related *via* the twofold screw axis) while the other consists of molecules *B* (also interrelated by the twofold screw axis). Within each chain the molecules are linked through N(4)—H···O(1) bridges with an N(4)···O(1) distance of 2·93 (chain *A*) and of 2·91 Å (chain *B*). Between the chains only van der Waals forces are present. The fact that O(1) is engaged in hydrogen bonding, whereas O(2) is not, also shows itself in a small, but distinct elongation of C(2)=O(1) compared to C(5)=O(2).

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Structure and Molecular Orbital Studies of Potentially Mutagenic Methylchrysenes and their π–π^* Electron Donor–Acceptor Molecular Complexes

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Abstract

The mutagenic and carcinogenic potency of 5-methylchrysene contrasts strongly with the lack of such activity in any other monomethylchrysene. In order to improve our understanding of the biochemical properties of these compounds, their electronic and molecular structures and π–π^* electron donor–acceptor complexes have been examined by X-ray diffraction and molecular orbital methods. The crystal structures of the hydrocarbons chrysene (redetermination), 1-methylchrysene and 6-methylchrysene, and of the 1:1 complexes of 1,3,5-trinitrobenzene with chrysene, 2-methylchrysene, 3-methylchrysene, 4-methylchrysene, 5-methylchrysene, 6-methylchrysene, the 2:1 complex with 1-methylchrysene and the 1:1 complex of 5-methylchrysene with pyromellitic dianhydride have been determined. 5-Methylchrysene, the carcinogenic hydrocarbon, shows considerable disorder alone and in complexes. In the complexes the stacking of molecules involves an alternation of hydrocarbon with complexing agent, with the aromatic ring of 1,3,5-trinitrobenzene lying over a hydrocarbon bond involved in ring fusion, as

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suggested by a consideration of HOMO's and LUMO's in molecular orbital theory.

Introduction

The mechanism of action of carcinogenic polycylic aromatic hydrocarbons (PAH's) depends on their metabolism to activated products, such as diol epoxides (Sims, Grover, Swaisland, Pal & Hewer, 1974) and the subsequent interaction of these metabolites *in vivo* with biological macromolecules. The identity of the 'critical target' for carcinogenesis, attacked by these activated PAH's, is not yet known. However, it is believed to be an information-containing macromolecule in the nucleus of the cell, since any change in one cancerous cell is transmitted to all daughter cells, implying some disruption of the genetic apparatus.

In order to investigate the process of chemical carcinogenesis by PAH's, many studies of a biochemical or structural nature have been carried out. These indicate that, while one PAH may be highly carcinogenic, chemically similar PAH's may be inactive. One variable in such studies of biological activity is the presence or absence of methyl groups in the PAH. In certain positions on PAH's, methyl groups can enhance carcinogenicity, in other positions they decrease it. For example, of the six possible monomethylchrysenes, only 5-methylchrysene (5MeC) is appreciably carcinogenic (Hoffmann, Bondinell & Wynder, 1974). Furthermore, 7,12-dimethylbenz[*a*]anthracene (DMBA) and 11-methylbenzo[*a*]pyrene (11-MeBaP) are more carcinogenic than their parent compounds lacking methyl groups (Wislocki, Fiorentini, Fu, Yang & Lu, 1982; Iyer, Lyga, Secrist, Daub & Slaga, 1980).

If the methyl group enhances carcinogenicity when in certain positions in a PAH, it may do so in one or more of several ways. It may change the charge distribution around the PAH ring system and so affect its chemical reactivity. It may impose stereochemical strain on the PAH ring system or, more importantly, on its activated metabolite and cause it to react in a specific way. It may have a better shape or electronic structure to fit into the active site of the metabolizing enzyme. Alternatively, it may, when its activated metabolite is bound to DNA, affect the overall conformation of the nucleic acid.

In view of these possibilities, we have studied the crystal structures of the various monomethylchrysenes in order to obtain information on steric strain or bonding variation among these compounds. We have also studied their interactions with other molecules by an examination both of their crystal packing and of complex formation and the packing that results from π–π^* interactions. The complexes studied in this work have mainly involved 1,3,5-trinitrobenzene (TNB), but a number of other complexing agents have been used (Herbstein, 1971; Prout & Kamenar, 1973). The structures of 5MeC and of 5,6- and 5,12-dimethylchrysenes (5,6diMeC and 5,12diMeC) have been published (Zacharias, Kashino, Glusker, Harvey, Amin & Hecht, 1984; Kashino, Zacharias, Prout, Carrell, Glusker, Hecht & Harvey, 1984).

Experimental

Preparation of methylated chrysenes

1-Methylchrysene was obtained from 5-methyl-1-tetralone using a three-step sequence (Hecht, Bondinell & Hoffmann, 1974). 2-Bromotoluene was converted to 2-(2-hydroxyethyl)toluene (Dreger, 1926), which was reacted with thionyl chloride to obtain 2-(2-chloroethyl)toluene (Drake & McVey, 1939). Reaction with ethyl malonate (Wessely & Wang, 1940) gave 4-(2-tolyl)butanoic acid, which was converted to 5-methyl-1-tetralone by treatment with P_2O_5 (Ochiai, Okamoto, Sekijima, Nishikawa & Shono, 1957).

2-Methylchrysene was synthesized according to the method of Hecht *et al.* (1974) from 6-methyl-1-tetralone. 3-Bromotoluene was converted to 6-methyl-1-tetralone by a six-step reaction sequence (Nasipuri & Roy, 1963).

3-Methylchrysene was obtained from 1-(2-chloroethyl)naphthalene in three steps (Ansell & Brooks, 1961). The chloride was obtained by conversion of 1-(2-hydroxyethyl)naphthalene (Aldrich) using thionyl chloride (Cook & Hewett, 1933).

6-Methylchrysene was synthesized from 4-methyl-1-tetralone (Aldrich) by the method of Hecht *et al.* (1974).

Crystals of the hydrocarbons were obtained from ethanol solvent. The TNB molecular complexes were obtained by dissolving the hydrocarbon in hot ethanol and adding an excess of TNB in ethanol solution. The 5-methylchrysene–pyromellitic dianhydride complex (5MeC:PMDA) was formed by mixing the two components in anhydrous butan-2-one, warming and allowing to cool. So far crystals of 2-methyl- and 3-methylchrysene suitable for X-ray diffraction studies have not been obtained.

X-ray analyses

For each structure analysis Table 1 reports crystal data and most experimental details. The X-ray diffraction data were collected on a Nicolet/Siemens $P2_1$ four-circle automated diffractometer using variable θ–2θ scans in the range 2·02–58·6° min^{-1}, depending on reflection intensity. For each crystal, the lattice parameters were determined, using a least-squares procedure, from 14 centered reflections. All measurements were made at the ambient temperature

