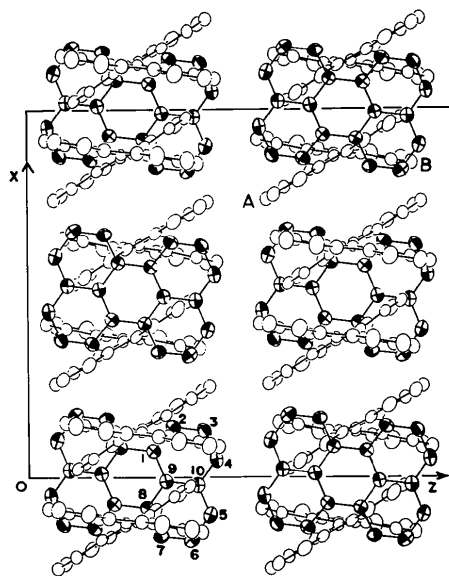

Fig. 4. 2/1 BFL–perylene complex in y projection showing perylene atomic numbering corresponding to (x, y, z) of Table 5. A and B fragments of BFL are $(x, y, 1+z)$ of Table 5.

$\frac{1}{2}$. In the perylene complex (Fig. 6) the columns within a given xy plane are related by **a** glides located at $y = \frac{1}{4}, \frac{3}{4}$. The result is closely similar packing within these planes. Thus note that, in the pyrene complex, the y displacement of BFL midpoints in adjacent columns is $\pm(0.678-0.322) = \pm 0.356$ [or, in an adjacent yz plane, $\pm(0.822-0.178) = \pm 0.644$, which is the same]. In the perylene complex, the y displacement between adjacent columns is $\pm(0.446-0.054) = \pm 0.392$. Thus the packing of columns in the yz planes of the pyrene complex is closely similar to that in the xy planes of the perylene complex. This correspondence is shown by the appropriate sections (Figs. 7 and 8). The difference between the structures lies in the relation between the yz planes ($x = \frac{1}{2}$ apart) in the pyrene complex and the xy planes ($z = \frac{1}{2}$ apart) in the perylene complex. In the former, packing in these planes is related by net glides at $y = \frac{1}{4}, \frac{3}{4}$ whereas in the latter they are related by **c** glides at $y = 0, \frac{1}{2}$. These differences can be seen on close inspection of Figs. 3 and 4.

Discussion. Tables 6 and 7 show averaged bond lengths and bond angles with their deviations from the mean for chemically equivalent bonds in BFL molecules.* On the

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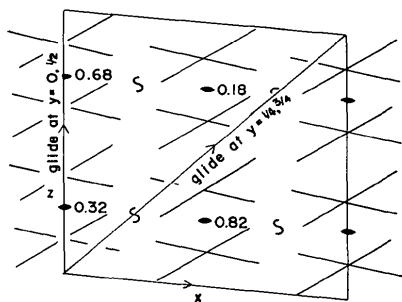
* See deposition footnote.

Fig. 5. 2/1 BFL–pyrene complex corresponding to Fig. 3 showing symmetry elements. Large X's are BFL molecules related in pairs by the diad axes together with fractional y coordinates of their midpoints.
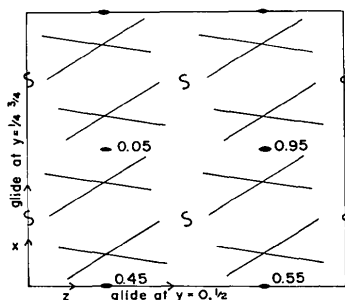

Fig. 6. 2/1 BFL–perylene complex corresponding to Fig. 4. Note that columns of BFL molecules in xy planes are related in a similar way to those in yz planes of the pyrene complex (Figs. 3, 5).

whole, the mean bond lengths and angles obtained from the complexes of BFL appear somewhat more concordant than those obtained from the α- and β-polymorphs.

