Molecular Compounds and Complexes.
V.* Crystallography of Equimolar Aromatic Hydrocarbon:1-X-2,4,6-Trinitrobenzene Molecular Compounds. Crystal Structure of Fluoranthene:Picryl Bromide, Polymorph I

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Crystal data are reported for the binary π-molecular compounds with naphthalene, anthracene, phenanthrene, acenaphthene, fluoranthene, pyrene or triphenylene as donor and 1,3,5-trinitrobenzene, picric acid, picryl chloride or picryl bromide as acceptor (33 different crystals have been studied). In three out of seven pairs, the trinitrobenzene and picric acid molecular compounds of a particular hydrocarbon are isomorphous, and in four out of seven pairs the picryl chloride and picryl bromide molecular compounds are isomorphous. The structure of fluoranthene:picryl bromide, polymorph I [monoclinic; $a = 7\cdot664$ (8), $b = 8\cdot035$ (2), $c = 31\cdot631$ (8) Å, $\beta = 91\cdot8$ (1)°, space group $P2_1/c$, $Z = 4$] has been solved by Patterson and Fourier methods and refined by block-diagonal least-squares calculations to a final R of $0\cdot062$. The structure consists of quasi-hexagonally close-packed mixed stacks of alternating donor and acceptor molecules. The stack axes are parallel to [100]. The interplanar spacing is $3\cdot49$ Å, suggesting a rather weak charge-transfer interaction.

1. Introduction

Aromatic hydrocarbons and the molecules 1,3,5-trinitrobenzene (TNB), picric acid, picryl chloride and picryl bromide form crystalline π-molecular compounds. The TNB and picric acid molecular compounds are usually isomorphous [for a summary see Herbstein (1971), especially pp. 196–201 and Table 20] but little is known about the picryl halide molecular compounds. We have therefore prepared molecular compounds of naphthalene, anthracene, phenanthrene, acenaphthene, fluoranthene, pyrene and triphenylene with the four acceptors TNB, picric acid, picryl chloride and picryl bromide and have determined the cell dimensions and space groups of 33 different crystalline compounds (Table 1). Examples of exact and approximate isomorphism were found, as well as examples of polymorphism and disorder. The results indicate many relationships among the structures of the molecular compounds of a particular donor with the several acceptors used.

Five of the six fluoranthene molecular compounds listed in Table 1 have one unusually long cell axis (~ 30 or ~ 60 Å) and their crystal structures do not follow at once from the cell dimensions. Excellent crystals of one of the fluoranthene:picryl bromide polymorphs were obtained and this structure was determined in the hope that it would serve as a prototype

of the fluoranthene molecular compounds. Furthermore the structure of fluoranthene itself has not yet been determined so these results provide a set of experimental dimensions for the fluoranthene molecule [cell dimensions of fluoranthene have been given by Chakravarti (1954)].

A rather stable pyrene:picryl bromide molecular compound with the component ratio 3:2 was encountered during this work and its structure is described in the following paper (Herbstein & Kaftory, 1974).

2. Crystallography of aromatic hydrocarbon:1-X-2,4,6-trinitrobenzene molecular compounds

2.1. *Experimental*

Crystals of the various molecular compounds were obtained by slow cooling of hot solutions of the components, which were taken in approximately equimolar ratios. The solvents used were benzene for picric acid molecular compounds, ethanol for TNB and picryl bromide molecular compounds and cyclohexane for the picryl chloride molecular compounds. The crystal data, obtained by standard methods, are given in Table 1, classified according to the electron donor (Lewis base) component.

2.2. *Discussion of results*

Of the 33 crystals studied here, 26 have a ~ 7 Å periodicity along their stack (or needle) axes, 5 have a ~ 14 Å periodicity and in 2 (naphthalene:picryl chloride and naphthalene:picryl bromide) the direction of the stack axis is not clear from the cell dimensions.

Table 1. *Crystal data for various equimolar π-molecular compounds*

The table has been arranged to emphasize structural relationships. The values for the stack axes (or needle axis for unknown structure types) are in bold type.

