$C_{18}H_{22}O_3S_2$

Fig. 1. Perspective view of molecule (I) with atomic labeling.

The phenyl rings are in quite different orientations with respect to the rest of the molecule, as shown by the torsion angles along the O(11')—C(12') and C(12')—

C(13') bonds. This is probably a consequence of the packing in the crystal, where only normal van der Waals contacts are observed.

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A 1:1 Complex of 2,9-Dimethyl-1,10-phenanthroline and Resorcinol, C₁₄H₁₂N₂.C₆H₆O₂

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Abstract. $M_r = 318.38$, triclinic, $P\bar{1}$, $a = 7.461$ (1), $b = 11.942$ (2), $c = 14.392$ (3) Å, $\alpha = 139.25$ (1), $\beta = 91.16$ (2), $\gamma = 94.87$ (1)°, $V = 826.9$ (2) Å³, $Z = 2$, $D_x = 1.28$ g cm⁻³, Cu $K\alpha$, $\lambda = 1.54178$ Å, $\mu = 6.79$ cm⁻¹, $F(000) = 336$, room temperature, $R = 0.078$ for 1755 unique reflections with $I > 3\sigma(I)$. Parallel sheets of 2,9-dimethyl-1,10-phenanthroline molecules are almost perpendicular, 81.7 (4)°, to parallel sheets of resorcinol molecules. There is extensive hydrogen bonding with each phenanthroline bound from above and below by resorcinol molecules. The title

complex represents a class of molecular complex which is different from three reported in the earlier papers.

Experimental. Complex prepared by mixing equimolar quantities of the reactants in alcoholic solvents. Recrystallization from acetone–methanol (3:1) yielded faceted prismatic crystals. Although the crystals were of poor quality, a useable single crystal was obtained; 0.5 × 0.5 × 0.5 mm. Syntex $P2_1$ diffractometer, $\theta:2\theta$ scan, $2\theta_{max} = 116°$, graphite-monochromated Cu $K\alpha$. Lattice parameters from least-squares refinement of 15 medium-angle reflections; angles measured by centering routine associated with the diffractometer system. No systematic absences. Monitored reflection showed no significant change in intensity. 1878 independent reflections measured ($0 \le h \le 8$, $-9 \le k \le 9$, $-11 \le l \le 11$), 1755 with $I > 3\sigma(I)$. Lorentz and polarization corrections; no absorption correction. Direct methods (*MULTAN*78: Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Several heavy atoms and all H atoms found in difference Fourier map.

Introduction. Interactions between neutral organic molecules are of biological interest as well as of importance in nonaqueous laboratory systems. We have investigated a series of crown-ether complexes with neutral organic molecules (Galloy, Watson, Vögtle & Müller, 1982; Grossie, Watson, Vögtle & Müller, 1982; Watson, Galloy, Grossie, Vögtle & Müller, 1983) and bipyridyl complexes with barium and calcium (Watson, Grossie, Vögtle & Müller, 1983). The title

Full-matrix least-squares anisotropic refinement (H atoms isotropic), $R = 0.078$, $S = 0.71$, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/\sigma^2(F_o)$. Largest peak in final difference Fourier $0.4e$ Å^{-3}. Average and maximum Δ/σ 0.18 and 0.71. Atomic scattering factors from XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Locally written programs used for data reduction and initial block-diagonal least-squares refinement. MULTAN78 used for the direct-methods calculations and XRAY76 for all other computations.

Discussion. Table 1 lists atomic positional parameters and U_{eq} values while Table 2 gives bond lengths, valence angles and hydrogen-bonding parameters.* Fig. 1 is an ORTEPII drawing (Johnson, 1971) which shows the molecular packing of the complex. Least-squares planes fitted to the phenanthroline skeleton indicate it to be planar with the two methyl substituents out of the plane by 0.07 and 0.06 Å. The atoms of the phenyl ring are planar within 0.012 (6) Å with the two hydroxyl atoms out of the plane by 0.07 Å. The dihedral angle between the two planes is 81.7 (4)°. The two N atoms of the phenanthroline molecule participate in hydrogen bonding. The hydroxyl H of one resorcinol binds in a bifurcated manner to the two N atoms from above while the second hydroxyl H binds from below to the two N atoms of another molecule.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and interatomic distances and valence angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38925 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
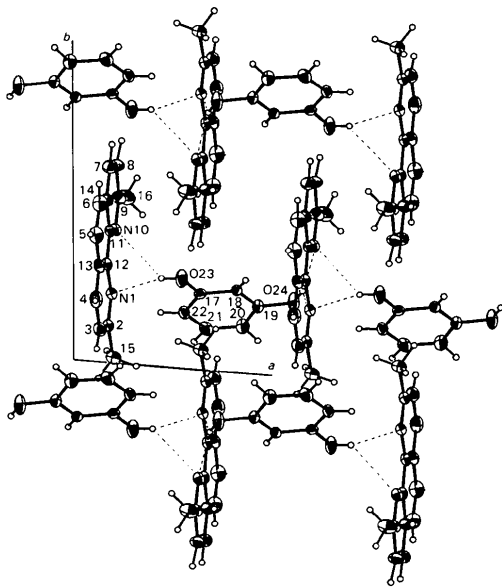