Table 1. *Crystal and experimental data*

	Chrysene	1MeC	4MeC	6MeC	Chrysene: TNB	1MeC: 2TNB	2MeC: TNB	3MeC: TNB	4MeC: TNB	5MeC: TNB	6MeC: TNB	5MeC: PMDA
Formula	$C_{18}H_{12}$	$C_{19}H_{14}$	$C_{19}H_{14}$	$C_{19}H_{14}$	$C_{18}H_{12}$, $C_6H_3N_3O_6$	$C_{19}H_{14}$, $2C_6H_3N_3O_6$	$C_{19}H_{14}$, $C_6H_3N_3O_6$	$C_{19}H_{14}$, $C_6H_3N_3O_6$	$C_{19}H_{14}$, $C_6H_3N_3O_6$	$C_{19}H_{14}$, $C_6H_3N_3O_6$	$C_{19}H_{14}$, $C_6H_3N_3O_6$	$C_{19}H_{14}$, $C_{10}H_2O_6$
M_r	228·29	242·32	242·32	242·32	441·40	668·54	455·43	455·43	455·43	455·43	455·43	460·44
Space group	$I2/c$	$P2_1/c$	$Pbam$	$Pna2_1$	$Pna2_1$	$P\bar{1}$	$P2_1$	$Pna2_1$	$P\bar{1}$	$P2_12_12_1$	$P2_1/a$	$P2_1/a$
Cell data												
a (Å)	8·367 (4)	11·902 (2)	7·487 (1)	10·840 (2)	10·253 (4)	7·567 (1)	18·306 (2)	10·621 (2)	8·336 (2)	8·332 (4)	19·567 (4)	17·434 (7)
b (Å)	6·214 (2)	6·186 (1)	7·538 (1)	20·812 (4)	27·523 (4)	13·357 (1)	7·522 (1)	27·620 (4)	16·928 (3)	31·866 (13)	7·290 (1)	7·826 (3)
c (Å)	25·183 (8)	8·719 (2)	22·957 (3)	5·6587 (8)	7·206 (2)	7·457 (1)	7·559 (1)	7·209 (2)	7·716 (2)	7·729 (2)	15·545 (3)	8·665 (5)
α (°)						98·73 (1)			92·81 (2)			
β (°)	115·70 (3)	91·44 (1)				93·47 (1)	95·00 (1)		101·64 (2)		107·95 (2)	113·76 (3)
γ (°)						97·54 (1)			96·06 (2)			
V (Å^3)	1179·8 (8)	641·7 (3)	1295·6 (3)	1276·6 (3)	2034 (1)	736·1 (2)	1036·9 (2)	2114·8 (8)	1057·7 (4)	2052 (1)	2109·2 (7)	1082·1 (8)
Z	4	2	4	4	4	1	2	4	2	4	4	2
D_x (Mg m^{-3})	1·285	1·254	1·242	1·261	1·442	1·508	1·459	1·430	1·430	1·474	1·434	1·413
Radiation	Mo	Cu	Cu	Cu	Mo	Cu	Cu	Cu	Cu	Mo	Cu	Mo
μ (cm^{-1})	0·365	4·606	4·562	4·63	0·647	9·09	7·88	7·728	7·725	1·004	7·747	0·586
$F(000)$	480	256	512	512	912	344	472	944	472	944	944	476
R_{obs}	0·054	0·064		0·041	0·048	0·065	0·040	0·080	0·10	0·132	0·069	0·090
R_{all}	0·066	-		0·050	0·075	0·079	0·042	0·120	0·11	0·20	0·099	0·133
wR_{obs}	0·076	0·083		0·039	0·039	0·055	0·054	0·092	0·15	0·122	0·079	0·095
wR_{all}	0·063	-		0·040	0·044	0·056	0·054	0·110	0·15	0·15	0·082	0·092
Data used	958	804	1241	1169	2060	2292	1865	1416	3337	1699	2685	1762
Total data	1368	1202	1574	1321	2543	2733	2232	2474	3949	2727	3923	2827
σ cutoff	$2·0\sigma$	$2·5\sigma$	$2·0\sigma$	$1·0\sigma$	$1·0\sigma$	$1·0\sigma$	$2·0\sigma$	$2·5\sigma$	$2·0\sigma$	$2·5\sigma$	$2·0\sigma$	$2·5\sigma$
δ	0·022	0·020	0·023	0·018	0·0182	0·019	0·029	0·020	0·015	0·023	0·021	0·017
Max $\sin\theta/\lambda$ (Å^{-1})	0·65	0·61	0·61	0·61	0·65	0·61	0·61	0·61	0·61	0·65	0·61	0·677
Parameters refined	160	197	-	228	358	270	375	316	351	307	375	339
S	3·34	-	-	1·53	1·36	1·40	2·54	1·53	1·36	1·42	2·54	-
(Δ/σ)max.	0·13	0·1		0·34	0·97	0·98	1·5	0·56	1·57	2·09	1·48	1·32
ρ_{max}, ρ_{min} (e Å^{-3})	0·21, −0·13	0·24, −0·18	-	0·11, −0·10	0·16, −0·20	0·10, −0·12	0·16, −0·18	0·54, −0·57	0·54, −0·65	0·60, −0·46	0·20, −0·24	0·32, −0·43
R_{int}	0·013	0·015	NA	NA	NA	0·022	0·016	NA	0·021	NA	0·016	0·017
θ, cell parameters (°)	16·5 20·5	11·6–23·4	19·6 26·4	15·5–26·5	10·4–19·1	16·7 26·6	24·2–42·5	6·7 20·5	16·5–20·5	5·5 23·3	12·2–26·5	10·3–18·9
Index range, data												
h	0 to 10	0 to 14	0 to 9	0 to 13	0 to 13	0 to 9	0 to 22	0 to 12	−10 to 0	0 to 10	0 to 23	0 to 23
k	0 to 8	0 to 7	0 to 9	0 to 25	0 to 35	−16 to 16	0 to 9	0 to 33	−20 to 20	0 to 39	0 to 8	0 to 10
l	29 to 28	−10 to 10	0 to 27	0 to 6	0 to 9	−9 to 8	−9 to 9	0 to 8	−9 to 9	0 to 9	−18 to 17	−11 to 10
Absorption correction	No	No	No	No	Yes	Yes	Yes	No	Yes	No	No	No
Crystal												
Size (mm)	0·2 × 0·2 × 0·4	0·4 × 0·4 × 0·4	0·4 × 0·4 × 0·1	0·05 × 0·07 × 0·5	0·2 × 0·4 × 0·2	0·2 × 0·5 × 0·1	0·2 × 0·3 × 0·1	0·06 × 0·08 × 0·4	0·2 × 0·4 × 0·5	0·2 × 0·1 × 0·5	0·04 × 0·1 × 0·55	0·3 × 0·3 × 0·6
Habit	Prism	Prism	Tablet	Needle	Prism	Lath	Prism	Needle	Tablet	Lath	Needle	Prism
Color	Colorless	Colorless	Colorless	Colorless	Deep orange	Orange	Orange	Yellow-orange	Brown-orange	Yellow	Orange	Deep red

of the instrument room (293–297 K) except for measurements on the 5-methylchrysene complex with trinitrobenzene which were made at 163 K. Four standard reflections were measured at periodic intervals in order to check the crystal decay. For each data set, these standard reflections showed a variation of less than 1%. When $(\mu t)_{max}$ exceeded 0·5 (see Jones, 1984), an analytical absorption correction, approximating the crystal to an ellipsoid of revolution, was applied. The data were corrected for Lorentz and polarization effects. The radiation wavelengths, λ, are 0·71069 (Mo $K\alpha$) and 1·5418 Å (Cu $K\alpha$). Except where otherwise stated, the weights for reflections used in the least-squares refinements $w = 1/\sigma^2(F)$ and were derived from counting statistics using the relation $\sigma(F) = (F/2)[\sigma^2(I)/(I)^2 + \delta^2]^{1/2}$ in which δ is an instrumental uncertainty based on the variation in the intensities of the standard reflections monitored throughout the data collections. The values in Table 1 for M_r, V, D_x, $F(000)$ and μ were obtained from a locally modified version of the program *INFORM* (Zalkin & Ward, 1974).

*MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) was used for direct-methods calculations, *CRYSTALS* (Watkin, Carruthers & Betteridge, 1986) for generalized Fourier sections and the refinement of disordered models with Waser (1963) restraints. For all other crystallographic calculations in-house programs were used (Carrell, Shieh & Takusagawa, 1981). Thermal ellipsoid plots were produced with *SNOOPI* (Davies, 1983) and the overlap diagrams with the computer program *VIEW* (Carrell, 1976). The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Except for the 1MeC and 5MeC:PMDA structures, all other structure refinements on F were carried out using a least-squares procedure, first with isotropic and then anisotropic thermal parameters. H atoms were located from difference maps and included in the final refinements using isotropic B equal to the B_{eq} of the C atoms they are bonded to.

The structure of 4-methylchrysene has not yet been solved. For the other crystals the atomic coordinates and equivalent isotropic temperature factors are given in Table 2. Fig. 1 shows the atomic numbering used throughout. Figs. 2(*a–j*) (deposited) show the thermal ellipsoids and atomic numbering of the individual structures reported. The anisotropic temperature factors and the observed and calculated structure factors have been deposited.* Relevant details of individual analyses follow.

* Lists of structure factors, anisotropic temperature factors, interatomic distances and bond angles (Table 3), least-squares planes (Table 6) and figures showing the thermal ellipsoid representations with atomic numbering (Figs. 2*a-j*) and molecular packing (Fig. 6) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53477 (206 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional atomic coordinates with e.s.d.'s in parentheses and equivalent isotropic temperature factors*

$B_{av} = \frac{1}{3}$ (trace orthogonalized B_{ij} matrix). The C atoms of chrysenes are numbered as in Fig. 1 and the methyl substituent is always C19. C(xT) indicates a C atom of *s*-trinitrobenzene. Primed numbers represent the alternative site in a disordered structure except in 5-methylchrysene–pyromellitic dianhydride where atom numbers beginning 1 and 2 indicate the two chrysene sites, and those beginning 3 and 4 the two pyromellitic dianhydride sites.