Donor:Acceptor	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Space group	Z	Density (g cm⁻³) Meas.	Calc.	Melting point (°C) Meas.[1]	Lit.[2]	Structural group	Note
Naphthalene:														
TNB	14·5	**6·97**	16·19	–	97·6	–	$P2_1/c$	4	1·41	1·40	152	151	4(b)	3,4
Picric acid	14·34	**6·80**	16·14	–	97·0	–	$P2_1/c$	4	1·527	1·519	150	149·5	4(b)	5
Picryl chloride	7·71*	**6·80***	**13·81**	130·3		61†	$P1$ or $P\bar{1}$	2	1·480	1·507	91·8	91·2		6
Picryl bromide	8·71	10·04	**13·94**	130·3	74·7	97·2	$P1$ or $P\bar{1}$	2	1·655	1·701	93·5			
Anthracene:														
TNB	11·33	16·27	**13·02**	–	133·2	–	$C2/c$	4	1·43	1·414	162	164	–	7
Picric acid	**7·191**	12·902	19·211	–	91·13	–	$P2_1/c$	4	1·466	1·513	138	138	3(b)	5,8,9
Picryl chloride	9·99	13·94	**7·37**	99·8	105·6	99·8	$P1$ or $P\bar{1}$	2	1·475	1·478	136	64·6	6(b)	
Picryl bromide	14·33	**6·90**	19·48	–	103·0	–	$P2_1/c$	4	1·63	1·668	118		4(b)	
Phenanthrene:														
TNB	7·7	17·13	**13·7**	–	101·5	–	$P2_1/c$	4	1·410	1·435	164	158	–	4
Picric acid	8·99	14·81	**7·12**	101·5	99·2	102·1	$P1$ or $P\bar{1}$	2	1·450	1·483	133	144	6(b)	4,10
Picryl chloride	15·89	15·48	**7·40**	–	91·0	–	$P2_1/c$	4	1·511	1·554	80	82·4	3(c)	
Picryl bromide	16·11	15·48	**7·40**	–	91·0	–	$P2_1/c$	4	1·652	1·696	84		3(c)	
Acenaphthene:														
TNB	16·21	**6·85**	16·55	–	119	–	$P2/a$ or $P2_1/a$	4	1·521	1·518	167·5	168	4(b)	11
Picric acid	14·4	8·92	**6·85**	–	102	–	$C2$	2	1·442	1·487	159	162	–	
Picryl chloride	14·5	?	**6·85**	?	?	?	?	?	1·548	?	109	113	–	12
Picryl bromide	15·36	17·13	**6·92**	–	102·5	–	$P2_1$	4	1·619	1·671	102			
Fluoranthene:														
TNB	8·48	**7·27**	30·35	–	96	–	$P2_1/c$	4	1·472	1·498	204	209	4(b)	
Picric acid	8·68	**7·27**	31·0	–	96	–	$P2_1/c$	4	1·487	1·472	190	185	4(b)	
Picryl chloride I	**7·41**	13·95	19·39	–	96·5	–	$P2_1/c$	4	1·492	1·500	115	120	3(b)	19
Picryl chloride II	37·0	**7·06**	60·64	–	91	–	Cc or $C2/c$	32	1·471	1·509	115		–	
Picryl bromide II	18·46	**7·01**	30·34	–	92	–	$B2_1/c$	8	1·634	1·677	82		4(b)	13
Picryl bromide I	**7·664**	8·035	31·631	–	91·8	–	$P2_1/c$	4	1·66	1·689	84		3(b)	
Pyrene:														
TNB	**6·77**	16·35	8·55	93·0	101·3	95·6	$P\bar{1}$	2	1·49	1·50	204	246	6(b)	14,19
Picric acid I	8·44*	**16·17***	**6·80**			81†	$P\bar{1}$	2	1·568	1·563			6(b)	15
Picric acid II	17·65	**6·80**	17·19	–	112·5	–	$P2_1/c$	4	1·464	1·507	225	222	4(b)	16
Picryl chloride I	17·17	**6·90**	16·64	–	94·0	–	$P2_1/c$	4	1·532	1·519	148	154	4(b)	19
Picryl bromide	17·38	**6·90**	16·56	–	94·0	–	$P2_1/c$	4	1·63	1·656	148		4(b)	
Picryl chloride II	9·98	16·01	**13·93**	101·7	118·2	86·2	$P1$ or $P\bar{1}$	4	1·500	1·555	145			
Triphenylene:														
TNB	16·29	8·75	**7·19**	–	97·6	–	$P2_1$	2	1·413	1·443	248			17
Picric acid	32·60	8·72	**7·11**	–	98·4	–	$P2_1/a$	4	1·524	1·519	222	222	3(b)	
Picryl chloride I	16·28	18·70	**7·16**	–	104·5	–	$P2/a$	4	1·511	1·498	156		3(b)	
Picryl chloride II	32·80	18·30	**14·40**	–	94	–	F-centred	16						13
	18·20	18·30	**14·40**	–	116	–	Aa or $A/2a$	8	–	1·466	152·5			18
Picryl bromide	32·22	18·30	**14·54**	–	92	–	F-centred cell	16						13
	17·90	18·30	**14·54**	–	116	–	Aa or $A2/a$	8	1·601	1·617	133 – 137			18