Fig. 1. ORTEP drawing showing packing of the title 1:1 complex.

Table 1. *Atomic positional parameters* ($\times 10^4$) *and equivalent isotropic thermal parameters*

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^* a_j^* (\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	U_{eq}(Å^2)
N(1)	2580 (2)	6017 (3)	4212 (2)	41
C(2)	2504 (3)	5561 (4)	4798 (4)	52
C(3)	2330 (4)	6796 (5)	6286 (4)	66
C(4)	2280 (4)	8478 (5)	7111 (4)	65
C(5)	2338 (4)	10733 (4)	7333 (3)	61
C(6)	2433 (4)	11170 (3)	6720 (3)	61
C(7)	2590 (4)	10311 (4)	4524 (4)	64
C(8)	2674 (4)	9043 (4)	3076 (4)	60
C(9)	2664 (4)	7333 (4)	2311 (3)	49
N(10)	2580 (2)	6894 (2)	2927 (2)	40
C(11)	2537 (2)	8161 (3)	4369 (2)	34
C(12)	2496 (3)	7693 (3)	5030 (2)	37
C(13)	2362 (3)	8998 (4)	6520 (3)	44
C(14)	2524 (3)	9904 (3)	5212 (3)	44
C(15)	2602 (4)	3714 (4)	3860 (4)	70
C(16)	2718 (5)	5886 (5)	713 (3)	75
C(17)	3315 (3)	5897 (3)	-1888 (2)	39
C(18)	1463 (3)	5627 (2)	-1965 (2)	36
C(19)	563 (3)	7005 (3)	-945 (2)	42
C(20)	1523 (3)	8689 (3)	161 (3)	55
C(21)	3378 (3)	8916 (3)	226 (3)	54
C(22)	4318 (3)	7542 (3)	-780 (2)	47
O(23)	4088 (2)	4455 (2)	-2977 (2)	72
O(24)	-1245 (2)	6802 (2)	-942 (2)	67

Table 2. *Interatomic distances* (Å), *valence angles* (°) *and hydrogen-bonding parameters* (Å *and* deg)

N(1)–C(2)	1.304 (8)	C(9)–C(16)	1.506 (4)
N(1)–C(12)	1.360 (4)	N(10)–C(11)	1.360 (3)
C(2)–C(3)	1.428 (6)	C(11)–C(12)	1.422 (7)
C(2)–C(15)	1.488 (6)	C(11)–C(14)	1.409 (5)
C(3)–C(4)	1.359 (7)	C(12)–C(13)	1.417 (4)
C(4)–C(13)	1.382 (9)	C(17)–C(18)	1.375 (3)
C(5)–C(6)	1.323 (8)	C(17)–C(22)	1.385 (3)
C(5)–C(13)	1.413 (6)	C(17)–O(23)	1.368 (3)
C(6)–C(14)	1.433 (5)	C(18)–C(19)	1.372 (3)
C(7)–C(8)	1.371 (5)	C(19)–C(20)	1.396 (3)
C(7)–C(14)	1.395 (8)	C(19)–O(24)	1.352 (3)
C(8)–C(9)	1.404 (6)	C(20)–C(21)	1.374 (3)
C(9)–N(10)	1.329 (7)	C(21)–C(22)	1.385 (3)

