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C—H···π interactions in 4,5-bis(2-isopropyl-5-methylphenoxy)phthalonitrile

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.044
wR factor = 0.120
Data-to-parameter ratio = 19.2

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

The supramolecular structure of the title compound, $C_{28}H_{28}N_2O_2$, is defined by weak C—H···π interactions. The peripheral aromatic rings lie in approximately orthogonal planes, conferring on the molecule a twisted conformation.

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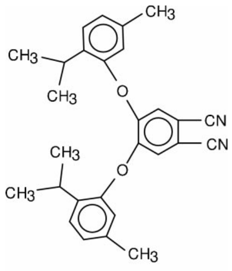
Comment

Substituted phthalonitriles are generally used for preparing symmetrically and unsymmetrically peripherally substituted phthalocyanine complexes and subphthalocyanines (McKeown, 1998; Leznoff & Lever, 1989–1996). The annual worldwide production of phthalocyanines, used in the preparation of dyes and pigments, is around 80 000 tons (Worhle, 2001). Phthalocyanines are excellent pigments with good thermal and chemical stabilities. They have been widely studied for many different purposes, finding applications in fields including liquid crystals, chemical sensors, photodynamic therapy for cancer (Decreau *et al.*, 2001), non-linear optics, molecular electronics, gas sensors, photosensitisers, catalysts, semiconducting materials, photovoltaic cells and electrochromic displays (McKeown, 1998; Leznoff & Lever, 1989–1996). For these reasons, the structures of substituted phthalonitrile derivatives have been a subject of many studies in our laboratory. Examples include 4,4′-(*N*-phenyl-2,2′-iminodiethanoxy)diphthalonitrile (Ocak *et al.*, 2003), 4-(2-isopropyl-5-methylphenoxy)phthalonitrile (Atalay *et al.*, 2003), 4,4′-[2,2′-(piperidine-1,4-diyldiethylene)di(tosylimino)]diphthalonitrile (Çoruh, Akdemir, Ağar, Vazquez-Lopez & Erdönmez, 2002) and dimethyl 2,2′-(4,5-dicyano-*o*-phenylenedithio)diacetate (Çoruh, Akdemir, Ağar, Kim & Erdönmez, 2002).



(I)

Compound (I) (Fig. 1) contains a phthalonitrile moiety which is 4,5-disubstituted by 2-isopropyl-5-methylphenoxy groups, giving a system of three benzene rings: C1–C6 (ring *A*), C9–C14 (ring *B*) and C19–C24 (ring *C*). The dihedral angles between these rings are 67.8 (6)° for *A*/*B*, 81.8 (5)° for *A*/*C* and 82.5 (5)° for *B*/*C*, indicating absence of coplanarity between the three rings and a twisted conformation for the molecule. The reason for this conformation is steric. The

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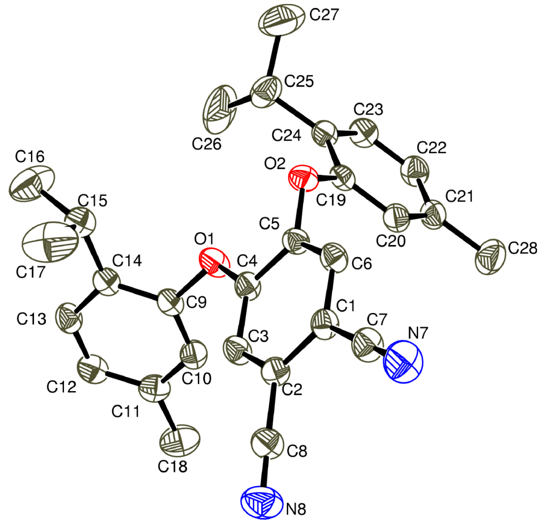