Notes: (1) Sealed tube. (2) Values from standard compilations, *e.g.* Beilstein, Heilbron. (3) See Wallwork (1961) for approximate structure. (4) Kofler (1944) reports two polymorphs and gives reference to earlier work. (5) Phase diagram by Mindovich (1956). (6) Isomorphous with naphthalene: picryl bromide. (7) Structure by Brown, Wallwork & Wilson (1964); also see Kofler (1944). (8) Kofler (1944) reports a phase transformation at 88°; we find that the high-temperature polymorph cannot be retained at room temperature. (9) We have determined this crystal structure (Herbstein & Kaftory, in preparation). (10) At least three polymorphs exist (Matsunaga, 1971). (11) Space group uncertain because of weak low-angle 0k0 reflexions. (12) OD structure, not investigated in detail. (13) Non-standard cell chosen to emphasize structural relationships. (14) Structure reported by Prout & Tickle (1973); cell dimensions also given by Hertel & Bergk (1936). (15) Isomorphous with pyrene: TNB. (16) Weak reflexions have been ignored in determining cell dimensions and space group. (17) Also 00*l* absent for *l* odd. (18) Re-orientation of *F*-centred monoclinic cell to give standard *A*-centred cell. (19) m.p. from Sinomiya (1940).

* Interplanar spacing. † Reciprocal angle.

Previous study of available results (Herbstein, 1971, Table 20) has shown that equimolar π-molecular compounds with ~ 7 Å periodicity along their stack axes can be sorted into a number of groups of quasi-isomorphous structures. 21 (of 26) crystals of Table 1 with ~ 7 Å stack axes can be assigned to these groups. Some equimolar π-molecular compounds have periodicities of ~ 14 Å along their stack axes (Herbstein, 1971, Table 16). The pyrene:picryl chloride II crystal and the isomorphous pair triphenylene:picryl chloride II and triphenylene:picryl bromide are new examples of this structure type. However too few examples are known to allow further classification into quasi-isomorphous groups.

The structural relationships among the various molecular compounds are quite complicated. The trinitrobenzene and picric acid compounds of each of naphthalene, fluoranthene and pyrene are strictly isomorphous, while those of triphenylene are clearly related. Different structures are found for each pair of the TNB and picric acid molecular compounds of anthracene, phenanthrene and acenaphthene. Picryl chloride and picryl bromide molecular compounds of each of naphthalene and phenanthrene are isomorphous and one pair of polymorphs is isomorphous when fluoranthene, pyrene and triphenylene are the electron donors. There is also a pair of non-isomorphous polymorphs of fluoranthene with picryl chloride and picryl bromide; a second pyrene:picryl chloride molecular compound (polymorph II), different from that in the isomorphous pair, is found. Furthermore the pyrene molecular compounds of picric acid (polymorph II), picryl chloride (polymorph I) and picryl bromide are isomorphous, while the triphenylene molecular compounds of TNB, picric acid and picryl chloride (polymorph I) are related but not strictly isomorphous.