	x	*y*	*z*	B_{av},B_{iso}(Å^2)
(*a*) Chrysene				
C15	−0·0261 (1)	0·0848 (2)	0·1274 (5)	3·40 (5)
C14	0·0193 (1)	0·0805 (2)	0·07548 (5)	3·48 (5)
C4	−0·0304 (2)	0·2430 (3)	0·10434 (6)	4·30 (6)
C3	0·0138 (2)	0·2291 (3)	0·16328 (7)	5·37 (7)
C2	0·1097 (2)	0·0548 (3)	0·19659 (7)	5·40 (8)
C1	0·1601 (2)	−0·1044 (3)	0·17031 (6)	4·83 (7)
C13	0·1166 (2)	−0·0977 (2)	0·10940 (6)	3·91 (6)
C12	0·1682 (2)	−0·2650 (3)	0·08183 (7)	4·41 (6)
C11	0·1259 (2)	−0·2592 (2)	0·02460 (7)	3·85 (6)
H4	−0·100 (2)	0·376 (2)	0·0804 (6)	5·7 (4)
H3	−0·026 (2)	0·341 (3)	0·1816 (7)	6·0 (4)
H2	0·138 (2)	0·047 (3)	0·2385 (7)	6·5 (4)
H1	0·222 (2)	−0·225 (3)	0·1916 (7)	5·4 (4)
H12	0·241 (2)	−0·394 (3)	0·1071 (7)	5·7 (4)
H11	0·161 (2)	−0·371 (2)	0·0075 (6)	4·2 (3)
(*b*) 1-Methylchrysene				
C1	0·3248 (3)	−0·0971 (7)	0·0819 (6)	6·5 (2)
C2	0·3710 (3)	0·0608 (9)	0·1737 (6)	7·4 (3)
C3	0·3052 (4)	0·2294 (8)	0·2250 (6)	7·4 (2)
C4	0·1937 (3)	0·2376 (6)	0·1828 (5)	6·5 (2)
C11	0·0490 (3)	−0·2535 (6)	−0·0904 (6)	5·8 (2)
C12	0·1601 (3)	−0·2598 (5)	−0·0526 (5)	6·1 (2)
C13	0·2083 (2)	−0·0933 (6)	0·0405 (5)	5·4 (2)
C14	0·1410 (3)	0·0787 (6)	0·0878 (5)	5·2 (2)
C15	0·0227 (2)	0·0848 (5)	0·0459 (5)	5·1 (2)
C19	0·3942 (5)	−0·273 (1)	0·029 (1)	7·8 (5)
C1′	0·3078 (6)	0·110 (2)	0·163 (1)	8·7 (8)
C2′	0·3816 (6)	−0·044 (2)	0·116 (2)	10· (1)
C3′	0·3438 (7)	−0·216 (2)	0·028 (2)	8·9 (9)
C4′	0·2334 (6)	−0·228 (1)	−0·016 (1)	9·2 (8)
C11′	0·0086 (6)	0·255 (2)	0·116 (2)	9·0 (8)
C12′	0·1175 (6)	0·267 (1)	0·161 (1)	8·3 (6)
C13′	0·1928 (5)	0·101 (1)	0·118 (1)	7·3 (7)
C14′	0·1533 (5)	−0·071 (1)	0·025 (1)	8·2 (7)
C15′	0·0365 (3)	−0·0822 (9)	−0·0235 (9)	4·5 (5)
C19′	0·3485 (8)	0·292 (3)	0·254 (2)	12 (2)
(*c*) 6-Methylchrysene				
C1	0·1402 (2)	0·11836 (9)	0·0792 (5)	4·8 (1)
C2	0·0561 (2)	0·13146 (9)	0·2537 (6)	5·1 (1)
C3	0·0361 (2)	0·0869 (1)	0·4315 (5)	5·0 (1)
C4	0·1006 (2)	0·0299 (1)	0·4387 (5)	4·44 (9)
C5	0·2437 (2)	−0·09189 (9)	0·4383 (5)	3·90 (9)
C6	0·3097 (2)	−0·14706 (9)	0·4457 (5)	3·98 (9)
C7	0·4821 (2)	−0·21276 (9)	0·2817 (6)	5·0 (1)
C8	0·5753 (2)	−0·2213 (1)	0·1212 (6)	5·6 (1)
C9	0·5963 (2)	−0·1755 (1)	−0·0527 (6)	5·2 (1)
C10	0·5244 (2)	−0·1213 (1)	−0·0644 (5)	4·6 (1)
C11	0·3693 (2)	−0·0052 (1)	−0·0884 (5)	4·3 (1)
C12	0·3004 (2)	0·0490 (1)	−0·0923 (6)	4·7 (1)
C13	0·2094 (2)	0·06101 (9)	0·0843 (5)	3·88 (9)
C14	0·1900 (2)	0·01553 (9)	0·2641 (5)	3·68 (9)
C15	0·2624 (2)	−0·04308 (9)	0·2648 (5)	3·51 (9)
C16	0·3529 (2)	−0·05260 (9)	0·0904 (6)	3·53 (9)
C17	0·4279 (2)	−0·11045 (8)	0·0983 (4)	3·82 (9)
C18	0·4061 (2)	−0·15734 (9)	0·2748 (5)	3·75 (9)
C19	0·2810 (2)	−0·19724 (9)	0·6309 (5)	5·0 (1)
HC1	0·153 (2)	0·1475 (9)	−0·057 (5)	6·2 (6)
HC2	0·009 (2)	0·171 (1)	0·247 (5)	6·7 (6)
HC3	−0·022 (2)	0·0958 (9)	0·560 (5)	6·7 (6)
HC4	0·088 (2)	0·0011 (8)	0·565 (4)	4·6 (5)
HC5	0·180 (2)	−0·0839 (9)	0·552 (4)	4·9 (5)
HC7	0·466 (2)	−0·247 (1)	0·407 (4)	5·4 (5)
HC8	0·624 (2)	−0·2563 (9)	0·127 (5)	5·2 (5)
HC9	0·664 (2)	−0·1769 (9)	−0·158 (4)	4·7 (5)
HC10	0·546 (2)	−0·0870 (9)	−0·190 (5)	5·2 (5)
HC11	0·434 (2)	−0·013 (1)	−0·215 (5)	6·2 (6)
HC12	0·311 (2)	0·0826 (9)	−0·220 (5)	5·3 (5)
H1C19	0·221 (2)	−0·182 (1)	0·738 (6)	6·2 (7)
H2C19	0·348 (3)	−0·209 (1)	0·725 (7)	7·7 (9)
H3C19	0·247 (3)	−0·237 (1)	0·554 (5)	7·3 (7)
(*d*) Chrysene–*s*-trinitrobenzene 1:1 complex				
O1	0·4699 (1)	0·32684 (6)	0·2507 (3)	6·48 (9)
O2	0·4779 (1)	0·40494 (6)	0·2465 (3)	6·50 (9)
O3	0·8158 (2)	0·23462 (5)	−0·0267 (4)	8·4 (1)
O4	0·9989 (2)	0·26974 (6)	−0·0951 (3)	7·5 (1)
O5	1·0351 (2)	0·44389 (7)	−0·0359 (4)	9·2 (1)
O6	0·8838 (2)	0·48343 (6)	0·1016 (4)	9·4 (1)
N1	0·5246 (2)	0·36498 (8)	0·2180 (3)	4·7 (1)
N2	0·8871 (2)	0·27000 (8)	−0·0380 (3)	5·7 (1)
N3	0·9297 (2)	0·44677 (9)	0·0385 (4)	6·4 (1)
C1T	0·6577 (2)	0·36284 (7)	0·1406 (3)	3·71 (9)
C2T	0·7077 (2)	0·31854 (7)	0·0892 (3)	3·9 (1)
C3T	0·8322 (2)	0·31754 (7)	0·0190 (4)	4·0 (1)
C4T	0·9069 (2)	0·35862 (9)	0·0008 (4)	4·5 (1)
C5T	0·8514 (2)	0·40182 (8)	0·0551 (3)	4·3 (1)
C6T	0·7282 (2)	0·40535 (7)	0·1246 (3)	4·1 (1)
C1	1·0319 (2)	0·29971 (8)	0·4044 (4)	5·4 (1)
C2	1·1371 (3)	0·3267 (1)	0·3567 (4)	6·4 (2)
C3	1·1374 (2)	0·3762 (1)	0·3882 (4)	6·3 (2)
C4	1·0300 (2)	0·39878 (8)	0·4614 (4)	5·2 (1)
C5	0·7876 (2)	0·44637 (7)	0·6074 (3)	4·5 (1)
C6	0·6837 (3)	0·46644 (8)	0·6728 (4)	5·8 (1)
C7	0·4544 (3)	0·46183 (9)	0·7793 (5)	6·5 (2)
C8	0·3465 (3)	0·4355 (1)	0·8174 (5)	7·4 (2)
C9	0·3483 (3)	0·3855 (1)	0·7924 (5)	6·7 (2)
C10	0·4573 (3)	0·36173 (9)	0·7319 (4)	5·5 (1)
C11	0·7007 (2)	0·31384 (7)	0·5951 (3)	4·0 (1)
C12	0·8081 (2)	0·29344 (7)	0·5288 (4)	4·7 (1)
C13	0·9188 (2)	0·32122 (8)	0·4801 (3)	4·3 (1)
C14	0·9161 (2)	0·37208 (7)	0·5086 (3)	3·90 (9)
C15	0·7985 (2)	0·39456 (7)	0·5799 (3)	3·73 (9)
C16	0·6899 (2)	0·36549 (7)	0·6219 (3)	3·78 (9)
C17	0·5712 (2)	0·38807 (7)	0·6880 (3)	4·09 (9)
C18	0·5695 (2)	0·43906 (8)	0·7136 (4)	4·8 (1)
HC2T	0·661 (1)	0·2911 (6)	0·101 (3)	3·4 (4)
HC4T	0·986 (2)	0·3613 (6)	−0·044 (3)	3·6 (4)
HC6T	0·696 (2)	0·4335 (6)	0·167 (3)	3·9 (4)
HC1	1·024 (2)	0·2667 (7)	0·392 (3)	5·9 (6)
HC2	1·215 (2)	0·3115 (7)	0·291 (4)	6·0 (6)
HC3	1·217 (2)	0·3986 (8)	0·347 (4)	8·3 (7)
HC4	1·030 (2)	0·4324 (6)	0·489 (3)	4·8 (5)
HC5	0·858 (2)	0·4629 (8)	0·583 (4)	6·1 (6)
HC6	0·684 (2)	0·5021 (7)	0·699 (3)	5·5 (5)
HC7	0·458 (2)	0·4960 (9)	0·796 (4)	6·6 (6)
HC8	0·260 (3)	0·451 (1)	0·856 (6)	13· (1)
HC9	0·272 (2)	0·3638 (7)	0·809 (4)	6·2 (6)
HC10	0·462 (2)	0·3234 (9)	0·718 (5)	8·8 (7)
HC11	0·622 (2)	0·2938 (8)	0·617 (4)	5·9 (6)
HC12	0·810 (2)	0·2578 (8)	0·522 (4)	5·9 (5)
(*e*) 1-Methylchrysene–*s*-trinitrobenzene 1:2 complex				
O1	0·8187 (2)	0·0367 (1)	0·4406 (2)	7·36 (9)
O2	0·9521 (3)	−0·0033 (1)	0·2009 (2)	8·1 (1)
O3	1·0646 (3)	0·2458 (1)	−0·2047 (2)	7·6 (1)
O4	1·0836 (3)	0·4045 (1)	−0·0915 (3)	9·8 (1)
O5	0·7424 (3)	0·3873 (2)	0·6360 (2)	8·7 (1)
O6	0·7946 (3)	0·4974 (1)	0·4570 (3)	8·6 (1)
N1	0·8900 (3)	0·0574 (1)	0·3065 (3)	5·15 (9)
N2	1·0440 (3)	0·3138 (2)	−0·0850 (3)	6·0 (1)
N3	0·7924 (3)	0·4119 (2)	0·4956 (3)	6·0 (1)
C1T	0·8983 (3)	0·1632 (2)	0·2713 (3)	4·16 (9)
C2T	0·9634 (3)	0·1862 (2)	0·1103 (3)	4·32 (9)
C3T	0·9731 (3)	0·2862 (2)	0·0835 (3)	4·46 (9)
C4T	0·9201 (3)	0·3618 (2)	0·2073 (3)	4·9 (1)
C5T	0·8544 (3)	0·3338 (2)	0·3627 (3)	4·8 (1)
C6T	0·8435 (3)	0·2356 (2)	0·3988 (3)	4·7 (1)
C1	0·4568 (3)	0·2971 (2)	0·0967 (3)	5·5 (1)
C2	0·3993 (3)	0·3222 (2)	0·2653 (4)	6·2 (1)
C3	0·3635 (3)	0·2496 (2)	0·3793 (3)	6·0 (1)
C4	0·3844 (3)	0·1497 (2)	0·3226 (3)	5·3 (1)
C5	0·4346 (3)	−0·0645 (2)	0·1950 (3)	5·4 (1)
C6	0·5393 (3)	0·1627 (2)	−0·1377 (3)	5·5 (1)
C7 (15)	0·4692 (3)	0·0129 (2)	0·0858 (3)	4·51 (9)
C8 (14)	0·4420 (3)	0·1182 (2)	0·1500 (3)	4·59 (9)
C9 (13)	0·4788 (3)	0·1930 (2)	0·0362 (3)	4·9 (1)
C (19)	0·4970 (7)	0·3782 (4)	−0·0122 (8)	7·0 (3)
HC2T	1·001 (2)	0·138 (1)	0·028 (2)	4·2 (4)
HC4T	0·935 (3)	0·428 (2)	0·183 (3)	6·6 (6)
HC6T	0·807 (2)	0·220 (1)	0·509 (2)	5·2 (5)
HC2	0·385 (3)	0·391 (2)	0·299 (3)	6·7 (6)
HC3	0·328 (3)	0·267 (1)	0·497 (3)	5·9 (5)
HC4	0·363 (3)	0·096 (2)	0·394 (3)	6·9 (6)
HC5	0·397 (3)	−0·044 (1)	0·305 (2)	5·1 (5)
HC6	0·565 (3)	0·216 (1)	−0·211 (3)	6·2 (5)
H1C19	0·590 (6)	0·374 (3)	−0·053 (6)	8· (1)
H2C19	0·427 (5)	0·367 (3)	−0·113 (5)	4·8 (9)
H3C19	0·460 (8)	0·439 (4)	0·041 (8)	10· (2)