The dihedral angles at the six central atoms of BFL (Table 8) accord with those given by B & H. Best least-squares planes were calculated for molecular half-fragments A and B and for all five- and six-membered rings. The angles between these planes were averaged over all the BFL molecules. The average angle between molecular half-fragments was 39.3 $(1)°$; that
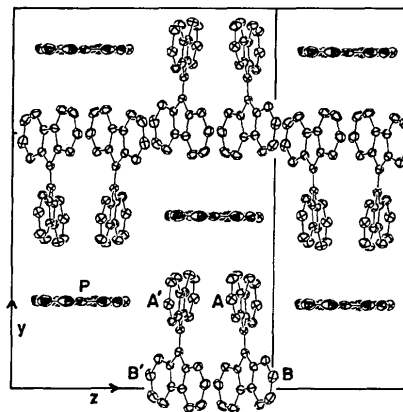

Fig. 7. The yz section of the 2/1 BFL–pyrene complex at $x = \frac{1}{2}$ (Fig. 3). A, B and A', B' fragments of BFL have coordinates (x, y, z) and $(1-x, y, 1\frac{1}{2}-z)$ of Table 4. P (pyrene) has coordinates (x, y, z) and $(1-x, y, \frac{1}{2}-z)$.
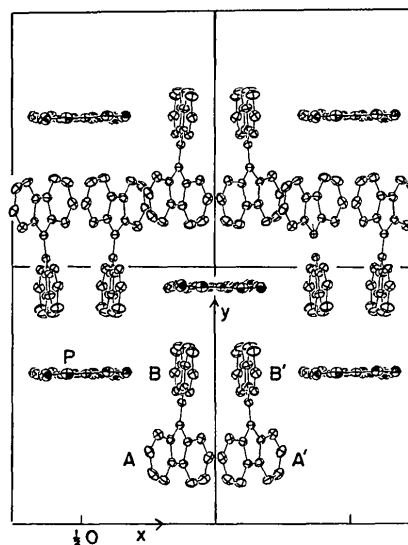

Fig. 8. The xy section of the 2/1 BFL–perylene complex at $z = \frac{3}{4}$ (Fig. 4). A, B and A', B' fragments of BFL have coordinates $(x, y, 1+z)$ and $(1-x, y, \frac{1}{2}-z)$ of Table 5. P (perylene) has coordinates $(\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}+z)$ and $(\frac{1}{2}-x, \frac{1}{2}+y, \bar{z})$.

Table 6. *Mean values of chemically equivalent bond lengths* (Å) *in BFL molecules; standard deviations, in parentheses, calculated from* $[(\sum \Delta^2)/(n-1)]^{1/2}$; (i) α-BFL, (ii) β-BFL, (iii) *pyrene complex,* (iv) *perylene complex*

Bonds	(i)*	(ii)	(iii)	(iv)
1–2; 7–8	1·399 (5)	1·391 (5)	1·384 (5)	1·387 (4)
2–3; 6–7	1·371 (4)	1·384 (13)	1·380 (3)	1·376 (6)
3–4; 5–6	1·372 (8)	1·371 (9)	1·374 (7)	1·372 (6)
4–11; 5–13	1·394 (5)	1·394 (7)	1·384 (3)	1·391 (3)
10–11; 12–13	1·399 (8)	1·410 (10)	1·400 (3)	1·403 (5)
11–13	1·453 (8)	1·450 (7)	1·470 (6)	1·453 (7)
1–10; 8–12	1·397 (4)	1·394 (7)	1·397 (4)	1·389 (2)
9–10; 9–12	1·475 (7)	1·484 (11)	1·482 (3)	1·481 (1)
Central double bond				
9–9'	1·367 (5)	1·364 (15)	1·359 (4)	1·373 (3)

* Mean lengths for ordered fragments *A* and *B* only.