Structure analyses may show further relationships which do not appear from comparison of cell dimensions and space groups.

References to previous work on the crystals of Table 1 are given in the notes to this table. In general there is good agreement between present and earlier results, although there are some discrepancies in melting points. However, there is some controversy in the literature about anthracene–picric acid molecular compounds. Our present work indicates that there is only one such compound, of equimolar composition and melting at 138°. This is in agreement with the three (compatible) phase diagrams that have been reported for the system anthracene–picric acid (Kremann, 1905; Reinholdt, Kircheisen & Henning, 1925; Mindovich, 1956) and with the results of Kofler (1944). Andersen (1956) has reported an equimolar anthracene:picric acid compound melting over the range 148–180°; after recrystallization from chloroform the melting point was 183°. Details are not given of the X-ray work performed, which is said to show that 'the high and the low melting picrates prepared from ethanol and chloroform were two definite modifications'. Sandqvist & Hagelin (1918) reported an anthracene–picric acid molecular compound with a broad melting range (up to 175°) and composition, based on nitrogen analysis, of anthracene:2 (picric acid). Neither of these proposals is compatible with the phase diagram or with our crystallographic results.

3. Crystal structure of fluoranthene:picryl bromide, polymorph I

The crystal data for fluoranthene:picryl bromide, polymorph I, are summarized in Table 2; the cell dimensions were measured from back-reflexion Weissen-
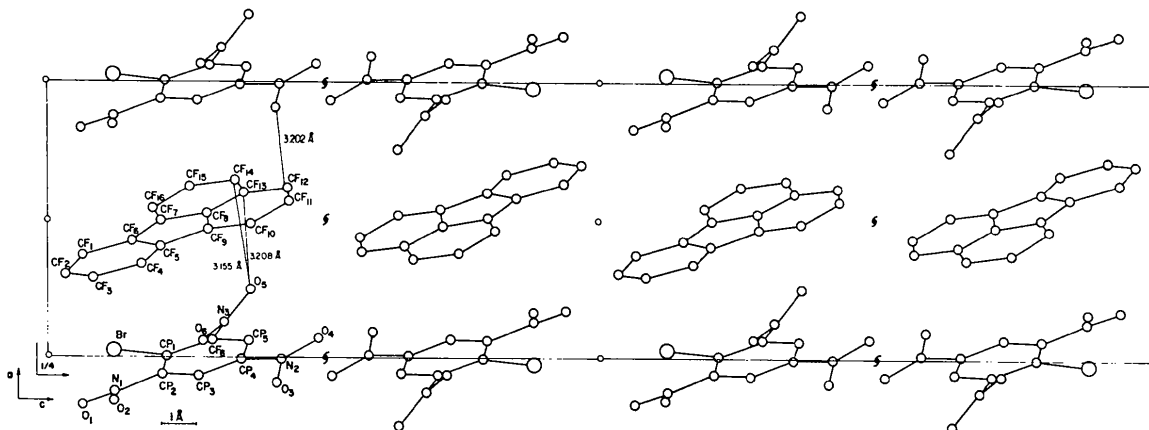

Fig. 1. Projection along [010]. The coordinates of the labelled atoms are given in Table 4. Hydrogen atoms have been omitted.

berg and Mathieson inclined-beam oscillation photo-graphs (Herbstein, 1963).

Table 2. *Crystal data for fluoranthene:picryl bromide* I

Fluoranthene: picryl bromide I	$C_{16}H_{10}:C_6H_2Br(NO_2)_3$
Monoclinic	F.W. 493·9
Space group $P2_1/c$	m.p. 84°C
$a = 7·664$ (8) Å	$Z = 4$
$b = 8·035$ (2)	$D_m = 1·66$ g cm^{-3}
$c = 31·631$ (8)	$D_x = 1·68$
$\beta = 91·8$ (1)°	$\mu = 36$ cm^{-1} for Cu $K\alpha$
$V = 1947$ Å^3	λ(Cu $K\alpha_1$) = 1·54050 Å
	λ(Cu $K\alpha_2$) = 1·54434

3.1. *Measurement and correction of intensities*

Intensities of 2205 0*kl*–4*kl* independent reflexions ($2\theta'_{max} = 130°$) were measured on a Stoe Weissenberg diffractometer with graphite-monochromated Cu $K\alpha$ radiation and the ω–2θ scan method (scan speed 1° 2θ/min; scan width 2·4° 2θ; backgrounds were counted for 20 s at the extrema of the scans). The crystal had

dimensions $0·38 \times 0·22 \times 0·08$ mm. Appropriate geometrical and absorption corrections (Busing & Levy, 1957) were applied.

