

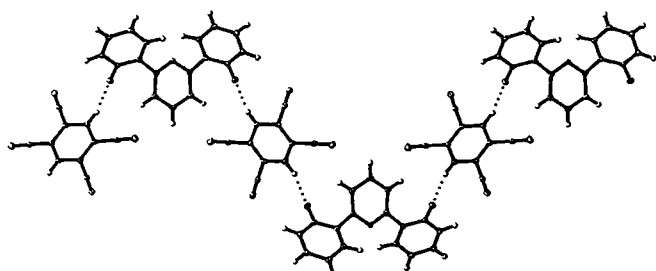
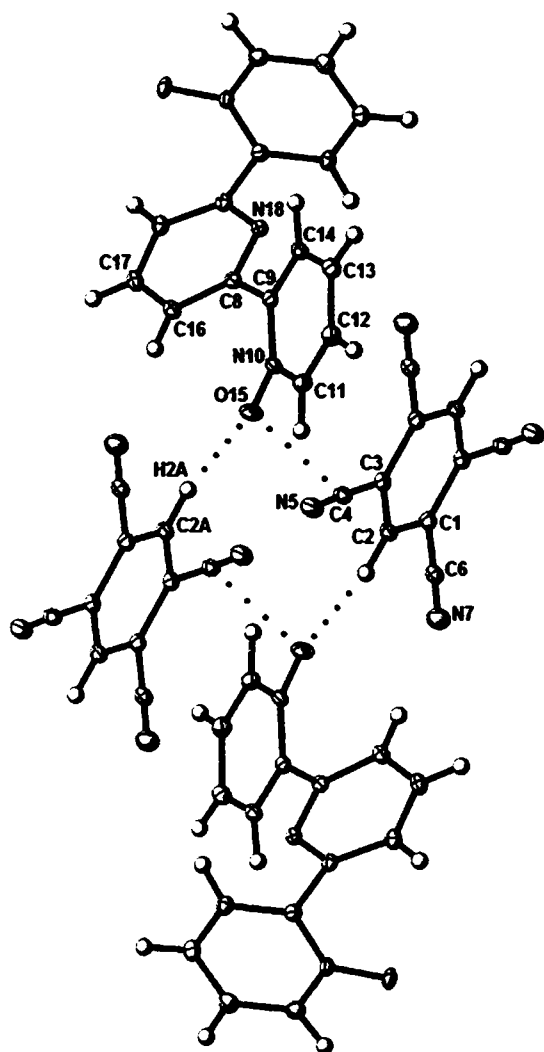
Crystal structure of 2,2':6',2''-terpyridine 1,1''-dioxide 1,2,4,5-tetracyanobenzene, $C_{15}H_{11}N_3O_2 \cdot C_6H_4(CN)_4$

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Abstract

$C_{25}H_{13}N_7O_2$, monoclinic, $C12/c1$ (no. 15), $a = 24.404(3)$ Å, $b = 6.487(1)$ Å, $c = 13.487(2)$ Å, $\beta = 108.29(1)^\circ$, $V = 2027.4$ Å³, $Z = 4$, $R_{gt}(F) = 0.038$, $wR_{ref}(F^2) = 0.099$, $T = 173$ K.

Source of material

We have prepared the title compound as a continuing effort to understand the intermolecular contact preferences of the *N*-oxide group in molecular crystals [1–4]. 2,2':6',2''-Terpyridine 1,1''-dioxide was prepared using a modification of the procedure for direct oxidation of pyridine and pyrazine moieties [5]. Dimethyldioxirane (17.71 ml, 0.08 M) in acetone was stirred with terpyridine (150.4 mg, 0.6447 mol, Aldrich 98 %) in acetone (2 ml, Fisher reagent grade) for 5 d at 300 K. Filtration of the mixture provided terpyridine dioxide as a colorless solid (92.2 %, 157.6 mg; m.p. 502–507 K, cf. 505–506 K [6]). The title cocrystals were obtained by slow evaporation of a 1:1 mixture using the previously prepared 2,2':6',2''-terpyridine 1,1''-dioxide and commercially available 1,2,4,5-tetracyanobenzene in methylene chloride solution at room temperature. The oxidizing agent, dimethyldioxirane, was prepared by reacting potassium peroxomonosulfate (0.0390 mol) and $NaHCO_3$ (0.138 mol) in acetone (38.4 ml) and water (50 ml) [7]. Vigorous stirring of the mixture at 263 K followed by distillation (40–100 Torr) at ambient temperature resulted in 0.06–0.08 M dimethyldioxirane as verified by titration against thioanisole.

Experimental details

The aryl hydrogen atoms were located in a difference density map and refined isotropically. The C—H distances were normalized to 1.08 Å for subsequent investigation of C—H $\cdots$ O interactions.

