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Synthesis and crystal structure of 1,3-bis[(3,4-dicyano)phenoxy]-4,6-dinitro-benzene, $C_{22}H_8N_6O_6$

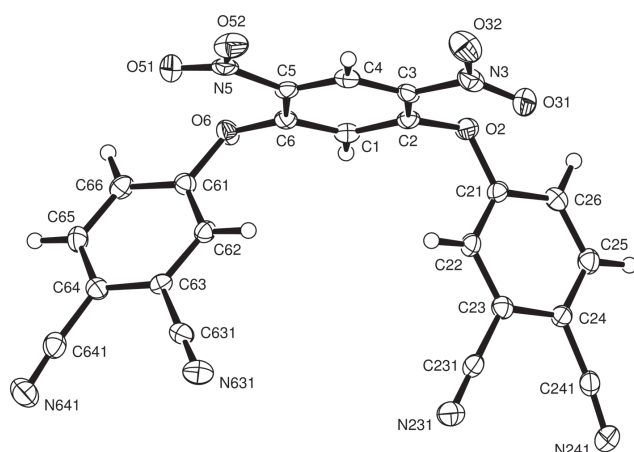


Table 1: Data collection and handling.

Crystal:	Plate, pale yellow
Size:	0.08 × 0.03 × 0.01 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.12 mm ⁻¹
Diffractometer, scan mode:	Xcalibur 3/Sapphire3, Thin slice φ and ω -scans
θ_{\max} , completeness:	25°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	23318, 3333, 0.085
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2315
$N(\text{param})_{\text{refined}}$:	339
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX and ORTEP [4, 5]

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Abstract

$C_{22}H_8N_6O_6$, monoclinic, $P2_1/n$ (no. 14), $a = 15.3939(6)$ Å, $b = 7.3053(3)$ Å, $c = 16.8282(6)$ Å, $\beta = 91.567(3)^\circ$, $V = 1891.74(13)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0510$, $wR_{\text{ref}}(F^2) = 0.0867$, $T = 140(2)$ K.

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Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

1,5-Difluoro-2,4-dinitrobenzene (0.2 g, 1 mmol), 4-hydroxyphthalonitrile (0.3 g, 2.1 mmol) and potassium carbonate (0.274 g, 2.0 mmol) were added to acetone (7 mL) and the

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mixture was stirred at room temperature for 24 h. The solvent was removed and the residue redissolved in DCM. This was washed with water and the washings were extracted with DCM three times. The combined organic extracts were dried over $MgSO_4$ and the solvent removed under reduced pressure. The product was purified by column chromatography (eluting with DCM). Recrystallization from acetone gave the title compound as a yellow crystalline solid (0.3 g, 66%). Mp. 197 °C; ¹H NMR (500 MHz, Acetone) δ 9.04 (s, 1H), 8.14 (d, $J = 8.8$ Hz, 2H), 7.96 (d, $J = 2.5$ Hz, 2H), 7.80 (dd, $J = 8.8, 2.5$ Hz, 2H), 7.73 (s, 1H); ¹³C NMR (126 MHz, Acetone) δ 160.10, 153.48, 139.12, 137.36, 126.49, 124.56, 124.31, 118.82, 117.81, 116.11, 115.74, 112.56; IR (KBr, cm⁻¹): 3047, 2240, 1630, 1536.

Experimental details

The structure was determined by the intrinsic phasing routines in the SHELXT program [2] and refined by full-matrix least-squares methods, in SHELXL [3]. Hydrogen atoms were included in idealized positions, but then allowed to refine freely. The figure was drawn with ORTEP [4, 5].