Table 4. *Fractional coordinates and isotropic temperature factors of hydrogen atoms*

$T = \exp(-8\pi^2 U \sin^2 \theta/\lambda^2)$. The mean standard deviations o. the hydrogen parameters are: $\sigma(x) = 0·008$, $\sigma(y) = 0·007$, $\sigma(z) = 0·002$, $\sigma(U) = 0·02$ Å^2

	x	y	z	U (Å^2)
HP(3)	−0·109	0·429	0·135	0·03
HP(5)	−0·095	−0·073	0·213	0·03
HF(1)	0·427	−0·099	−0·014	0·03
HF(2)	0·275	−0·339	0·017	0·02
HF(3)	0·227	−0·572	0·030	0·01
HF(4)	0·319	−0·553	0·104	0·02
HF(10)	0·403	−0·465	0·190	0·04
HF(11)	0·596	−0·326	0·246	0·03
HF(12)	0·672	−0·036	0·241	0·03
HF(14)	0·702	0·211	0·185	0·03
HF(15)	0·649	0·327	0·121	0·01
HF(16)	0·521	0·155	0·067	−0·01

Table 3. *Final parameters (and their e.s.d.'s) of the non-hydrogen atoms*

The U_{ij} values (in Å^2) are defined by $T = \exp(-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U'_{ij}h_ih_ja_i^*a_j^*)$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Picryl bromide									
Br	0·0276 (1)	0·10673 (8)	0·06079 (2)	0·053 (1)	0·0679 (5)	0·0481 (4)	0·0008 (3)	0·0273 (4)	0·0072 (3)
CP(1)	0·0006 (8)	−0·0376 (6)	0·1067 (1)	0·022 (3)	0·041 (2)	0·036 (2)	0·005 (3)	0·003(2)	0·013 (2)
CP(2)	−0·0606 (8)	−0·1968 (6)	0·1027 (1)	0·012 (6)	0·048 (3)	0·031 (2)	0·002 (3)	−0·005 (2)	0·004 (2)
CP(3)	−0·0689 (8)	−0·3073 (5)	0·1359 (1)	0·010 (6)	0·031 (2)	0·045 (3)	0·003 (2)	−0·002 (2)	0·009 (2)
CP(4)	−0·0032 (8)	−0·2528 (5)	0·1751 (1)	0·020 (6)	0·037 (2)	0·035 (2)	0·012 (2)	0·006 (2)	0·008 (2)
CP(5)	0·0610 (8)	−0·0976 (5)	0·1815 (1)	0·009 (6)	0·040 (3)	0·035 (3)	0·004 (2)	0·004 (2)	0·004 (2)
CP(6)	0·0635 (8)	0·0101 (5)	0·1472 (1)	0·021 (6)	0·035 (2)	0·041 (2)	0·001 (2)	0·000 (2)	0·004 (2)
N(1)	−0·1307 (7)	−0·2694 (6)	0·0614 (1)	0·048 (6)	0·071 (3)	0·036 (2)	−0·005 (3)	−0·007 (2)	0·001 (2)
N(2)	−0·0111 (8)	−0·3685 (5)	0·2113 (1)	0·051 (6)	0·045 (2)	0·045 (2)	0·014 (2)	0·008 (2)	0·014 (3)
N(3)	0·1249 (8)	0·1800 (5)	0·1576 (2)	0·020 (6)	0·041 (3)	0·064 (3)	−0·001 (2)	−0·003 (2)	0·018 (3)
O(1)	−0·1701 (9)	−0·1767 (6)	0·0332 (1)	0·120 (7)	0·115 (4)	0·047 (3)	−0·030 (4)	0·015 (3)	−0·021 (3)
O(2)	−0·1471 (11)	−0·4169 (7)	0·0601 (2)	0·197 (9)	0·082 (3)	0·085 (4)	−0·028 (4)	−0·024 (3)	−0·057 (5)