Table 2 (*cont.*)

	x	y	z	B_{av}, B_{iso}(Å^2)
(*f*) 2-Methylchrysene–*s*-trinitrobenzene 1:1 complex				
O1	0·2354 (1)	0·5423 (4)	0·9281 (3)	5·8 (1)
O2	0·3423 (1)	0·4404 (4)	1·0207 (3)	6·3 (1)
O3	0·4431 (1)	0·0806 (5)	0·3512 (3)	7·1 (1)
O4	0·4904 (1)	0·1511 (5)	0·6108 (3)	6·9 (1)
O5	0·1948 (1)	0·2441 (4)	0·1632 (3)	5·6 (1)
O6	0·1329 (1)	0·4036 (4)	0·3331 (3)	6·6 (1)
N1	0·2916 (2)	0·4617 (4)	0·9076 (3)	4·7 (1)
N2	0·4401 (2)	0·1505 (5)	0·4953 (4)	5·2 (1)
N3	0·1875 (2)	0·3215 (4)	0·3011 (4)	4·5 (1)
C1*T*	0·2998 (2)	0·3842 (4)	0·7296 (4)	4·0 (1)
C2*T*	0·3650 (2)	0·3088 (5)	0·6984 (4)	4·1 (1)
C3*T*	0·3708 (2)	0·2366 (5)	0·5335 (4)	4·3 (1)
C4*T*	0·3135 (2)	0·2395 (4)	0·3996 (4)	4·0 (1)
C5*T*	0·2495 (2)	0·3173 (4)	0·4401 (4)	3·9 (1)
C6*T*	0·2395 (2)	0·3921 (4)	0·6047 (4)	3·9 (1)
C1	0·6277 (2)	0·3008 (4)	0·3144 (4)	4·2 (1)
C2	0·6121 (2)	0·3505 (4)	0·1398 (4)	4·5 (1)
C3	0·6677 (2)	0·4300 (5)	0·0525 (4)	4·6 (1)
C4	0·7364 (2)	0·4584 (4)	0·1349 (4)	4·4 (1)
C5	0·8828 (2)	0·5239 (4)	0·3238 (4)	4·1 (1)
C6	0·9487 (2)	0·5536 (4)	0·4127 (4)	4·6 (1)
C7	1·0338 (2)	0·5294 (5)	0·6827 (5)	5·1 (2)
C8	1·0491 (2)	0·4719 (5)	0·8543 (4)	5·1 (2)
C9	0·9960 (2)	0·3842 (5)	0·9403 (4)	5·1 (2)
C10	0·9272 (2)	0·3565 (5)	0·8572 (4)	4·6 (1)
C11	0·7805 (2)	0·3025 (4)	0·6719 (3)	3·7 (1)
C12	0·7130 (2)	0·2770 (4)	0·5854 (4)	4·0 (1)
C13	0·6968 (2)	0·3286 (4)	0·4048 (4)	3·6 (1)
C14	0·7535 (2)	0·4099 (4)	0·3145 (4)	3·5 (1)
C15	0·8250 (2)	0·4385 (4)	0·4077 (4)	3·7 (1)
C16	0·8383 (2)	0·3829 (4)	0·5859 (4)	3·4 (1)
C17	0·9097 (2)	0·4131 (4)	0·6790 (4)	3·8 (1)
C18	0·9646 (2)	0·4990 (4)	0·5922 (4)	4·1 (1)
C19	0·5369 (2)	0·3193 (6)	0·0446 (5)	6·4 (2)
HC2*T*	0·396 (1)	0·304 (4)	0·785 (3)	3·4 (6)
HC4*T*	0·315 (2)	0·193 (4)	0·292 (4)	5·4 (7)
HC6*T*	0·195 (2)	0·449 (5)	0·630 (4)	6·5 (8)
HC1	0·593 (2)	0·253 (4)	0·377 (4)	4·5 (7)
HC3	0·663 (2)	0·464 (4)	−0·082 (4)	4·3 (6)
HC4	0·776 (1)	0·507 (4)	0·070 (4)	4·2 (7)
HC5	0·876 (2)	0·562 (4)	0·197 (3)	4·2 (6)
HC6	0·990 (2)	0·612 (5)	0·358 (4)	5·8 (8)
HC7	1·073 (2)	0·597 (5)	0·628 (4)	5·7 (8)
HC8	1·103 (2)	0·487 (5)	0·905 (5)	5·8 (8)
HC9	1·013 (2)	0·332 (5)	1·057 (4)	5·6 (9)
HC10	0·888 (2)	0·288 (4)	0·913 (4)	4·0 (6)
HC11	0·789 (2)	0·279 (4)	0·793 (4)	4·2 (7)
HC12	0·674 (2)	0·222 (4)	0·649 (4)	4·2 (7)
H1C19	0·507 (4)	0·30 (1)	0·093 (8)	17· (3)
H2C19	0·516 (4)	0·414 (9)	−0·02 (1)	12· (2)
H3C19	0·540 (3)	0·223 (9)	−0·049 (8)	11· (2)
(*g*) 3-Methylchrysene–*s*-trinitrobenzene 1:1 complex				
O1	0·4815 (6)	0·3297 (3)	0·249 (1)	9·1 (5)
O2	0·4880 (7)	0·4078 (3)	0·241 (1)	9·4 (5)
O3	0·8280 (8)	0·2391 (3)	0·009 (2)	11·7 (6)
O4	0·999 (1)	0·2759 (3)	−0·083 (1)	10·9 (6)
O5	1·0232 (9)	0·4502 (3)	−0·043 (2)	12·6 (7)
O6	0·8750 (8)	0·4888 (3)	0·087 (1)	11·3 (6)
N1	0·5358 (7)	0·3677 (3)	0·214 (1)	6·8 (4)
N2	0·894 (1)	0·2747 (4)	−0·015 (1)	8·6 (7)
N3	0·921 (1)	0·4518 (3)	0·030 (1)	8·4 (6)
C1*T*	0·6683 (9)	0·3665 (3)	0·138 (1)	5·6 (4)
C2*T*	0·7121 (9)	0·3221 (3)	0·097 (1)	6·4 (4)
C3*T*	0·836 (2)	0·3221 (5)	0·031 (2)	6·7 (9)
C4*T*	0·906 (1)	0·3640 (3)	0·003 (1)	7·0 (5)
C5*T*	0·847 (2)	0·4066 (5)	0·054 (2)	5·6 (7)
C6*T*	0·7289 (8)	0·4090 (3)	0·117 (1)	5·9 (4)
C1	1·024 (1)	0·2988 (4)	0·412 (2)	8·4 (7)
C2	1·123 (1)	0·3268 (5)	0·359 (2)	9·4 (8)
C3	1·1189 (8)	0·3775 (3)	0·385 (1)	9·3 (8)
C4	1·011 (1)	0·3966 (3)	0·455 (2)	8·2 (6)
C5	0·783 (1)	0·4436 (3)	0·598 (1)	6·8 (5)
C6	0·678 (1)	0·4641 (3)	0·659 (2)	8·0 (6)
C7	0·457 (1)	0·4589 (4)	0·771 (2)	8·6 (7)
C8	0·3492 (9)	0·4316 (6)	0·808 (2)	9·9 (8)
C9	0·3500 (8)	0·3814 (3)	0·791 (1)	8·6 (7)
C10	0·463 (1)	0·3595 (3)	0·732 (2)	7·6 (6)
C11	0·6970 (9)	0·3123 (3)	0·604 (1)	6·1 (4)
C12	0·806 (1)	0·2918 (3)	0·538 (1)	6·8 (5)
C13	0·9135 (9)	0·3195 (3)	0·486 (1)	6·5 (5)
C14	0·905 (1)	0·3696 (3)	0·511 (1)	6·1 (5)
C15	0·7912 (9)	0·3924 (3)	0·577 (1)	5·6 (4)
C16	0·687 (1)	0·3641 (3)	0·624 (1)	6·0 (5)
