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Dimethyl 2,2′-(4,5-dicyano-*o*-phenylenedioxy)dibenzoate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.044
wR factor = 0.118
Data-to-parameter ratio = 14.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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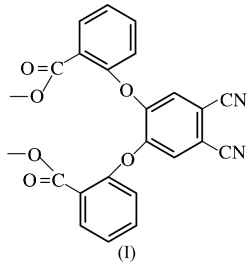
There are two independent molecules in the structure of the title compound, $C_{24}H_{16}N_2O_6$, one in a general position, the other on a twofold axis of space group *Pbcn*. There are thus one and a half molecules in the asymmetric unit. C—H···O, C—H···N and C—H···π interactions exert some influence on the molecular conformation and packing in the crystal structure.

Comment

Phthalonitriles are known precursors to phthalocyanines, an important class of molecules with wide applications, ranging from catalysis to solid-state materials (McKeown, 1998). For many years, phthalocyanines have attracted continued interest in various research fields, such as chemical sensors, electrochromism, batteries, photodynamic therapy, semiconductive materials, liquid crystals and non-linear optics (Leznoff & Lever, 1989–1996).

For these reasons, the structure of phthalonitrile derivatives with different substituents have been of much interest in our laboratory (Ocak *et al.*, 2003; Ocak, Çoruh *et al.*, 2004; Ocak, Işik *et al.*, 2004). The molecular structure of the title compound, (I), is shown in Fig. 1. Tables 1 and 2 list selected geometric parameters and the hydrogen-bonding geometry, respectively.



(I)

The molecules consist of a phthalonitrile moiety carrying two 2-hydroxybenzoic acid methyl ester substituents at C6, C7 (Fig. 2), C28 and C28^{i} [symmetry code: (i) $1-x, y, \frac{3}{2}-z$]. The N≡C distances of 1.141 (3), 1.139 (3) and 1.133 (3) Å are similar to other values reported in the literature (Subbiah Pandi *et al.*, 2002; Ocak, Işik *et al.*, 2004). The O1—C7, O2—C6 and O7—C28 distances are 1.371 (3), 1.370 (3) and 1.377 (3) Å, respectively, and also show good agreement with corresponding distances reported previously. All bond lengths in the ester groups agree with those of other esters (Çoruh *et al.*, 2002; Bujak *et al.*, 2002).

The crystal structure is stabilized by intramolecular C5—H5···O6 and C27—H27···O6 interactions, and intermolecular C21—H21···O1^{ii} and C30—H30···N2^{iii} close contacts (see Table 2 for details and symmetry codes). The crystal structure also shows an intermolecular C—H···π

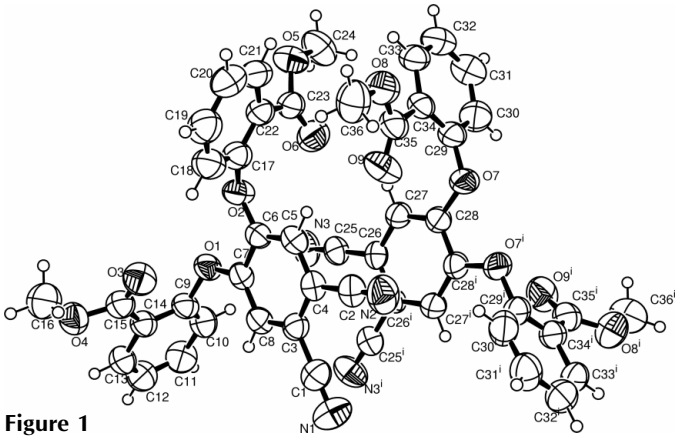


Figure 1
An *ORTEP*III drawing of the two molecules of the title compound, showing the atomic numbering. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level.

interaction (C24—H24*B*···*Cg*5, where *Cg*5 is the centroid of the C29–C34 ring; Table 2).

Experimental

Methyl 2-hydroxybenzoate (1.60 g, 10.53 mmol) and 4,5-dichloro-1,2-dicyanobenzene (1.00 g, 5.08 mmol) were heated at 333 K in dry DMSO (50 ml) with stirring under nitrogen. Dry fine-powdered potassium carbonate (1.70 g, 12.32 mmol) was added in portions (12 × 1 mmol) every 10 min. The mixture was heated for a further 48 h. After cooling, the mixture was poured into ice water (200 g). The product was filtered off and washed with (10% *w*/*w*) NaOH solution and water until the filtrate was neutral. Recrystallization from ethanol gave a yellow product. Yield 0.45 g, 20.74%. Single crystals were obtained from absolute ethanol at room temperature *via* slow evaporation (m.p. 377 K). Analysis calculated for $C_{24}H_{16}N_2O_6$: C 67.29, H 3.76, N 6.54%; found: C 67.40, H 3.60, N 6.40%. IR (ν_{max}, cm^{-1}): 3110–3037 (Ar-CH), 2995–2839 (CH), 2225 (CN) 1728 (C═O), 1608, 1587, 1568, 1502, 1483, 1444, 1425, 1402, 1336, 1277, 1219, 1126, 1080, 955, 885, 847, 804, 764, 702, 671, 633, 532.