O(3)	−0·0961 (7)	−0·4947 (5)	0·2071 (1)	0·086 (6)	0·047 (2)	0·079 (3)	−0·008 (2)	0·017 (2)	0·017 (2)
O(4)	0·0663 (8)	−0·3282 (6)	0·2436 (1)	0·086 (6)	0·087 (3)	0·050 (2)	0·000 (3)	0·024 (2)	−0·011 (2)
O(5)	0·2452 (7)	0·1924 (5)	0·1836 (2)	0·030 (5)	0·072 (3)	0·090 (3)	−0·013 (2)	−0·022 (2)	−0·005 (3)
O(6)	0·0503 (7)	0·2967 (5)	0·1397 (2)	0·072 (5)	0·044 (2)	0·093 (3)	0·005 (2)	0·007 (2)	0·013 (3)
Fluor-anthene									
CF(1)	0·3682 (10)	−0·1814 (7)	0·0323 (2)	0·051 (7)	0·047 (3)	0·051 (3)	−0·009 (3)	0·008 (2)	0·003 (3)
CF(2)	0·3030 (10)	−0·3304 (8)	0·0163 (2)	0·052 (7)	0·065 (3)	0·048 (3)	−0·009 (3)	−0·005 (3)	−0·010 (3)
CF(3)	0·2870 (11)	−0·4705 (7)	0·0412 (2)	0·067 (8)	0·048 (3)	0·073 (4)	−0·016 (3)	−0·008 (3)	−0·012 (4)
CF(4)	0·3352 (10)	−0·4634 (7)	0·0840 (2)	0·060 (7)	0·041 (2)	0·056 (3)	−0·007 (3)	0·001 (2)	0·002 (3)
CF(5)	0·4022 (8)	−0·3176 (6)	0·1010 (1)	0·014 (6)	0·043 (2)	0·047 (3)	0·002 (2)	0·000 (2)	0·003 (2)
CF(6)	0·4204 (8)	−0·1750 (6)	0·0750 (1)	0·018 (6)	0·042 (2)	0·044 (2)	−0·005 (2)	0·000 (2)	0·004 (2)
CF(7)	0·4974 (8)	−0·0400 (6)	0·1012 (2)	0·022 (6)	0·039 (2)	0·049 (3)	−0·005 (2)	0·006 (2)	0·006 (2)
CF(8)	0·5229 (8)	−0·1072 (5)	0·1418 (2)	0·003 (6)	0·035 (2)	0·048 (3)	−0·003 (2)	0·001 (2)	0·006 (3)
CF(9)	0·4669 (6)	−0·2744 (6)	0·1439 (1)	0·014 (6)	0·038 (2)	0·047 (3)	−0·001 (2)	0·004 (2)	0·007 (2)
CF(10)	0·4819 (10)	−0·3584 (7)	0·1819 (2)	0·042 (7)	0·049 (3)	0·054 (3)	0·004 (3)	0·008 (2)	0·006 (3)
CF(11)	0·5614 (10)	−0·2718 (8)	0·2172 (2)	0·050 (7)	0·068 (3)	0·042 (3)	0·004 (3)	0·010 (2)	0·008 (3)
CF(12)	0·6149 (10)	−0·1103 (7)	0·2151 (2)	0·014 (7)	0·070 (4)	0·049 (3)	0·000 (3)	−0·008 (2)	0·003 (3)
CF(13)	0·5967 (8)	−0·0186 (6)	0·1756 (2)	0·004 (6)	0·050 (3)	0·050 (3)	0·002 (2)	−0·007 (2)	0·002 (3)
CF(14)	0·6466 (10)	0·1455 (7)	0·1679 (2)	0·025 (7)	0·040 (2)	0·070 (4)	−0·011 (3)	−0·014 (3)	0·004 (3)
CF(15)	0·6194 (10)	0·2130 (6)	0·1282 (2)	0·032 (7)	0·038 (3)	0·078 (4)	−0·001 (3)	0·003 (3)	−0·002 (3)
CF(16)	0·5413 (10)	0·1219 (6)	0·0941 (2)	0·038 (7)	0·034 (2)	0·062 (4)	−0·012 (2)	0·002 (2)	0·001 (3)

Table 5. *Observed and calculated structure factors on an absolute scale*

Table 5 (cont.)