C17	0·573 (1)	0·3855 (3)	0·687 (1)	6·3 (5)
C18	0·570 (1)	0·4380 (3)	0·707 (1)	6·9 (5)
C19	1·2180 (9)	0·4071 (6)	0·317 (3)	13· (2)
C19′	0·238 (1)	0·3537 (5)	0·834 (3)	7· (1)
(*h*) 4-Methylchrysene–*s*-trinitrobenzene 1:1 complex				
O1	−0·1942 (3)	0·2941 (2)	0·3512 (5)	10·3 (2)
O2	−0·2013 (3)	0·1861 (3)	0·4836 (5)	13·3 (2)
O3	0·5502 (3)	0·3984 (2)	0·4594 (5)	9·2 (2)
O4	0·3238 (4)	0·4371 (1)	0·3160 (4)	8·6 (1)
O5	0·5368 (3)	0·1520 (2)	0·7349 (4)	9·6 (2)
O6	0·3052 (4)	0·0821 (2)	0·7329 (4)	9·1 (1)
N1	−0·1272 (4)	0·2437 (3)	0·4360 (5)	8·1 (2)
N2	0·4010 (4)	0·3916 (2)	0·4065 (4)	7·0 (1)
N3	0·3875 (4)	0·1398 (2)	0·6966 (4)	7·2 (1)
C1*T*	0·0536 (3)	0·2508 (2)	0·4754 (4)	5·8 (1)
C2*T*	0·1368 (3)	0·3155 (2)	0·4213 (4)	5·5 (1)
C3*T*	0·3066 (4)	0·3218 (2)	0·4617 (4)	5·5 (1)
C4*T*	0·3907 (3)	0·2649 (2)	0·5495 (4)	5·6 (1)
C5*T*	0·3003 (4)	0·2014 (2)	0·6004 (4)	5·6 (1)
C6*T*	0·1291 (4)	0·1927 (2)	0·5650 (4)	5·9 (1)
C1	0·3149 (5)	0·4514 (2)	−0·1873 (5)	7·3 (2)
C2	0·1817 (6)	0·4878 (2)	−0·2602 (6)	8·6 (2)
C3	0·0291 (5)	0·4554 (3)	−0·2459 (5)	8·2 (2)
C4	−0·0009 (4)	0·3865 (2)	−0·1663 (5)	7·0 (2)
C5	−0·0444 (4)	0·2224 (2)	−0·0321 (5)	6·7 (2)
C6	−0·0547 (6)	0·1500 (3)	0·0457 (6)	8·7 (2)
C7	0·0629 (9)	0·0421 (3)	0·2171 (7)	11·3 (3)
C8	0·217 (1)	0·0138 (3)	0·2892 (6)	12·9 (4)
C9	0·3614 (9)	0·0523 (4)	0·2823 (8)	12·2 (4)
C10	0·3766 (7)	0·1178 (3)	0·2081 (6)	11·8 (2)
C11	0·4090 (4)	0·2696 (2)	0·0544 (4)	6·4 (1)
C12	0·4271 (4)	0·3409 (3)	−0·0231 (5)	7·6 (2)
C13	0·2914 (4)	0·3801 (2)	−0·1051 (4)	6·5 (1)
C14	0·1316 (4)	0·3438 (2)	−0·0990 (4)	5·9 (1)
C15	0·1119 (4)	0·2649 (2)	−0·0229 (4)	6·3 (1)
C16	0·2554 (4)	0·2317 (2)	0·0531 (4)	6·7 (1)
C17	0·2424 (6)	0·1554 (2)	0·1339 (4)	7·9 (2)
C18	0·0840 (6)	0·1176 (2)	0·1312 (5)	9·2 (2)
C19	−0·1743 (6)	0·3705 (4)	−0·1373 (8)	11·4 (3)
(*i*) 5-Methylchrysene–*s*-trinitrobenzene 1:1 complex				
O1	−0·2847 (7)	0·1840 (2)	0·2142 (6)	4·1 (3)
O2	−0·0554 (8)	0·2179 (2)	0·2306 (6)	4·6 (3)
O3	0·4032 (6)	0·1510 (2)	0·4909 (8)	5·7 (3)
O4	0·3731 (6)	0·0957 (2)	0·6394 (7)	4·1 (3)
O5	−0·1351 (7)	0·0224 (2)	0·6205 (8)	4·9 (3)
O6	−0·3260 (7)	0·0476 (2)	0·4718 (8)	5·6 (3)
N1	−0·1440 (9)	0·1874 (2)	0·2553 (7)	3·1 (3)
N2	0·3201 (8)	0·1231 (2)	0·5465 (8)	3·3 (3)
N3	−0·1932 (8)	0·0494 (2)	0·5270 (9)	3·3 (3)
C1*T*	−0·0701 (9)	0·1514 (2)	0·3590 (8)	2·2 (3)
C2*T*	0·0883 (9)	0·1543 (2)	0·4050 (9)	2·6 (3)
C3*T*	0·1516 (8)	0·1213 (2)	0·4956 (9)	1·9 (3)
C4*T*	0·0663 (9)	0·0868 (2)	0·5398 (8)	2·3 (3)
C5*T*	−0·0948 (8)	0·0866 (2)	0·4869 (9)	2·5 (3)
C6*T*	−0·1625 (9)	0·1187 (2)	0·3934 (8)	2·6 (3)
C1	−0·2778 (9)	0·1967 (3)	−0·3123 (9)	4·1 (4)
C2	−0·2037 (9)	0·2337 (2)	−0·3646 (9)	3·3 (3)
C3	−0·050 (1)	0·2416 (2)	−0·321 (1)	3·9 (4)
C4	0·039 (1)	0·2140 (3)	−0·227 (1)	4·3 (5)
C5	0·2356 (9)	0·1538 (2)	−0·0192 (9)	3·7 (4)
C6	0·319 (1)	0·1200 (3)	0·071 (1)	4·5 (5)
C7	0·340 (1)	0·0496 (3)	0·210 (1)	4·7 (4)
C8	0·261 (1)	0·0149 (3)	0·2602 (9)	5·1 (5)
C9	0·106 (1)	0·0092 (3)	0·220 (1)	5·3 (5)
C10	0·021 (1)	0·0366 (3)	0·129 (1)	5·0 (5)
C11	−0·1653 (9)	0·0987 (2)	−0·0652 (9)	2·7 (3)
C12	−0·249 (1)	0·1294 (3)	−0·151 (1)	4·5 (5)
C13	−0·182 (1)	0·1674 (2)	−0·209 (1)	3·4 (4)
C14	−0·0212 (9)	0·1761 (3)	−0·1658 (9)	3·5 (4)
C15	0·0761 (9)	0·1432 (3)	−0·0647 (9)	3·6 (4)
C16	0·001 (1)	0·1071 (2)	−0·0264 (9)	3·1 (4)
C17	0·091 (1)	0·0739 (3)	0·0760 (8)	3·9 (4)
C18	0·253 (1)	0·0813 (2)	0·118 (1)	4·0 (4)
C19	0·338 (1)	0·1904 (3)	−0·039 (2)	7·5 (7)
(*j*) 6-Methylchrysene–*s*-trinitrobenzene 1:1 complex				
O1	0·4776 (1)	0·6725 (4)	0·0462 (1)	8·5 (1)
O2	0·5874 (1)	0·5946 (4)	0·1159 (2)	9·4 (1)
O3	0·6500 (1)	0·3489 (3)	0·4180 (1)	7·6 (1)
O4	0·5703 (1)	0·3319 (3)	0·4852 (1)	7·3 (1)
O5	0·3255 (1)	0·4816 (4)	0·3299 (2)	8·6 (1)
O6	0·2970 (1)	0·6049 (3)	0·1965 (2)	7·3 (1)
N1	0·5244 (2)	0·6110 (4)	0·1112 (2)	7·0 (1)