Figure 1
A view of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

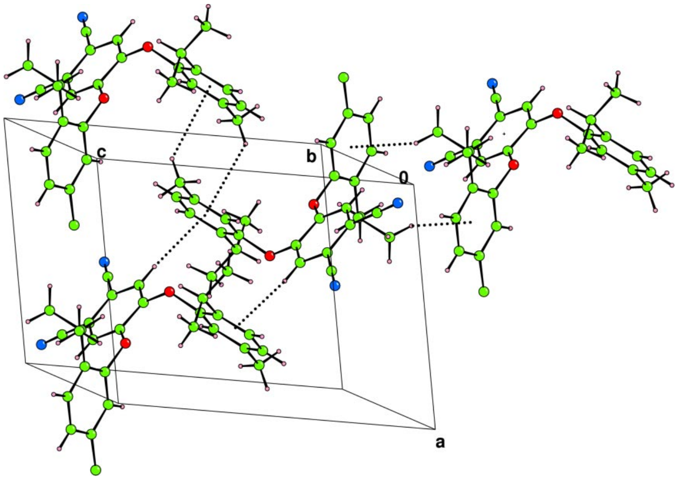

Figure 2
Packing showing the weak C—H$\cdots\pi$ interactions as dotted lines.

placement of the cyano groups and their triple-bond lengths lie very close to previously reported examples (Ocak *et al.*, 2003; Atalay *et al.*, 2003; Çoruh, Akdemir, Ağar, Vazquez-Lopez & Erdönmez, 2002; Çoruh, Akdemir, Ağar, Kim & Erdönmez, 2002).

The geometry around the O atoms shows good agreement with the literature (Atalay *et al.*, 2003; Ocak *et al.*, 2003), with the values for the C—O—C angles C19—O2—C5 and C9—O1—C4 being 116.65 (16) and 120.75 (12)°, respectively. Four C—H$\cdots\pi$ intermolecular interactions can also be observed in (I) (Fig. 2), thereby completing the capacity of the aromatic π-electrons to act as acceptors. These weak interactions are reported in Table 2. It has been recognized that these weak C—H$\cdots\pi$ interactions play an appreciable role in determining the conformation of organic compounds (Umezawa *et al.*, 1999).

Experimental

5-Methyl-2-(1-methylethyl)phenol (5.11 g, 34.02 mmol) and 4,5-dichloro-1,2-dicyanobenzene (1.04 g, 5.28 mmol) were heated at 363 K in dry DMSO (20 ml) with stirring under N_2. Dry finely powdered potassium carbonate (1.40 g, 10 mmol) was added in portions (8 × 10 mmol) every 5 min. The mixture was heated for a further 60 min. After cooling, the mixture was added to ice water (200 g). The product was filtered off and washed with NaOH solution (10% *w*/*w*) and water until the filtrate was neutral. Recrystallization from methanol gave a green product (yield: 1.25 g, 55.85%). Single crystals (m.p. 412 K) were obtained from absolute ethanol at room temperature *via* slow evaporation; elemental analysis, calculated for $C_{28}H_{28}N_2O_2$: C 79.22, H 6.65, N 6.66%; found: C 79.10, H 6.70, N 6.50%. ^{1}H NMR ($CDCl_3$, 293 K): 1.18 (*s*, 3H), 1.19 (*s*, 3H), 2.34 (*s*, 3H), 3.01 (*m*, 1H), 6.75–7.30 (*m*, 4H); ^{13}C NMR ($CDCl_3$, 293 K): 20.37, 22.99, 23.19, 27.39, 109.84, 115.23, 120.45, 120.84, 127.22, 127.64, 136.98, 137.73, 151.00, 152.11; IR ($\nu_{\rm max}$/cm^{-1}): 3045–3022 (aryl CH), 2960–2870 (aliphatic CH), 2220 (CN).