3.2. Structure determination and refinement

The position of the bromine atom was found from the Harker sections $(2x,\frac{1}{2},\frac{1}{2}+2z)$ and $(0,\frac{1}{2}+2y,\frac{1}{2})$. The positions of all the other non-hydrogen atoms were found from a Fourier synthesis. After refinement of the coordinates and anisotropic temperature parameters the hydrogen atoms were located from a difference synthesis. Final least-squares refinement was carried out in two blocks, the parameters of one molecule in each. The parameters refined were coordinates and anisotropic temperature factors for the non-hydrogen atoms, coordinates and isotropic temperature factors for the hydrogen atoms. The weighting scheme used was $w=\frac{1}{4}$ for $|F_o|<4\cdot0$ and $w=1/|F_o|$ for $|F_o|\geq4\cdot0$.

The scattering factors were taken from Hanson, Herman, Lea & Skillman (1964), dispersion corrections for bromine were taken from *International Tables for X-ray Crystallography* (1962). Refinement was stopped with the conventional R equal to $0\cdot062$, the weighted $R=0\cdot091$ and the 'goodness of fit' $=0\cdot45$. The latter value suggests that the weights have been underestimated on an absolute scale. Observed and calculated structure factors based on the final atomic parameters (Tables 3 and 4) are listed in Table 5.

3.3. Description of the structure

The structure is shown in projection on (010) in Fig. 1 and on (100) in Fig. 2. The alternating donor and acceptor molecules are arranged in mixed stacks whose axes lie along [100], each stack being surrounded by six others in an approximately hexagonal array. Two of these six first-neighbour stacks are identical with the reference stack and are related to it by translation along b, while the remaining stacks are related to the reference stack by inversion. A stereoscopic drawing (*ORTEP*) of the unit-cell contents is shown in Fig. 3. The molecules are inclined at 22° to (100), the angle between the planes (as defined below) of donor and acceptor molecules is 2·1° and the two independent interplanar spacings are 3·49 and 3·59 Å. However, there are some appreciably shorter approaches between oxygen atoms of the nitro-groups and carbon atoms of the fluoranthene molecule (Fig. 1). The distances between stacks correspond to normal van der Waals distances.

The fluoranthene molecule is approximately planar, the equation of its mean plane (referred to orthogonal axes a,b,c^*) being $-0\cdot9201x+0\cdot3273y+0\cdot2151z=0\cdot7142$. The deviations of the atoms from this plane are given in Fig. 5.

3.4. Discussion

The molecular geometry of picryl bromide (Fig. 5) is discussed in more detail in the following paper (Herbstein & Kaftory, 1975).

The molecular geometry of fluoranthene is shown in Fig. 4. Hydrocarbon molecules in which five-membered rings are fused to six-membered aromatic rings must either be non-planar, have unusual bond lengths, have bond angles differing from 120°, or have some combination of these three features. The present results show that fluoranthene is planar and can be considered, *insofar as bond lengths are concerned*, to be a combination of unperturbed naphthalene and benzene portions joined by single bonds between sp^2-hybridized carbon atoms. This is a remarkably good first approximation as the differences between corresponding bond lengths

Fig. 2. Projection along [100], showing quasi-hexagonal packing of mixed stacks. The molecules shown in this figure are those that appear in Fig. 1 or are related to those of Fig. 1 by translation along [001]. Hydrogen atoms have been omitted.

calculated for naphthalene and benzene, on the one hand, and for fluoranthene, on the other, do not exceed 0·007 Å (Dewar & Trinajstic, 1971). These differences are beyond the sensitivity of our present measurements. However, when naphthalene and benzene are joined together via a five-membered ring, appreciable angle strains result; these are fairly evenly spread over the fluoranthene molecule but some concentration of the angle strain appears in the naphthalene portion. Any effect of angle strain on bond lengths is not detectable. A rather similar situation exists in acenaphthene (Ehrlich, 1957), in the cis-dimer of acenaphthylene (Welberry, 1971) and, presumably, in acenaphthylene. [The crystal structure of acenaphthylene has been reported (Welberry, 1973) but disorder prevented determination of the details of the molecular geometry.]

