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Molecular Compounds and Complexes. XV.† Pyrene–1,4,5,8-Naphthalenetetrone (1:1), C₁₆H₁₀.C₁₀H₄O₄

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Abstract. $M_r = 390\cdot4$, monoclinic, $P2_1/a$, $a = 10\cdot536$ (5), $b = 12\cdot877$ (5), $c = 7\cdot314$ (4) Å, $\beta = 114\cdot1$ (5)°, $V = 905\cdot5$ (9) Å³, $Z = 2$, $D_x = 1\cdot43$ g cm⁻³, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 0\cdot56$ cm⁻¹, $F(000) = 404$, $T = 298$ K, $R_F = 0\cdot057$ ($R_w = 0\cdot049$) for 878 intensities. The familiar mixed stacking of donor and acceptor molecules is found, with carbonyl groups aligned above six-membered rings of the pyrene molecule. The deviations from planarity in the $C_{10}H_4O_4$ acceptor molecule are slightly but significantly smaller than those found in the neat compound.

Introduction. 1,4,5,8-Naphthalenetetrone (NT), first synthesized from naphthazarin by oxidation with lead tetraacetate (Zahn & Ochwat, 1928), is a very powerful oxidizing agent and Lewis acid, and hence a likely electron acceptor in the formation of π–π^* charge-transfer molecular compounds. Black needles of perylene–NT have been described (Hellmuth, 1930) and Tatarsky (private communication) has prepared equimolar molecular compounds of acenaphthene, hexamethylbenzene and pyrene with NT. We have determined the crystal structure of pyrene–NT as a representative of this group and in order to investigate whether molecular-compound formation has any effect on the naphthalenetetrone molecule, which was found to be appreciably non-planar in its neat crystals (Herbstein & Kapon, 1982).

Experimental. Black needles elongated along [001] obtained by slow cooling of a 1:1 solution of the components in CH_3CN under nitrogen atmosphere; crystals stable in air and X-ray beam; cell dimensions from 25 strong high-angle reflections; intensities of about 1100 reflections ($-7 \leq h \leq 7$; $0 \leq k \leq 13$, $0 \leq l \leq 10$) measured, Philips PW 1100/20 four-circle diffractometer, graphite-monochromated Mo $K\alpha$, $\omega/2\theta$ measurement mode, no absorption correction; crystal $0\cdot1 \times 0\cdot1 \times 0\cdot3$ mm; scan range, speed and width $5° \leq 2\theta \leq 45°$, $1\cdot5°\omega$ min⁻¹ and $1\cdot2°\omega$, respectively, standard reflections 031, 02̄2̄ and 200; R_{int} (by merging $hk0$ and $\bar{h}k0$ equivalent reflections) $= 2\cdot5\%$; structure solved using *SHELX*76 direct methods; refinement on F (also by *SHELX*76) converged after inclusion of all atoms at $R_F = 5\cdot7\%$, $R_w = 4\cdot9\%$ (anisotropic temperature factors for non-hydrogen atoms and H atoms from difference Fourier synthesis with isotropic thermal parameters); 878 reflections used [reflections for which $F_o < 1\cdot5\sigma(F_o)$ suppressed], 164 parameters refined in final cycle; weighting scheme $1\cdot496/[\sigma^2(F_o)]$; terminal Δ/σ about 0·2 and a final difference synthesis revealed $\Delta\rho$ excursions within $-0\cdot20$ and $0\cdot18$ e Å⁻³; atomic scattering factors from *International Tables for X-ray Crystallography* (1974).*

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† Part XIV: Herbstein, Kapon, Reisner & Rubin (1983).

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* Lists of structure factors, thermal parameters and least-squares planes details have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38737 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. Atomic parameters are given in Table 1.

The mixed-stack molecular arrangement is shown in a stereodiagram (Fig. 1) and molecular geometries of the components are in Fig. 2. The reference pyrene molecule is centred at $(\frac{1}{2}\frac{1}{2}0)$ and the reference naphthalenetetrone molecule at $(00\frac{1}{2})$. The pyrene molecule is planar within experimental error. The naphthalenetetrone molecule is non-planar, its overall shape being similar to that found in the neat crystals (Herbstein & Kapon, 1982). The angle between pyrene and the best plane through the C, O atoms of naphthalenetetrone is 4·3 (1)°.