Crystal data

$C_{28}H_{28}N_2O_2$
M_r = 424.52
Triclinic, $P\bar{1}$
a = 9.268 (9) Å
b = 10.150 (10) Å
c = 13.115 (13) Å
α = 93.919 (8)°
β = 101.078 (8)°
γ = 95.278 (8)°
V = 1201 (2) Å^3
Z = 2
D_x = 1.174 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 10727 reflections
θ = 2.0–27.6°
μ = 0.07 mm^{-1}
T = 293 (2) K
Prism, green
0.50 × 0.36 × 0.27 mm

Data collection

Stoe IPDS 2 diffractometer
ω scans
Absorption correction: none
20244 measured reflections
5615 independent reflections
2920 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.059
$\theta_{\rm max}$ = 27.8°
$h = -12 \rightarrow 12$
$k = -13 \rightarrow 12$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.120
S = 0.87
5615 reflections
292 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0657P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.21 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.12 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.022 (3)

Table 1
Selected geometric parameters (Å, °).

C4—O1	1.3579 (19)	N7—C7	1.136 (2)
C5—O2	1.374 (2)	N8—C8	1.136 (2)
C4—O1—C9	120.76 (12)	C5—O2—C19	116.65 (13)

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

*Cg*2 and *Cg*3 are the centroids of rings *B* and *C*, respectively.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C6—H6$\cdots Cg3^{\rm i}$	0.93	2.784	3.705 (4)	171
C17—H17$C\cdots Cg2^{\rm ii}$	0.96	3.21	3.818 (5)	122
C26—H26$C\cdots Cg2^{\rm iii}$	0.96	3.31	4.143 (4)	146
C28—H28$B\cdots Cg3^{\rm iv}$	0.96	3.06	3.793 (5)	134

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $-x, -y, -z$; (iii) $-x, -y, 1 - z$; (iv) $-x, 1 - y, 1 - z$.

All H atoms were placed in calculated positions and refined using a riding model, with aromatic C—H distances of 0.93 Å and methylene C—H distances of 0.96 Å, and with $U_{\rm iso}$(H) = 1.20$U_{\rm eq}$(C).

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), *ORTEP*-3 *for Windows* (Farrugia, 1997) and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PARST* (Nardelli, 1995).

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References

Atalay, Ş., Ağar, A., Akdemir, N. & Ağar, E. (2003). *Acta Cryst.* E**59**, o1111–o1112.

Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Çoruh, U., Akdemir, N., Ağar, E., Kim, Y. & Erdönmez, A.,(2002). *Acta Cryst.* E**58**, o994–o996.

Çoruh, U., Akdemir, N., Ağar, E., Vazquez-Lopez, E. M. & Erdönmez, A. (2002). *Acta Cryst.* E**58**, o896–o897.

Decreau, R., Richard, M. J. & Julliard, M. (2001). *J. Porphyrins Phthalocyanines*, **5**, 390–396.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Leznoff, C. C. & Lever, A. B. P. (1989–1996). *Phthalocyanines: Properties and Applications*, Vols. 1, 2, 3 & 4. Weinheim/New York: VHC Publishers Inc.

McKeown, N. B. (1998). *Phthalocyanine Materials: Synthesis, Structure and Function*. Cambridge University Press.

Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.

Ocak, N., Ağar, A., Akdemir, N., Ağar, E., Garcia-Granda,S. & Erdönmez, A. (2003). *Acta Cryst.* E**59**, o1000–o1001.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Göttingen, Germany.

Stoe & Cie (2002). *X-AREA* (Version 1.118) and *X-RED*32 (Version 1.04). Stoe & Cie, Darmstadt, Germany.

Umezawa, Y., Tsuboyama, S., Takahashi, H., Uzawa, J. & Nishio, M.(1999). *Tetrahedron*, **55**, 10047–10056.

Watkin, D. M., Pearce, L. & Prout, C. K. (1993). *CAMERON*. Chemical Crystallography Laboratory, University of Oxford, England.

Worhle, D. (2001). *Macromol. Rapid Commun.* **22**, 68–97.