The bond lengths and angles found here for fluoranthene agree well with those found for the cis-dimer of acenaphthylene. There is also good agreement with the less accurate dimensions of acenaphthene.

The overlap diagram of fluoranthene onto the plane of picryl bromide is shown in Fig. 6. The orientations of the benzene ring in picryl bromide and the five-membered ring in fluoranthene resemble those in the azulene:TNB (Hanson, 1965), skatole:TNB and indole:TNB (Hanson, 1964) molecular compounds. This suggests that the Mulliken overlap and orientation principle holds for all these molecular compounds. However the charge-transfer interaction in fluoranthene:picryl bromide seems to be considerably weaker than in azulene:TNB and skatole:TNB (interplanar spacings 3·49, 3·30 and 3·33 Å respectively).

All calculations were carried out on the IBM 370/165 computer at the Technion with standard programs.

We are grateful to many colleagues for copies of their programs.

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Fig. 3. *ORTEP* stereo diagram of unit-cell contents ([001] vertical). Hydrogen atoms have been omitted.

Fig. 4. Fluoranthene: bond lengths (Å) and angles (°) and displacements (10^{-2} Å) of atoms from mean plane of molecule.
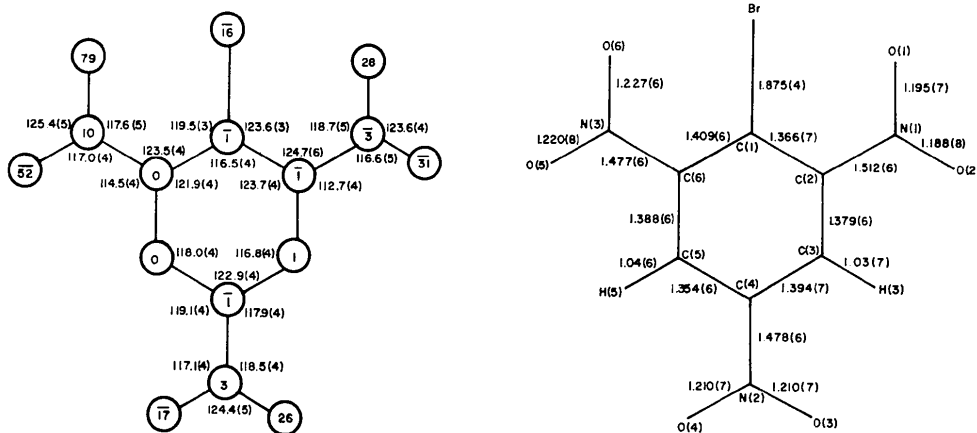
Fig. 5. Picryl bromide: bond lengths (Å) and angles (°) and displacements $(10^{-2}$ Å$)$ of atoms from mean plane of benzene ring.
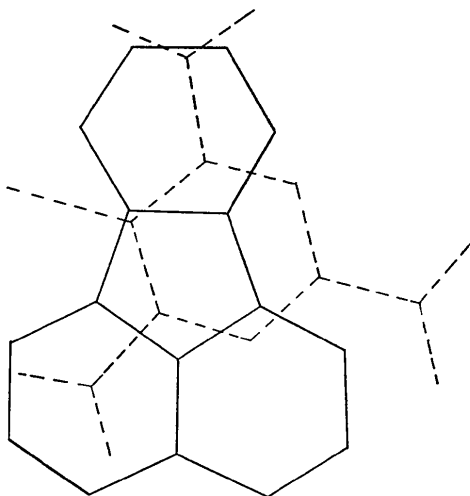
Fig. 6. Fluoranthene:picryl bromide overlap diagram.

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