The crystals belong to group 3a of the classification given by Herbstein (1971); the TCNE (tetracyanoethylene), PMDA (pyromellitic dianhydride) and chloranil π-molecular compounds of pyrene also belong to this group. The alternating arrangement of donor and acceptor molecules in quasi-hexagonally arranged stacks is typical of neutral ground-state π–π^* molecular compounds. The overlap diagram (Fig. 3) suggests that there is marked interaction between polarizable six-membered rings of the pyrene molecule and carbonyl groups of NT, a feature found in many molecular compounds of aromatic hydrocarbons with quinones (Prout & Wallwork, 1966).

The pyrene molecule does not deviate significantly from *mmm* (D_{2h}) symmetry. Bond lengths averaged in accordance with this symmetry agree well with those found in pyrene at 113 K (Kai, Hama, Yasuoka & Kasai, 1978), except for the bond C(A)—C(G'), where our value is ~0·037 Å shorter than the values found by

other workers (Table 2; earlier work is summarized by Kai *et al.*, 1978). Presumably this is a systematic error due to the appreciable in-plane libration of the pyrene molecule as indicated by the thermal ellipsoids shown in Fig. 3.
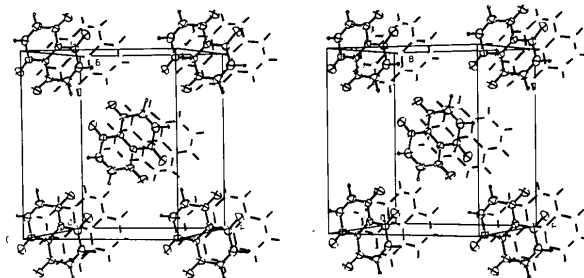

Fig. 1. *ORTEP* (Johnson, 1965) stereodiagram of the unit cell. The ellipsoids are of 40% probability.
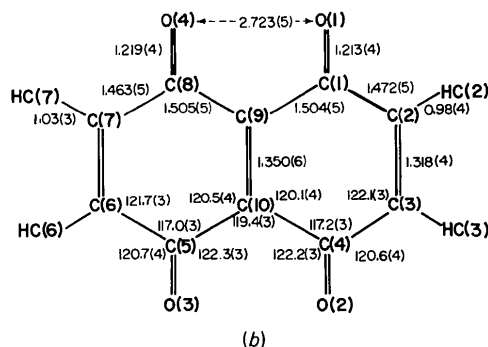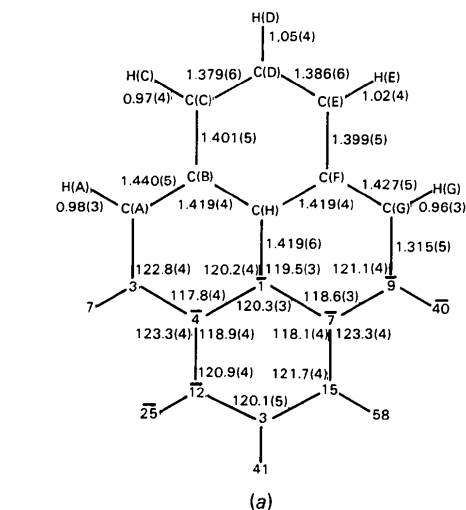

Fig. 2. (a) Molecular geometry of pyrene (deviations from planarity are given in the lower part of the diagram in units of 10^{-3} Å). (b) Molecular dimensions of naphthalenetetrone. (Distances in Å, angles in deg.)
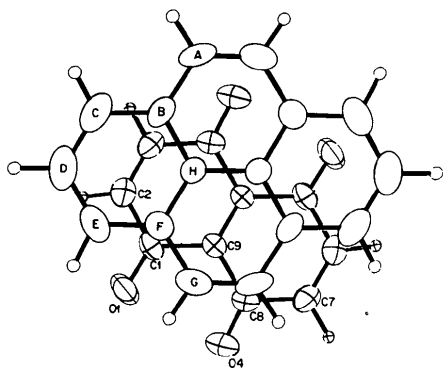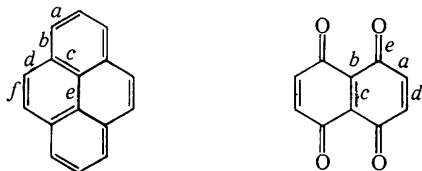
Table 1. *Atomic coordinates* ($\times 10^4$ *for non-hydrogen atoms;* $\times 10^3$ *for hydrogens), equivalent isotropic temperature factors for non-hydrogen atoms* ($\text{Å}^2 \times 10^3$) *and isotropic temperature factors for hydrogens* ($\text{Å}^2 \times 10^2$)