Table 7. *Mean values of chemically equivalent interbond angles* (°) *in BFL molecules* (*details as for Table* 6)

Bond angles	(i)	(ii)	(iii)	(iv)
2–1–10; 7–8–12	117·7 (7)	119·2 (3)	119·4 (3)	119·5 (3)
1–2–3; 6–7–8	122 (1)	120·8 (6)	120·7 (4)	120·9 (5)
2–3–4; 5–6–7	120 (1)	121·0 (6)	120·9 (4)	120·6 (3)
3–4–11; 6–5–13	119 (1)	119·0 (7)	118·8 (3)	119·3 (2)
10–9–9'; 12–9–9'	127·5 (3)	127·4 (6)	127·1 (1)	127·3 (3)
1–10–11; 8–12–13	119·4 (8)	119·1 (4)	118·8 (3)	119·0 (4)
9–10–11; 9–12–13	109·1 (7)	108·7 (4)	108·5 (4)	108·6 (3)
1–10–9; 8–12–9	131 (1)	131·4 (5)	132·0 (5)	131·8 (3)
4–11–10; 5–13–12	121·4 (4)	120·8 (6)	121·4 (2)	120·6 (2)
4–11–13; 5–13–11	130·2 (5)	130·5 (8)	130·0 (4)	130·6 (4)
10–11–13; 11–13–12	108·4 (5)	108·7 (4)	108·6 (3)	108·7 (4)
10–9–12	104·9 (2)	105·1 (3)	105·8 (3)	105·4 (0)

Table 8. *Dihedral angles* (°) *in BFL molecules*

	(i)	(ii)	(iii)	(iv)
10–9–9'–10'	−32·0 (3)	−33·8 (7)	−30·2 (6)	−34·1 (1)	−30·0 (3)
12–9–9'–12'	−34·0 (2)	−30·5 (6)	−33·7 (6)	−31·2 (2)	−33·8 (3)
10–9–9'–12'	152·0 (3)	150·5 (6)	152·0 (6)	147·0 (1)	148·4 (4)
12–9–9'–10'	142·1 (3)	145·2 (6)	144·1 (7)	147·8 (3)	147·8 (3)

Table 9. *Overcrowded ethylenes* R_2=C=C=R_2; *correlation of conformation with magnitude of internal angle* R–C–R

	Internal angle (°)	Reference
Twist conformation		
Five-membered rings		
Bifluorenylidene	104·9–105·8	This work
Perchlorofulvalene	104·5	(a)
Octobromofulvalene	104·9	(b)
'Doubly bent' conformation		
Six-membered rings		
Benzodifurazanylidene derivative	109–110	(c)
Bixanthylidene (α-form)	109	(d)
(β-form)	111	(d)
Bicyclohexylidene	110·6	(e)
Dianthronylidene	113	(f)
Seven-membered rings		
Heptafulvalene	117·6	(g)
Tetrabenzoheptafulvalenes	112–114	(h)

References: (a) Ammon, Wheeler & Agranat (1973); (b) Fallon, Ammon, West & Rao (1974); (c) Cameron & Prout (1969); (d) Mills & Nyburg (1963); (e) Sasvári & Löw (1965); (f) Harnik & Schmidt (1954); (g) Thomas & Coppens (1972); (h) Dichmann, Nyburg, Pickard & Potworowski (1974).

Table 10. *Averaged chemically equivalent bond lengths* (Å) *and interbond angles* (°) *in pyrene and perylene molecules of* 2/1 *BFL complexes*

Bond lengths		Interbond angles	
Pyrene			
1–2; 2–3	1·358 (9)	2–1–6; 2–3–8	118·5 (5)
1–6; 3–8	1·402 (7)	5–4–8; 4–5–6'	121·9 (4)
6–7; 7–8	1·412 (5)	1–6–5'; 3–8–4	122·9 (4)
5–6; 4–8	1·422 (7)	1–6–7; 3–8–7	119·2 (4)
4–5	1·335 (7)	7–6–5'; 7–8–4	118·0 (3)
7–7'	1·421 (6)	6–7–7'; 8–7–7'	120·1 (3)
		1–2–3	124·1 (5)
		6–7–8	119·8 (3)
Perylene			
1–2; 7–8	1·379 (4)	2–1–9; 7–8–9	118·3 (2)
1–9; 8–9	1·429 (4)	2–1–8'; 1'–8–7	122·5 (2)
2–3; 6–7	1·387 (5)	9–1–8'; 1'–8–9	119·2 (2)
3–4; 5–6	1·354 (5)	1–2–3; 6–7–8	122·4 (3)
5–10; 4–10	1·405 (5)	2–3–4; 5–6–7	120·0 (3)
9–10	1·423 (4)	3–4–10; 6–5–10	121·3 (3)
1–8'	1·472 (4)	1–9–10; 8–9–10	119·2 (2)
		1–9–8	121·7 (2)
		4–10–5	122·1 (3)
		4–10–9; 5–10–9	119·0 (2)