Table 2 (*cont.*)

	x	y	z	B_{av},B_{iso}(Å^2)
N2	0·5899 (1)	0·3671 (3)	0·4208 (2)	5·5 (1)
N3	0·3394 (1)	0·5368 (3)	0·2626 (2)	6·2 (1)
C1*T*	0·5028 (1)	0·5544 (4)	0·1915 (2)	5·2 (1)
C2*T*	0·5552 (1)	0·4868 (4)	0·2648 (2)	5·4 (1)
C3*T*	0·5345 (1)	0·4366 (3)	0·3376 (2)	4·6 (1)
C4*T*	0·4651 (1)	0·4516 (4)	0·3393 (2)	4·9 (1)
C5*T*	0·4150 (1)	0·5186 (4)	0·2627 (2)	4·9 (1)
C6*T*	0·4326 (1)	0·5721 (4)	0·1871 (2)	5·0 (1)
C1	0·6593 (2)	0·9037 (5)	0·3382 (3)	9·8 (2)
C2	0·6745 (2)	0·8371 (6)	0·4274 (4)	9·6 (2)
C3	0·6200 (2)	0·8209 (5)	0·4643 (2)	7·4 (2)
C4	0·5519 (1)	0·8736 (4)	0·4205 (2)	5·8 (1)
C5	0·4029 (1)	0·9803 (4)	0·3160 (2)	4·8 (1)
C6	0·3345 (1)	1·0280 (4)	0·2706 (2)	5·7 (1)
C7	0·2466 (2)	1·1635 (5)	0·1331 (2)	7·7 (2)
C8	0·2327 (2)	1·2351 (6)	0·0514 (3)	10·4 (3)
C9	0·2834 (3)	1·2556 (6)	0·0104 (3)	11·1 (3)
C10	0·3546 (2)	1·1973 (5)	0·0522 (2)	8·6 (2)
C11	0·5036 (2)	1·0776 (4)	0·1521 (2)	8·8 (2)
C12	0·5717 (2)	1·0269 (5)	0·2006 (3)	8·8 (2)
C13	0·5884 (1)	0·9581 (4)	0·2901 (3)	7·6 (2)
C14	0·5329 (1)	0·9426 (4)	0·3298 (2)	5·2 (1)
C15	0·4605 (1)	0·9963 (4)	0·2790 (2)	5·1 (1)
C16	0·4457 (2)	1·0644 (4)	0·1899 (2)	5·8 (1)
C17	0·3724 (2)	1·1209 (4)	0·1407 (2)	6·5 (2)
C18	0·3179 (2)	1·1036 (4)	0·1819 (2)	5·8 (2)
C19	0·2767 (2)	1·0010 (5)	0·3130 (3)	8·3 (2)
HC2*T*	0·609 (1)	0·477 (4)	0·262 (2)	8·0 (7)
HC4*T*	0·458 (1)	0·417 (3)	0·394 (2)	5·5 (5)
HC6*T*	0·401 (1)	0·616 (3)	0·138 (2)	6·1 (6)
HC1	0·684 (2)	0·937 (5)	0·311 (2)	12· (1)
HC2	0·729 (2)	0·802 (5)	0·436 (2)	12· (1)
HC3	0·631 (2)	0·775 (5)	0·541 (2)	10·2 (9)
HC4	0·510 (1)	0·863 (3)	0·437 (1)	4·7 (5)
HC5	0·4118 (9)	0·933 (3)	0·367 (1)	4·2 (5)
HC7	0·201 (2)	1·154 (5)	0·181 (2)	11· (1)
HC8	0·180 (2)	1·279 (6)	0·017 (3)	14· (1)
HC9	0·277 (2)	1·301 (5)	−0·058 (2)	10·9 (9)
HC10	0·383 (2)	1·179 (6)	0·018 (3)	14· (1)
HC11	0·489 (1)	1·128 (4)	0·089 (2)	7·5 (7)
HC12	0·608 (1)	1·046 (3)	0·154 (1)	4·8 (5)
H1C19	0·238 (2)	0·909 (5)	0·263 (2)	11· (1)
H2C19	0·258 (1)	1·130 (4)	0·320 (2)	8·1 (7)
H3C19	0·314 (4)	0·92 (1)	0·361 (5)	29· (3)
(*k*) 5-Methylchrysene–pyromellitic dianhydride 1:1 complex				
C11	0·2797 (2)	−0·2305 (7)	0·8652 (5)	6·5 (2)
C12	0·2692 (3)	−0·3043 (9)	0·9959 (7)	7·4 (2)
C13	0·3286 (3)	−0·2829 (7)	1·1558 (5)	6·9 (2)
C14	0·3999 (2)	−0·1928 (6)	1·1816 (4)	5·8 (2)
C111	0·4347 (2)	0·0100 (5)	0·7666 (4)	4·9 (1)
C112	0·3650 (2)	−0·0709 (5)	0·7458 (4)	5·8 (2)
C113	0·3542 (2)	−0·1398 (5)	0·8867 (4)	5·3 (2)
C114	0·4170 (2)	−0·1203 (4)	1·0474 (3)	4·5 (1)
C115	0·5044 (1)	0·0313 (4)	0·9273 (3)	4·3 (1)
C115′	0·4956 (1)	−0·0313 (4)	1·0727 (3)	4·3 (1)
C119	0·4440 (5)	0·073 (2)	0·6112 (8)	12·7 (6)
C21	0·3385 (5)	−0·259 (1)	1·1269 (7)	7·7 (3)
C22	0·2666 (6)	−0·294 (2)	0·994 (1)	9·2 (6)
C23	0·2584 (4)	−0·252 (1)	0·8353 (8)	6·0 (4)
C24	0·3189 (4)	−0·157 (1)	0·8141 (6)	5·7 (3)
C211	0·5407 (3)	−0·0424 (8)	1·2342 (5)	3·3 (2)
C212	0·4803 (4)	−0·1304 (9)	1·2529 (5)	5·1 (3)
C213	0·4044 (3)	−0·1650 (8)	1·1092 (5)	4·6 (2)
C214	0·3961 (3)	−0·1129 (7)	0·9493 (5)	3·6 (2)
C215	0·5375 (2)	0·0158 (7)	1·0734 (3)	4·1 (2)
C215′	0·4625 (2)	−0·0158 (7)	0·9267 (3)	4·1 (2)
C219	0·6215 (6)	−0·018 (2)	1·388 (1)	8·8 (9)
O31	1·0607 (3)	−0·2173 (6)	0·6758 (5)	8·7 (2)
O32	0·8205 (3)	0·0482 (7)	0·5773 (5)	8·2 (2)
O33	0·9344 (2)	−0·0934 (6)	0·5860 (4)	7·0 (2)
C31	1·0105 (6)	−0·1410 (6)	0·7091 (4)	6·2 (2)
C32	1·0159 (2)	−0·0669 (6)	0·8713 (4)	4·7 (2)
C33	0·9416 (2)	0·0150 (7)	0·8401 (4)	5·5 (2)
C34	0·8884 (2)	−0·0044 (7)	0·6590 (4)	6·6 (2)
C35	0·9227 (2)	0·0828 (7)	0·9685 (5)	5·0 (2)
O41	1·0077 (5)	−0·1667 (8)	0·6010 (6)	10·9 (2)
O42	0·7962 (4)	0·120 (1)	0·6446 (7)	9·5 (3)
O43	0·8909 (3)	−0·0284 (8)	0·5816 (5)	7·2 (2)
C41	0·9715 (4)	−0·0910 (8)	0·6699 (5)	7·1 (3)
C42	0·9938 (3)	−0·0602 (9)	0·8496 (5)	5·9 (2)
C43	0·9278 (3)	0·0271 (8)	0·8638 (5)	4·9 (2)
C44	0·8632 (3)	0·0515 (9)	0·6927 (5)	7·6 (3)
C45	0·9328 (3)	0·0909 (9)	1·0142 (7)	6·6 (2)

Chrysene. The structure of this compound has been previously determined (Iball, 1934) and refined using three-dimensional photographic data (Burns & Iball, 1960). The coordinates of Burns & Iball were further refined with new intensity data.

1-*Methylchrysene* (1*MeC*). The unit cell contains two non-centrosymmetric 1MeC molecules which, in the space group $P2_1/c$ (identified by unambiguous systematic absences), must be disordered about the crystallographic symmetry centers. The molecular orientation was deduced from the three-dimensional Patterson section computed in a plane of high vector density passing through the origin. Difference electron density maps, computed using phases given by an idealized chrysene molecule in the orientation observed in the Patterson function, showed peaks corresponding to a second chrysene molecule. These two molecules were related by an approximate noncrystallographic mirror plane passing through the origin and along the long axis of the molecule so that the whole arrangement had noncrystallographic symmetry *mmm*. This meant that there were two centrosymmetric chrysene molecules with 0·5 occupancy and four methyl C atoms with 0·25 occupancy. The model was refined, first assuming isotropic thermal motion and with Waser restraints based on the molecular dimensions observed for chrysene, and then with anisotropic thermal parameters with the additional restraint that for bonded pairs of atoms the difference in the components of the U_{ij} tensor along the bond must approximate to zero. The positions of hydrogen atoms were calculated and their positions were adjusted during the refinement using a riding model. The Chebyshev polynomial weighting scheme used was $w = [653t_0(x) + 267t_1(x) - 556t_2(x) - 175t_3(x)]$ where $x = F_{obs}/F_{max}$ (Carruthers & Watkin, 1979). The U_{ij} tensors were fitted with a *TLS* model with an r.m.s. discrepancy of 0·0049 Å^2.

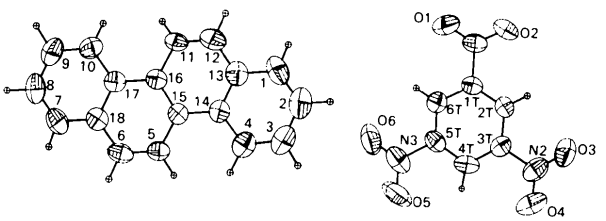


Fig. 1. Thermal ellipsoid (50% probability) representation of chrysene and *s*-trinitrobenzene showing the atomic numbering used throughout.

6-*Methylchrysene* (*6MeC*). The structure was determined by direct methods. There was no evidence of disorder in the crystal.

Chrysene–1,3,5-*trinitrobenzene* 1:1 *complex* (*Ch:TNB*). The structure was determined by direct methods. There was no evidence of disorder in the crystal.

1-*Methylchrysene*–1,3,5-*trinitrobenzene* 1:2 *complex* (*1MeC:2TNB*). The triclinic unit cell contains only one formula unit and if the crystal is assumed to be centrosymmetric, space group $P\bar{1}$, then the noncentrosymmetric 1-methylchrysene molecule must be disordered about the crystallographic symmetry center. The structure determination by direct methods and the subsequent refinement gave a well-defined centrosymmetric chrysene skeleton with half-occupancy carbon atoms attached at the 1- and 7-positions. Whilst the local symmetry over small regions of space must be $P1$, there is no evidence to suggest that the average structure seen by the diffraction experiment would be better represented by a noncentrosymmetric model.

2-*Methylchrysene*–1,3,5-*trinitrobenzene* 1:1 *complex* (*2MeC:TNB*). The structure was determined by direct methods. There was no evidence of disorder in the crystal.

3-*Methylchrysene*–1,3,5-*trinitrobenzene* 1:1 *complex* (*3MeC:TNB*). The structure was determined by direct methods. Surprisingly, even though the 3-methylchrysene occupies a general position in a non-centrosymmetric space group the molecules are disordered and appear as approximately centrosymmetric molecules with methyl carbon atoms at half-occupancy in the 3- and 9-positions but in the final refinement the half methyl group at C(9) has a non-positive-definite temperature factor.

4-*Methylchrysene*–1,3,5-*trinitrobenzene* 1:1 *complex* (*4MeC:TNB*). The structure, in space group $P\bar{1}$ with two formula units in the unit cell, was determined by direct methods. There was no evidence of disorder in the crystal.

5-*Methylchrysene*–1,3,5-*trinitrobenzene* 1:1 *complex* (*5MeC:TNB*) *and* 6-*methylchrysene*–1,3,5-*trinitrobenzene* 1:1 *complex* (*6MeC:TNB*). The structures were determined by direct methods. There was no evidence of disorder in either crystal structure.

5-*Methylchrysene–pyromellitic dianhydride* 1:1 *complex* (*5MeC:PMDA*). In space group $P2_1/a$ with two molecules in the unit cell, the two molecules must occupy two crystallographically distinct sets of symmetry centers, those at $\frac{1}{2}$,0,0 *etc.* and at 0,0,0 *etc.* The structure was modelled from generalized Patterson and electron density sections calculated in the molecular planes. About one symmetry center, two chrysene skeletons of half-occupancy can be distinguished and about a second symmetry center, two pyromellitic dianhydride molecules. This result is somewhat surprising, since the PMDA molecule is centrosymmetric. The analysis followed a pattern similar to that outlined for 1-methylchrysene. The Chebyshev polynomial weighting scheme had coefficients 653, 267, − 556 and − 175.