$U_{\text{iso}} = \frac{1}{8}\pi^2 B_{\text{iso}}$ and $U_{\text{eq}} = \frac{1}{3}\,\text{tr}(\mathbf{U})$.

	x	y	z	$U_{\text{eq}}/U_{\text{iso}}$
C(A)	4724 (5)	3186 (3)	−1479 (5)	53 (2)
C(B)	3748 (4)	3965 (3)	−1463 (4)	42 (2)
C(C)	2302 (5)	3835 (4)	−2410 (6)	62 (3)
C(D)	1398 (5)	4594 (4)	−2345 (6)	69 (3)
C(E)	1910 (4)	5520 (4)	−1350 (6)	63 (3)
C(F)	3342 (4)	5705 (3)	−414 (5)	44 (2)
C(G)	3928 (5)	6649 (3)	604 (6)	58 (3)
C(H)	4270 (3)	4919 (3)	−472 (4)	36 (2)
C(1)	3017 (4)	5237 (3)	4026 (5)	48 (2)
C(2)	2508 (4)	4177 (3)	3382 (6)	56 (3)
C(7)	6644 (4)	6580 (3)	6597 (6)	55 (3)
C(8)	5152 (4)	6411 (3)	5975 (5)	45 (2)
C(9)	4568 (4)	5386 (2)	5003 (5)	38 (2)
O(1)	2209 (3)	5950 (2)	3764 (4)	77 (2)
C(4)	4431 (3)	7072 (2)	6271 (4)	69 (2)
H(A)	430 (3)	254 (3)	−215 (5)	7 (1)
H(C)	197 (4)	319 (3)	−314 (5)	7 (1)
H(D)	32 (4)	449 (3)	−309 (6)	10 (1)
H(E)	130 (4)	611 (3)	−124 (6)	10 (2)
H(G)	326 (4)	715 (3)	61 (5)	7 (1)
H(2)	149 (5)	415 (3)	280 (6)	10 (1)
H(7)	703 (4)	732 (3)	700 (5)	8 (1)

Fig. 3. Overlap diagram with pyrene molecule projected onto mean plane of NT.

Averaged bond lengths (Table 2) and angles (not listed) of naphthalenetetrone agree well with those reported earlier. There are small differences in the deviations from the mean planes. These differences are statistically significant and are ascribed to packing effects. Similar small differences have been found between the shapes of the non-planar benzo[c]phenanthrene molecule in its neat crystals and in the π-molecular compound benzo[c]phenanthrene–2,3-di-chloro-5,6-dicyano-p-benzoquinone (Bernstein, Regev & Herbstein, 1977).

Table 2. *Comparisons of averaged bond lengths (Å) as defined in the molecular formulae*

The results have not been corrected for thermal vibrations. Figures in parentheses are e.s.d.'s of average values.

	Pyrene		Naphthalenetetrone	
Bond	Present results	Kai *et al.* (1978)	Present results	Herbstein & Kapon (1982)
a	1·383 (4)	1·385 (1)	1·468 (4)	1·474 (2)
b	1·400 (4)	1·402 (1)	1·505 (4)	1·502 (2)
c	1·419 (3)	1·422 (1)	1·350 (6)	1·349 (3)
d	1·434 (4)	1·436 (1)	1·318 (4)	1·325 (2)
e	1·419 (6)	1·427 (2)	1·216 (4)	1·215 (2)
f	1·315 (5)	1·352 (2)	—	—

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The Structure of p-Iodobenzoic Acid, $C_7H_5IO_2$

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Abstract. $M_r = 237·0$, monoclinic, $P2_1/a$, $a = 30·357$ (2), $b = 6·0300$ (7), $c = 4·1561$ (4) Å, $\beta = 97·35$ (1)°, $V = 754·6$ (1) Å³, $Z = 4$, $D_x = 2·148$ g cm⁻³, monochromated Mo $K\alpha$, $\lambda = 0·71034$ Å, $\mu = 43·5$ cm⁻¹, $F(000) = 464$, $T = 300$ K. $R = 0·072$ for 1002 observed reflections. Two of the asymmetric units form a planar dimeric species. The compound is isostructural with the bromine analog.

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