Discussion

The crystal structure of this 1:1 bimolecular compound contains tetracyanobenzene (TCNB) and terpyridinedioxide (TPDO) molecules positioned on inversion and two-fold rotation symmetry elements, respectively. Inspection of molecular conformation reveals the expected planar TCNB with TPDO skewed due to the pyridyl-*N*-oxide-pyridyl geometry ($\angle N10-C9-C8-N1 = 145.7(1)^\circ$). The crystal structure is stabilized by an assortment of nonbonded contacts that link adjacent TCNB and TPDO building blocks. Each TCNB moiety forms $C2A-H\cdots O15^- - N10^+$ contacts [$d(C\cdots O) = 3.038(2)$ Å, $\angle C-H\cdots O = 162^\circ$ (symmetry code: $\frac{1}{2}-x, \frac{1}{2}-y, -z$)] and $N5 \equiv C4\cdots O15^- - N10^+$ [$d(C\cdots O) = 3.004(2)$ Å, $\angle N \equiv C\cdots O = 104.9(1)^\circ$, $\angle N^+ - O^- \cdots C = 122.12(8)^\circ$ (symmetry code: x, y, z)] to neighboring *N*-oxide groups to give centrosymmetric tetrameric patterns (figure, top). The C—H $\cdots$ O motifs extend along the [101] direction resulting in an undulating supramolecular pattern (figure, bottom) that stacks with translation related motifs via *N*-oxide $\cdots$ nitrile contacts.

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Table 1. Data collection and handling.

Crystal:	light yellow transparent block, size 0.21 × 0.38 × 0.46 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.98 cm ⁻¹
Diffractometer, scan mode:	Rigaku R-axis Spider, ω/ϕ
$2\theta_{\max}$:	50.7°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	6967, 1819
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1657
$N(\text{param})_{\text{refined}}$:	181
Programs:	SHELXS-97 [8], SHELXL-97 [9], X-Seed [10]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(2)	8f	0.6871(7)	0.533(3)	-0.043(1)	0.022(4)
H(11)	8f	0.8176(7)	0.479(3)	-0.116(1)	0.024(4)
H(12)	8f	0.8618(7)	0.185(3)	-0.172(1)	0.030(4)
H(13)	8f	0.9548(7)	0.077(3)	-0.063(1)	0.019(4)
H(14)	8f	1.0036(7)	0.279(2)	0.094(1)	0.023(4)
H(16)	8f	0.9363(7)	0.894(3)	0.109(1)	0.026(4)
H(17)	4e	0	1.072(4)	¼	0.023(6)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(15)	8f	0.85259(4)	0.6764(2)	0.04289(8)	0.0185(5)	0.0172(6)	0.0287(5)	0.0066(4)	0.0060(4)	-0.0058(4)
N(5)	8f	0.76274(5)	0.7180(2)	0.19765(9)	0.0223(6)	0.0191(7)	0.0178(6)	0.0030(5)	0.0029(5)	-0.0022(5)
N(7)	8f	0.62168(5)	0.2753(2)	-0.26980(9)	0.0232(7)	0.0246(8)	0.0215(6)	0.0026(5)	0.0029(5)	0.0003(5)
N(10)	8f	0.88152(5)	0.5308(2)	0.01446(8)	0.0150(6)	0.0112(6)	0.0160(5)	0.0023(4)	0.0050(4)	0.0010(5)
N(18)	4e	0	0.4966(3)	¼	0.0142(7)	0.0123(9)	0.0134(7)	0	0.0046(6)	0
C(1)	8f	0.70617(6)	0.2556(2)	-0.0958(1)	0.0160(6)	0.0139(7)	0.0145(6)	0.0001(5)	0.0055(5)	0.0014(5)
C(2)	8f	0.71228(6)	0.4188(2)	-0.0260(1)	0.0173(7)	0.0126(7)	0.0166(6)	0.0020(5)	0.0061(5)	0.0022(5)
C(3)	8f	0.75612(5)	0.4140(2)	0.0698(1)	0.0181(6)	0.0122(7)	0.0142(6)	-0.0005(5)	0.0067(5)	0.0003(5)
C(4)	8f	0.76072(5)	0.5835(2)	0.1414(1)	0.0156(6)	0.0159(8)	0.0150(6)	0.0021(5)	0.0033(5)	0.0023(6)
C(6)	8f	0.65964(6)	0.2633(2)	-0.1935(1)	0.0192(7)	0.0135(7)	0.0177(7)	0.0021(5)	0.0065(6)	0.0004(5)
C(8)	8f	0.96575(5)	0.6043(2)	0.16892(9)	0.0144(6)	0.0139(7)	0.0139(6)	0.0005(5)	0.0058(5)	0.0006(5)
C(9)	8f	0.93605(5)	0.4780(2)	0.07606(9)	0.0145(6)	0.0127(7)	0.0130(6)	-0.0002(5)	0.0043(5)	0.0028(5)
C(11)	8f	0.85588(6)	0.4263(2)	-0.0762(1)	0.0162(7)	0.0178(8)	0.0153(6)	-0.0007(6)	0.0024(5)	0.0007(6)
C(12)	8f	0.88237(6)	0.2615(2)	-0.1058(1)	0.0200(7)	0.0181(8)	0.0138(6)	-0.0015(6)	0.0039(5)	-0.0005(6)
C(13)	8f	0.93663(6)	0.1991(2)	-0.0428(1)	0.0203(7)	0.0151(8)	0.0169(6)	0.0019(6)	0.0080(5)	-0.0005(5)
C(14)	8f	0.96330(6)	0.3109(2)	0.0470(1)	0.0168(7)	0.0139(8)	0.0159(6)	0.0020(5)	0.0054(5)	0.0022(5)
C(16)	8f	0.96274(6)	0.8190(2)	0.1676(1)	0.0189(7)	0.0140(8)	0.0166(7)	0.0020(5)	0.0064(6)	0.0019(6)
C(17)	4e	0	0.9271(3)	¼	0.023(1)	0.012(1)	0.0189(9)	0	0.0091(8)	0

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