between a five- and six-membered ring, 5·6 (1·4)°; that between six-membered rings attached to the same five-membered ring, 2·6 (1·1)°. The senses and magnitudes of these deviations from coplanarity are consistent with their being caused by a repulsive interaction between H atoms at positions 1 and 8. The distances between these H atoms all, with one exception, fall in the range 2·19–2·30 Å. The exception is H(A8)···H(B8) in the β-form of BFL, which is 1·87 Å. We cannot account for this and it is difficult to believe that it is genuine. Such positions, found by least-squares refinement, would correspond to displacements of these two particular H atoms out of their local six-membered rings in directions towards, rather than away from, each other. This is highly unlikely. Intermolecular H···H distances in all four crystal structures are 2·0 Å or longer.

Although there are, as yet, too few examples to make a definite generalization possible, the conformations adopted by overcrowded symmetric ethylenes R_2=C=C=R_2 appear to be correlated with the magnitude of the internal angle R–C–R (Table 9). When this angle is less than 105° (five-membered central rings) a twisted conformation is adopted; when this angle is greater than 109° (six- and seven-membered central rings) the 'doubly bent' conformation is adopted.

The bond lengths and interbond angles found for the pyrene and perylene molecules are in close accord with published values. Averaged dimensions are given in Table 10. As can be seen from the *y* coordinates listed in Table 4, the C atoms of pyrene are closely coplanar. Those of perylene on the other hand are far less coplanar showing deviations of order 0·1 Å from the mean molecular plane. This is not unusual; other crystal structure determinations of perylene all show deviations from planarity of this order of magnitude.

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Acide Bicyclo[4.1.0]heptanedicarboxylique-3,4-(1R*,3R*,4R*,6S*), C9H12O4

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Abstract. $M_r = 184.2$, triclinic, $P\bar{1}$, $a = 14.986$ (4), $b = 11.358$ (2), $c = 8.480$ (2) Å, $\alpha = 98.81$ (6), $\beta = 77.00$ (5), $\gamma = 98.91$ (6)°, $V = 1378.9$ (6) Å³, $Z = 6$, $D_x = 1.33$ Mg m⁻³, $\lambda(\text{Cu} K\alpha) = 1.5418$ Å, $\mu(\text{Cu} K\alpha) = 0.895$ mm⁻¹, $F(000) = 588$, final $R = 0.072$ for 3039 reflections. The three independent molecules of the asymmetric unit are associated through conventional hydrogen bonds to form a trimer, each molecule being bonded to the other two. The associated carboxyl groups mark the boundaries of a large cavity.

Introduction. Ce composé a été choisi pour servir de référence à une série d'études cristallographiques

consacrées principalement à des composés bicyclo-[4.1.0]heptaniques substitués par deux chlores en position 7 (Ebby, Lapasset, Pizzala, Aycard & Bodot, 1980).

Partie expérimentale. Préparation par saponification du diester correspondant (Pizzala, 1978). Densité mesurée par flottation. Monocristal de dimensions 0,38 × 0,22 × 0,13 mm. Diffractomètre Enraf–Nonius CAD-3. Paramètres de la maille obtenus à partir de 15 réflexions (15 < θ < 25°). 3975 réflexions indépendantes enregistrées (balayage $\theta/2\theta$; θ < 65°; $\sin\theta/\lambda$ < 0,588 Å⁻¹; h −16–16, k −13–13, l 0–12), 3039 réflexions conservées [$I > 3\sigma(I)$], puis corrigées des facteurs de Lorentz et de polarisation, mais pas