Results and discussion

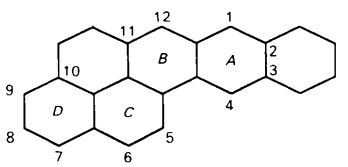
Molecular structure and dimensions

The structures reported here represent 13 independent determinations of the geometry of the chrysene skeleton. These have been found to varying degrees of accuracy, with different positions of a substituent methyl group. Bond lengths and interbond angles for each are listed in Table 3 (deposited). In four of these, 1MeC:2TNB, 3MeC:TNB, 1MeC and 5MeC:PMDA, there is a disorder about the principal axis of the chrysene skeleton; this disorder is resolved in the structure determination and, in the latter two structures, atoms were each assigned 50% occupancy in two sites. For 5MeC:TNB, the thermal ellipsoids are unsatisfactory (Fig. 2*i*) and may be indicative of substantial disorder, whilst, for the remaining molecules, the thermal ellipsoids (Fig. 2) are consistent with a significant librational motion about the principal skeleton axis of the chrysene portion of the molecule. For the disordered structures of 1MeC and 5MeC:PMDA, the expected bond lengths for chrysene and PMDA were used as input observations (Waser, 1963) in the least-squares analysis. Some internal measure of the self-consistency of the analyses may be obtained from the dimensions of the TNB molecules which are well known; the dimensions found in this study are typical of those recorded in other reported crystallographic studies.

The general pattern of bond lengths and angles in the methylchrysenes is the same as that predicted for chrysene itself by quantum mechanical calculations by the program *AMPAC* (Dewar, Zoebisch, Healy & Stewart, 1985). Examination of the standard deviations in Table 2 indicates that this crystallographic work is not sufficiently sensitive to bond-length variation for definitive conclusions to be made as to effects of methyl position. However, as in other crystallographic studies, the endocyclic angle at a C atom with a methyl substituent appears, in general, to be significantly less than the angle observed when the same C atom is unsubstituted (Domenicano, Vaciago & Coulson, 1975). At the site of methyl substituent the exocyclic bond angles are both approximately equal except for the cases of 4MeC and 5MeC. In these molecules, repulsions between hydrogen atoms across the bay region lead to distortions so that one exocyclic angle is markedly greater than 120° and the other angle smaller than 120°.

Such bond-angle distortions at the sites of bay-region substitution might be expected to be

Table 4. *Interplanar angles* (°)



	A–B	*A–C*	*A–D*	*B–C*	*B–D*	*C–D*
Chrysene	0·7	−0·7	0·0	0·0	0·7	−0·7
1MeC	1·25	−1·25	0·0	0·0	1·25	−1·25
6MeC	1·9	3·6	5·6	1·9	3·8	2·2
Ch:TNB	2·0	2·8	3·5	1·2	2·0	0·8
1MeC:2TNB	1·2	−1·2	0·0	0·0	1·2	−1·2
2MeC:TNB	0·4	1·9	2·9	1·8	2·6	1·5
3MeC:TNB	2·5	3·3	4·8	0·8	2·5	1·7
4MeC:TNB	4·1	6·7	−3·7	2·7	1·0	−3·0
5MeC:TNB	3·1	3·6	2·2	1·6	1·8	3·1
6MeC:TNB	0·5	0·9	2·6	1·0	3·0	2·2
5MeC:PMDA*	–	–		–	–	
5MeC†	2·2	3·6	2·7	1·5	−1·6	2·1
5,12diMeC						
Mol. 1	4·6	8·2	10·0	3·6	5·6	2·6
Mol. 2	5·4	10·7	14·9	5·3	9·8	4·9
11MeBaP						
Mol. 1	2·6	4·9	5·5	2·4	3·2	1·1
Mol. 2	8·5	13·5	13·7	6·3	6·0	0·7
DMBA	10·5	20·8	24·0	10·4	13·6	5·2

* Crystal disorder vitiates significance.
† For the ordered molecule.

accompanied by distortions throughout the chrysene skeleton. The greatest distortions, in the form of a twist of ring *A* relative to ring *C*, are expected for 4MeC and 5MeC because of the repulsions of the 4- and 5-methyl groups by the 5- and 4-H atoms, respectively. Also, the expectation is that chrysene itself, as well as 2MeC and 3MeC, will show the smallest deviations from planarity. 1MeC and 6MeC might show somewhat greater distortion because of the interaction of the methyl group with the *peri*-H atom (at the 12- or 7-positions).

The experimental results from this crystallographic study are presented in Table 4 which gives selected interplanar angles. These angles provide some measure of the deformation of the chrysene skeleton that occurs on monomethylation. If the molecule lies on a crystallographic center of symmetry, then rings *A* and *D* are necessarily coplanar, as are rings *B* and *C* (see Table 4), and chrysene, 1MeC and 1MeC:2TNB are found to be closest to planar. Our results, however, show that 4MeC is more distorted than 5MeC. The most surprising result is that the 3MeC molecule in 3MeC:TNB, which is at a general position in the unit cell and which would be expected to be planar, shows deviations from planarity that are as great as those of 5MeC in 5MeC:TNB and only slightly smaller than those of 4MeC in 4MeC:TNB (Table 4). The distortions observed for 5MeC in the 5MeC:TNB complex are small and similar to those observed in the ordered 5MeC molecule in crystalline 5MeC (Kashino *et al.*, 1984). In contrast, 11-MeBaP (Prout, Daub, Zacharias & Glusker, 1989) (in one of the two molecules in the asymmetric unit), DMBA and 5,12-diMeC all show much greater deviations from planarity. However, in these molecules the deformation of the exocyclic bond angles at C—CH_3 is still as great as that observed for 5MeC. Thus the smaller skeletal twist in 4MeC and 5MeC is not compensated for by increased bond-angle deformation.

It is therefore necessary to question the apparent lack of distortion in the crystals of 4MeC and 5MeC. This may be real, or it may be a manifestation of disorder in the crystal. If the 5MeC molecule is viewed parallel to the molecular plane with the methyl group towards the observer then the methyl group may be distorted to the left or the right to give two chiral forms. If these two forms both fit the crystal sites and are randomly distributed amongst those sites, then the electron density is averaged by the addition of a false mirror plane and will appear to be that of a near planar system. The bond angles seen for such an averaged molecule will be those observed for the projection of the molecule onto its best plane and will be closely similar to the values in the distorted true molecule. Disorder of this type might explain the rather poor diffraction intensities and the failure to achieve a low *R* value.

Crystal packing and complex formation

The crystal structures of chrysene, monomethylchrysenes and their complexes show great variety with surprisingly little isomorphism; only Ch:TNB and 3MeC:TNB are isomorphous. Chrysene has molecular symmetry $2/m$ and occupies a site with symmetry $\bar{1}$ in the crystal. The monomethylchrysenes, although without molecular symmetry, have a tendency to occupy sites at crystallographic inversion centers (1MeC, 1MeC:2TNB and 5MeC:PMDA) and are therefore necessarily disordered. In 3MeC:TNB, even though the crystals are noncentrosymmetric, the 3-MeC molecule is disordered about a molecular pseudo-inversion center (Fig. 6) (deposited).

Examination of the unit-cell volumes in Table 1 shows that the molecular volumes of the methylchrysenes, 1MeC, 4MeC and 6MeC, are roughly constant (319·2–323·9 Å^3) and for 5MeC, 323·0 Å^3. These values are 24–28 Å^3 greater than that of chrysene, a difference ascribable to the methyl group. The molecular volumes occupied by the 1:1 complexes of the methylchrysenes (except for 2MeC:TNB, see later) are again virtually constant (527·3–528·7 Å^3). In these cases, however, the molecular volume of the chrysene complex Ch:TNB is only 18·8–20·2 Å^3 less than those of the methylchrysene complexes, 3MeC:TNB, 4MeC:TNB, 5MeC:TNB and 6MeC:TNB. The effect is more marked in 2MeC:TNB which has a molecular

volume of 518·4 Å^3, only 9·9 Å^3 greater than that of Ch:TNB. The differences between methylchrysene volumes just listed and those of the TNB complexes are less than the volume of TNB (211·1 Å^3) (Choi & Abel, 1972). These contractions suggest strong intermolecular binding in the complexes.

All the crystals contain plane-to-plane molecular stacks, as would be expected for the closest packing of large, essentially planar molecules. In the complexes, the two molecular types alternate through the crystal, as is typical of the donor–acceptor stacks of π–π^* molecular complexes. The molecular stacks observed in the crystal structures are shown schematically in Fig. 3.

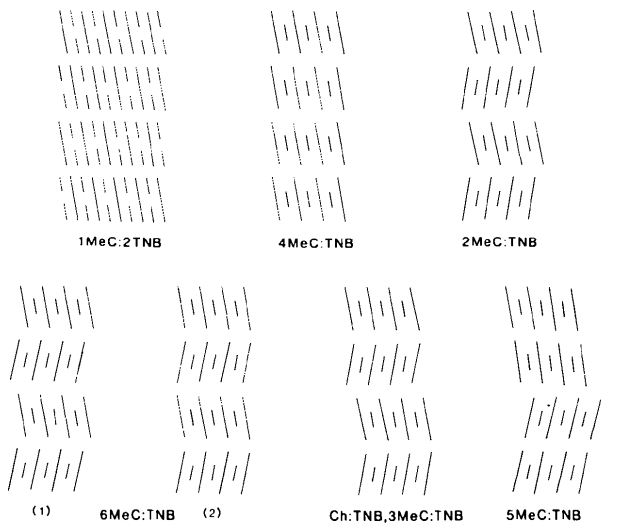


Fig. 3. Schematic representation of the donor–acceptor stacking in the π–π^* complexes.