Discussion

1,2-Cyano-containing benzene compounds or phthalonitriles are important precursors for phthalocyanine molecules [6] and have potential uses in composite matrices, adhesives, sensitizers and pigments [7–11]. As part of our ongoing work on the synthesis and study of phthalocyanine dimers, we targeted the title novel compound as a linker unit.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U_{iso}^*/U_{eq}
C1	0.57921(15)	0.8096(3)	0.20185(14)	0.0199(6)
C2	0.53242(14)	0.7043(3)	0.14712(13)	0.0193(5)
C3	0.53716(15)	0.5142(3)	0.15288(13)	0.0190(6)
C4	0.59101(15)	0.4339(3)	0.20993(14)	0.0212(6)
C5	0.63902(15)	0.5404(3)	0.26216(13)	0.0189(6)
C6	0.63195(14)	0.7311(3)	0.26008(13)	0.0182(5)
O2	0.48760(10)	0.7927(2)	0.08682(9)	0.0232(4)
C21	0.40277(15)	0.8442(3)	0.09919(14)	0.0196(6)
C22	0.36351(16)	0.8123(3)	0.17038(15)	0.0200(6)
C23	0.27956(15)	0.8749(3)	0.18027(13)	0.0198(6)
C24	0.23554(15)	0.9672(3)	0.11806(14)	0.0202(6)
C25	0.27591(17)	0.9935(3)	0.04637(15)	0.0241(6)
C26	0.35984(16)	0.9330(3)	0.03719(15)	0.0220(6)
C231	0.23842(15)	0.8575(3)	0.25549(14)	0.0227(6)
N231	0.20400(14)	0.8493(3)	0.31519(13)	0.0314(5)
C241	0.15022(17)	1.0347(3)	0.13437(14)	0.0237(6)
N241	0.08405(14)	1.0852(3)	0.15378(13)	0.0352(6)
N3	0.48709(13)	0.3912(3)	0.09940(12)	0.0267(5)
O31	0.42934(11)	0.4568(2)	0.05668(10)	0.0315(4)
O32	0.50654(12)	0.2285(2)	0.10111(10)	0.0379(5)
N5	0.70039(13)	0.4432(3)	0.31619(12)	0.0261(5)
O51	0.75237(12)	0.5349(2)	0.35598(10)	0.0360(5)
O52	0.69727(11)	0.2753(2)	0.31646(10)	0.0344(5)
O6	0.67834(10)	0.8492(2)	0.30921(9)	0.0239(4)
C61	0.65818(15)	0.8576(3)	0.38875(13)	0.0195(6)
C62	0.58248(15)	0.7833(3)	0.41665(14)	0.0196(6)
C63	0.56391(14)	0.8028(3)	0.49640(13)	0.0178(5)
C64	0.62098(15)	0.8988(3)	0.54776(13)	0.0197(6)
C65	0.69742(16)	0.9701(3)	0.51824(15)	0.0224(6)
C66	0.71587(16)	0.9497(3)	0.43899(14)	0.0217(6)
C631	0.48516(16)	0.7239(3)	0.52597(13)	0.0215(6)
N631	0.42304(14)	0.6595(3)	0.54914(12)	0.0308(5)
C641	0.59660(16)	0.9205(3)	0.62918(16)	0.0250(6)
N641	0.57146(15)	0.9336(3)	0.69278(13)	0.0365(6)
H1	0.5752(13)	0.941(3)	0.2002(11)	0.016(6)*
H22	0.3917(13)	0.754(3)	0.2123(12)	0.022(6)*
H25	0.2473(14)	1.055(3)	0.0023(13)	0.023(6)*
H26	0.3892(14)	0.952(3)	-0.0117(13)	0.017(6)*
H4	0.5943(15)	0.304(3)	0.2118(13)	0.035(7)*
H62	0.5419(14)	0.719(3)	0.3833(12)	0.023(6)*
H65	0.7371(14)	1.032(3)	0.5518(12)	0.017(6)*
H66	0.7688(13)	0.995(2)	0.4190(11)	0.010(6)*

The synthesis of the bis-phthalonitrile is a straightforward procedure which can be achieved by the substitution reaction method, mixing 4-hydroxyphthalonitrile with 1,5-difluoro-2,4-dinitrobenzene in acetone in the presence of freshly ground potassium carbonate. After workup, purification over silica gel gave the target compound as the second fraction. The ¹H-NMR spectrum shows singlets at *ca* 9.05 and 7.75 p.p.m. assigned to the two protons of the

Table 3: Short intermolecular contacts, ‘weak hydrogen bonds’, in Ångstroms and degrees.

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
C(22)–H(22)···N(241)#1	0.92(2)	2.59(2)	3.468(3)	160.1(17)
C(26)–H(26)···O(32)#2	0.96(2)	2.59(2)	3.362(3)	137.7(15)
C(62)–H(62)···N(241)#1	0.95(2)	2.24(2)	3.147(3)	157.9(17)
C(65)–H(65)···N(231)#3	0.94(2)	2.54(2)	3.416(3)	154.8(17)
C(25)–H(25)···O(51)#4	0.96(2)	2.55(2)	3.221(3)	126.8(16)

Symmetry transformations used to generate equivalent atoms: #1: $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; #2: $1 - x, 1 - y, -z$; #3: $1 - x, 2 - y, 1 - z$; #4: $x - \frac{1}{2}, 1\frac{1}{2} - y, z - \frac{1}{2}$.

bridging benzene ring. This easily prepared bis-phthalonitrile is a potential candidate for making a variety of dimers of phthalocyanines which are unique in their electronic and optical properties [12].

The crystal structure of the title compound shows an approximately planar central C₆H₂(NO₂)₂(O)₂ group. The two nitro groups are rotated about the C–N bonds by 10.93(14) and 9.05(14)°. The phthalonitrile groups are turned out of the central plane by rotation about the C(2)–O(2) and C(6)–O(6) bonds (by 88.05(14) and 68.16(11)°, respectively) and aligned so that the normals to these C₆ rings are approximately perpendicular (85.82(7) and 77.29(7)°, respectively) to the normal to the central ring plane. The bond lengths and angles are within normal ranges and are comparable to those observed in similar structures [13]. Molecules are connected through ‘weak hydrogen bonds’, the shortest of which is for C(62)–H(62)···N(241¹) where the H···N distance is 2.24(4) Å Table 3. The dicyanophenyl rings form a short-range stack and are close to parallel (the angles between their normals are zero or 10.53(11)°), but with, in some cases, limited overlap of the rings; shorter interactions within this stack include C(24)···C(64⁴) at 3.40 Å.

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