Crystal data

$C_{24}H_{16}N_2O_6$
M_r = 428.39
Orthorhombic, *Pbcn*
a = 22.1158 (16) Å
b = 12.8114 (9) Å
c = 21.802 (2) Å
V = 6177.2 (9) Å^3
Z = 12
D_x = 1.382 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 24 564 reflections
θ = 1.8–24.3°
μ = 0.10 mm^{-1}
T = 293 (2) K
Prism, yellow
0.33 × 0.27 × 0.20 mm

Data collection

Stoe IPDS–II diffractometer
ω scans
Absorption correction: none
82 028 measured reflections
6080 independent reflections
2621 reflections with $I > 2\sigma(I)$
R_{int} = 0.093
θ_{max} = 26.0°
h = −27 → 27
k = −15 → 15
l = −26 → 26

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.118
S = 0.80
6080 reflections
434 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0599P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00106 (16)

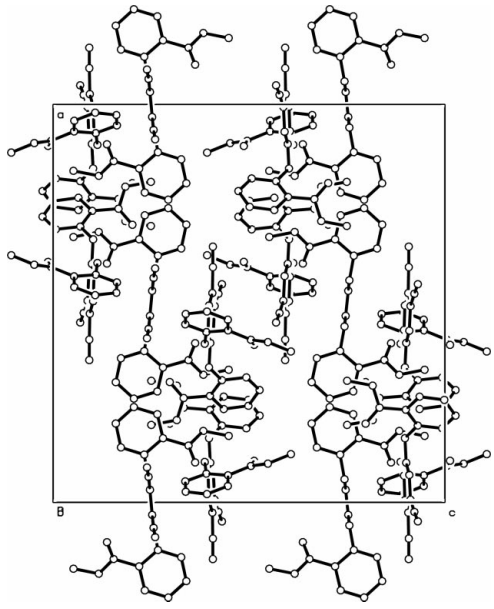


Figure 2
Packing diagram of the structure, viewed down the *b* axis.

Table 1
Selected geometric parameters (Å, °).

O1—C7	1.371 (3)	O6—C23	1.205 (3)
O1—C9	1.400 (3)	O7—C28	1.377 (3)
O2—C6	1.370 (3)	O7—C29	1.398 (3)
O2—C17	1.401 (3)	O8—C35	1.331 (3)
O3—C15	1.200 (3)	O8—C36	1.443 (4)
O4—C15	1.345 (3)	O9—C35	1.198 (3)
O4—C16	1.447 (3)	N1—C1	1.141 (3)
O5—C23	1.334 (3)	N2—C2	1.139 (3)
O5—C24	1.450 (3)	N3—C25	1.133 (3)
C7—O1—C9	117.26 (17)	O3—C15—O4	123.2 (3)
C6—O2—C17	115.67 (19)	O6—C23—O5	123.6 (3)
C28—O7—C29	120.00 (19)	O7—C28—C28^{i}	115.26 (12)
O2—C6—C5	123.4 (2)	O9—C35—O8	123.6 (3)
O1—C7—C6	115.3 (2)		
C17—O2—C6—C5	−29.3 (3)	C29—O7—C28—C27	−5.4 (4)
C9—O1—C7—C8	11.2 (3)		

Symmetry code: (i) $1-x, y, \frac{3}{2}-z$.

Table 2
Hydrogen-bonding geometry (Å, °).

*Cg*5 is the centroid of the C29–C34 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···O6	0.93	2.39	3.159 (3)	140
C27—H27···O6	0.93	2.53	3.293 (3)	139
C21—H21···O1^{ii}	0.93	2.58	3.450 (3)	157
C30—H30···N2^{i}	0.93	2.57	3.393 (4)	147
C24—H24B···*Cg*5^{iii}	0.96	2.75	3.624 (4)	152

Symmetry codes: (i) $1-x, y, \frac{3}{2}-z$; (ii) $\frac{3}{2}-x, \frac{1}{2}+y, z$; (iii) $\frac{3}{2}-x, y-\frac{1}{2}, z$.

H atoms were positioned geometrically and included in the refinement in a riding model, with aromatic C—H distances of 0.93 Å and methyl group C—H distances of 0.96 Å. U_{iso}(H) values were set at $1.2U_{eq}(C_{aromatic})$ and $1.5U_{eq}(C_{methyl})$ of the parent atom.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED*32 (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PARST* (Nardelli, 1995).

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