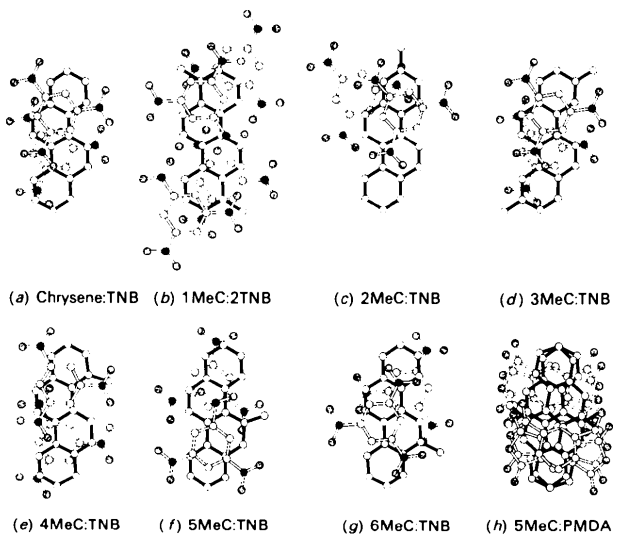


Fig. 4. Relationships of the donor and acceptor molecules in the molecular stacks.

Table 5. *Distance between least-squares best planes through chrysene and s-trinitrobenzene* C *atoms* (Å)

Chrysene:TNB	3·324	3·335
1MeC:2TNB	3·338	3·335
	3·534	3·142
2MeC:TNB	3·551	3·072
3MeC:TNB	3·282	3·445
4MeC:TNB	3·317	3·338
5MeC:TNB	3·342	3·285
6MeC:TNB	3·463	3·293

The stacking shows the similarities and differences between the various TNB complexes. 1MeC:2TNB differs in stoichiometry from the rest of the series since there are two TNB molecules per 1MeC molecule. Two coplanar TNB molecules lie between pairs of 1MeC molecules. All the other complexes contain 1:1 alternating stacks of TNB and hydrocarbon molecules. The simplest arrangement is that found in 4MeC:TNB in which the stacks are related by inversion centers in space group $P\bar{1}$ so that the crystal is effectively built up from planar sheets containing both 4MeC and TNB in a 1:1 molecular ratio. 2MeC:TNB has a simple herringbone packing with the molecular stacks related by the twofold screw axis in $P2_1$. In the direction perpendicular to the plane of the paper in this figure the stacks are identical. This same herringbone pattern is found in 6MeC:TNB crystals (1) but the glide plane in $P2_1/c$ introduces a different herringbone pattern perpendicular to the plane of the paper (2). These two patterns (1) and (2) are combined in the herringbone pattern found in Ch:TNB and 3MeC:TNB. In 5MeC:TNB the orientation of the molecular stacks in the herringbone pattern is reversed every two stacks instead of every stack.

The relationships of the molecules within a stack are illustrated in Figs. 4(*a–h*). The electron-acceptor molecules are projected onto the best plane of the (substituted) chrysene electron donors. In each diagram the chrysene is depicted with bold bonds, the electron-acceptor molecule above the chrysene with open bonds and the one below with dashed bonds. In all diagrams 'above' and 'below' are purely arbitrary. Interplanar spacings are given in Table 5.

Only if the chrysene is at an inversion center do the TNB (and PMDA) molecules above and below have the same relationship to the chrysene [1MeC:2TNB (Fig. 4*b*) and 5MeC:PMDA (Fig. 4*h*)]. In all other cases the orientation of the molecules above and below the chrysene are not equivalent but may, by coincidence, be similar, as in 4MeC:TNB (Fig. 4*e*).

It has been shown that for π–π^* electron donor–acceptor complexes where the charge-transfer interaction is superficial in the stabilization of the molecular complex (and hydrogen bonding is absent), the relative orientations of the donor and

acceptor molecules in the crystals are those that will maximize the overlap integral of the donor HOMO and the acceptor LUMO molecular orbitals (Mayoh & Prout, 1972). The symmetries of the highest and next highest energy occupied molecular orbitals of chrysene and the lowest and next lowest energy unoccupied molecular orbitals of TNB are shown in Fig. 5. Those for the substituted chrysenes are very similar to those of chrysene and those for PMDA are very similar to those of TNB. If HOMO–LUMO overlap is to be maximized, then the TNB molecule will lie over the center of the ring fusion bond of the *A* and *B* rings of chrysene, either with the benzene ring of TNB in the same orientation as in the chrysene or rotated about 30° as illustrated in Fig. 5. A comparison of Figs. 4 and 5 shows that these predicted positions are very close to that observed for 5MeC:TNB and not very different from those observed for 1MeC:2TNB, 4MeC:TNB, and 5MeC:PMDA.

In the stacks in Ch:TNB, the donor and the acceptor molecules are each related by a lattice translation along **c** so that the two planar faces of the chrysene molecule have a dissimilar environment with respect to the trinitrobenzene and *vice versa*. Within the stack the chrysene relates to one trinitrobenzene in an orientation well suited to maximize HOMO–LUMO interactions but the other is rather less well placed (Fig. 4*a*). This arrangement is repeated in the isomorphous 3MeC:TNB (Fig. 4*d*). In 2MeC:TNB, again the two TNB molecules are related by a lattice translation. One TNB molecule is close to the predicted orientation for a charge-transfer overlap but the other barely overlaps the chrysene at all and it may be that the complex is better thought of as composed of donor–acceptor pairs. In 6MeC:TNB it is a lattice translation that relates the two TNB molecules. The overlap is reasonable but quite far from the predicted position.

Abbreviations used: PAH polycyclic aromatic hydrocarbon; BaP benzo[*a*]pyrene; DMBA 7,12-dimethylbenz[*a*]anthracene; MeC methylchrysene; TNB 1,3,5-trinitrobenzene; PMDA pyromellitic dianhydride; 11-MeBaP 11-methylbenzo[*a*]pyrene.

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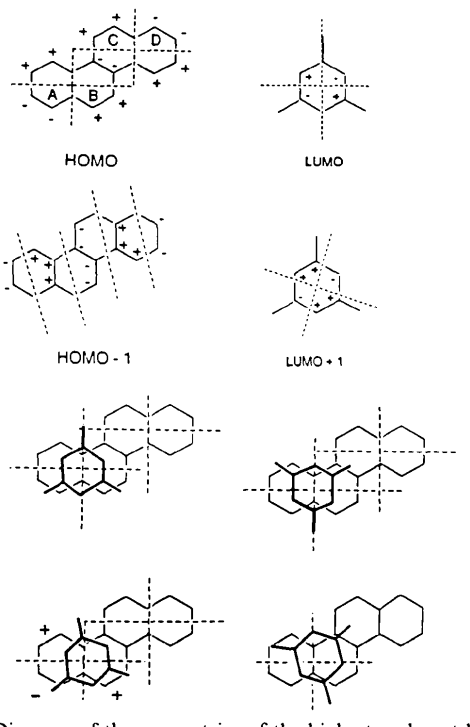

Fig. 5. Diagram of the symmetries of the highest and next highest energy occupied molecular orbitals (HOMO, HOMO-1) of the donor and lowest and next lowest energy unoccupied molecular orbitals (LUMO, LUMO + 1) of the acceptor.

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Comparison of the Structures of the Plant Growth Hormone Indole-3-acetic Acid, and Six of its Amino-Acid Conjugates

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Abstract

The crystal structures of six biologically active conjugates of the plant growth hormone, indole-3-acetic acid (IAA = auxin), with the amino acids L-alanine (1), α-amino-L-butyric acid (2), L-norvaline (3), DL-aspartic acid (4), L-isoleucine (5), and δ-aminovaleric acid (6) were determined. (1) $C_{13}H_{14}N_2O_3$, $M_r = 246{\cdot}26$, monoclinic, $P2_1$, $a = 6{\cdot}777\ (2)$, $b = 9{\cdot}611\ (2)$, $c = 10{\cdot}003\ (1)$ Å, $\beta = 106{\cdot}24\ (1)^\circ$, $V = 625{\cdot}1\ (2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}308$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71073$ Å, $\mu = 0{\cdot}88$ cm^{-1}, $F(000) = 260$, $T = 293\ (1)$ K, $R = 0{\cdot}048$, $wR = 0{\cdot}053$ for 1313 reflections with $I \geq 3\sigma(I)$. (2) $C_{14}H_{16}N_2O_3$, $M_r = 260{\cdot}30$, monoclinic, $P2_1$, $a = 7{\cdot}380\ (1)$, $b = 9{\cdot}727\ (1)$, $c = 9{\cdot}741\ (1)$ Å, $\beta = 105{\cdot}08\ (1)^\circ$, $V = 675{\cdot}2\ (1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}280$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71073$ Å, $\mu = 0{\cdot}85$ cm^{-1}, $F(000) = 276$, $T = 293\ (1)$ K, $R = 0{\cdot}045$, $wR = 0{\cdot}043$ for 1281 reflections with $I \geq 3\sigma(I)$. (3) $C_{15}H_{18}N_2O_3$, $M_r = 274{\cdot}32$, monoclinic, $P2_1$, $a = 8{\cdot}165\ (4)$, $b = 9{\cdot}635\ (4)$, $c = 9{\cdot}792\ (3)$ Å, $\beta = 106{\cdot}33\ (3)^\circ$, $V = 739{\cdot}3\ (2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}232$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71073$ Å, $\mu = 0{\cdot}81$ cm^{-1}, $F(000) = 292$, $T = 293\ (1)$ K, $R = 0{\cdot}065$, $wR = 0{\cdot}053$ for 1502 reflections with $I \geq 3\sigma(I)$. (4) $C_{14}H_{14}N_2O_5$, $M_r = 290{\cdot}28$, monoclinic, $P2_1/n$ (nonstandard, No. 14), $a = 7{\cdot}577\ (1)$, $b = 18{\cdot}939\ (3)$, $c = 9{\cdot}442\ (4)$ Å, $\beta = 97{\cdot}30\ (1)^\circ$, $V = 1343{\cdot}9\ (6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}434$ g cm^{-3}, Cu $K\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å, $\mu = 8{\cdot}88$ cm^{-1}, $F(000) = 608$, $T =$

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