C(2)–N(1)–C(12)	119.6 (3)	N(1)–C(12)–C(13)	122.6 (4)
N(1)–C(2)–C(3)	121.0 (4)	C(11)–C(12)–C(13)	118.4 (3)
N(1)–C(2)–C(15)	117.7 (4)	C(4)–C(13)–C(5)	123.0 (3)
C(3)–C(2)–C(15)	121.3 (6)	C(4)–C(13)–C(12)	116.5 (3)
C(2)–C(3)–C(4)	119.5 (7)	C(5)–C(13)–C(12)	120.5 (5)
C(3)–C(4)–C(13)	120.8 (4)	C(6)–C(14)–C(7)	123.1 (3)
C(6)–C(5)–C(13)	120.8 (3)	C(6)–C(14)–C(11)	119.2 (4)
C(5)–C(6)–C(14)	121.5 (3)	C(7)–C(14)–C(11)	117.7 (3)
C(8)–C(7)–C(14)	120.5 (4)	C(18)–C(17)–C(22)	121.4 (2)
C(7)–C(8)–C(9)	118.2 (5)	C(18)–C(17)–O(23)	116.0 (2)
C(8)–C(9)–N(10)	123.0 (3)	C(22)–C(17)–O(23)	122.6 (2)
C(8)–C(9)–C(16)	120.4 (5)	C(17)–C(18)–C(19)	120.1 (2)
N(10)–C(9)–C(16)	116.6 (4)	C(18)–C(19)–C(20)	120.1 (2)
C(9)–N(10)–C(11)	118.6 (3)	C(18)–C(19)–O(24)	122.3 (2)
N(10)–C(11)–C(12)	118.5 (3)	C(20)–C(19)–O(24)	117.6 (2)
N(10)–C(11)–C(14)	121.9 (4)	C(19)–C(20)–C(21)	118.5 (2)
C(12)–C(11)–C(14)	119.6 (3)	C(20)–C(21)–C(22)	122.4 (2)
N(1)–C(12)–C(11)	118.9 (3)	C(17)–C(22)–C(21)	117.5 (2)

D–H$\cdots A$	D–H	H$\cdots A$	$D\cdots A$	D–H$\cdots A$
O(23)–H(23)$\cdots$N(1^i)	0.75 (3)	2.41 (4)	2.925 (3)	127 (4)
O(23)–H(23)$\cdots$N(10^i)	0.75 (3)	2.56 (5)	3.103 (4)	131 (5)
O(24)–H(24)$\cdots$N(1^{ii})	0.75 (3)	2.63 (4)	3.116 (3)	124 (6)
O(24)–H(24)$\cdots$N(10^{ii})	0.75 (3)	2.23 (4)	2.944 (3)	160 (5)

Symmetry code: (i) $1 - x$, $1 - y$, $-z$; (ii) $-x$, $1 - y$, $-z$.

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Molecular Compounds and Complexes. XV.† Pyrene–1,4,5,8-Naphthalenetetrone (1:1), $C_{16}H_{10}.C_{10}H_4O_4$

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Abstract. $M_r = 390.4$, monoclinic, $P2_1/a$, $a = 10.536$ (5), $b = 12.877$ (5), $c = 7.314$ (4) Å, $\beta = 114.1$ (5)°, $V = 905.5$ (9) Å³, $Z = 2$, $D_x = 1.43$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.56$ cm⁻¹, $F(000) = 404$, $T = 298$ K, $R_F = 0.057$ ($R_w = 0.049$) 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 CH₃CN 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 $0.1 \times 0.1 \times 0.3$ mm; scan range, speed and width $5° \leq 2\theta \leq 45°$, $1.5°\omega$ min⁻¹ and $1.2°\omega$, respectively, standard reflections 031, $0\bar{2}\bar{2}$ and 200; R_{int} (by merging $hk0$ and $\bar{h}k0$ equivalent reflections) = 2.5%; structure solved using *SHELX*76 direct methods; refinement on F (also by *SHELX*76) converged after inclusion of all atoms at $R_F = 5.7\%$, $R_w = 4.9\%$ (anisotropic temperature factors for non-hydrogen atoms and H atoms from difference Fourier synthesis with isotropic thermal parameters); 878 reflections used [reflections for which $F_o < 1.5\sigma(F_o)$ suppressed], 164 parameters refined in final cycle; weighting scheme $1.496/[\sigma^2(F_o)]$; terminal Δ/σ about 0.2 and a final difference synthesis revealed $\Delta\rho$ excursions within -0.20 and 0.18 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).