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4,5-Bis(4-methylphenylsulfanyl)phthalonitrile

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean *σ*(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.040
wR factor = 0.060
Data-to-parameter ratio = 15.9

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

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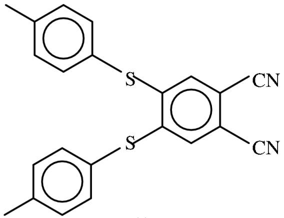
The title compound, $C_{22}H_{16}N_2S_2$, has one and a half molecules in the asymmetric unit. Each molecule has a twist conformation and distorted C_{2v} symmetry. The supramolecular structure of the title compound is defined by C—H···N, π–π stacking and C—H···π interactions.

Comment

4,5-Bis(4-methylthiophenoxy)phthalonitrile is a starting material in the synthesis of subphthalocyanines (Rey *et al.*, 1998). Phthalocyanines are an interesting class of compounds, with increasingly diverse industrial and biomedical applications, including photosensitization, linear optics, catalysis, liquid crystals and gas sensing (McKeown, 1998; Leznoff & Lever, 1989–1996).



(I)

The title compound, $C_{22}H_{16}N_2S_2$, (I), consists of a phthalonitrile moiety carrying two 4-methylthiophenoxy groups at positions 4 and 5 (Fig. 1). Discussion below refers mainly to the molecule in a general position; similar geometry is found for the molecule on a twofold rotation axis. Selected bond lengths, angles and hydrogen-bond parameters are given in Tables 1 and 2, respectively. The C1≡N1 and C2≡N2 bond distances are 1.131 (3) and 1.138 (3) Å, respectively, and show N≡C triple-bond character. They are also comparable to literature values (Öztürk *et al.*, 1999, 2000; Subbiah Pandi *et al.*, 2002; Çoruh, Akdemir, Aar, Kim *et al.*, 2002; Çoruh, Akdemir, Aar, Vázquez-López *et al.*, 2002; Çoruh, Işık, *et al.* 2002; Ocak *et al.*, 2003).

The title compound is distorted from the ideal C_{2v} symmetry, with dihedral angles between rings *A* (C3–C8) and *B* (C16–C21) of 81.03 (9)°, rings *A* and *C* (C9–C14) of 71.12 (9)°, and rings *B* and *C* of 15.34 (9)°.

In the molecule of (I), the S1···S2 distance is 3.063 (12) Å. Repulsions between atoms H21 and H4, H17 and H4, H14 and H7, and H10 and H7 lead to enlargement of the C4—C5—S2 and C7—C6—S1 angles. While the C4—C5—S2 angle is 122.5 (2)°, the C6—C5—S2 angle is 117.97 (18)°. Similarly the C7—C6—S1 angle is 122.40 (19)°, whereas the C5—C6—S1 angle is 118.43 (17)°.

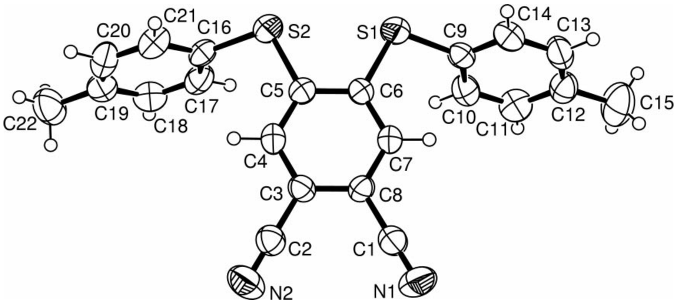


Figure 1
An *ORTEP*III (Burnett & Johnson, 1996) drawing of one molecule in the asymmetric unit of the title compound, showing the atomic numbering scheme. Displacement ellipsoids of non-H atoms are shown at the 50% probability level. Only one conformation of the disordered methyl groups is shown.

The crystal structure of (I) is stabilized by intermolecular C7—H7$\cdots$N3^{i} interactions [symmetry code: (i) $\frac{1}{2}-x$, $\frac{1}{2}-y$, $2-z$], a C—H$\cdots\pi$ interaction (Table 2) and two π–π stacking interactions.

In (I), the π–π stacking interactions involve rings *A* and *B*. Ring *A* in the molecule at (*x*, *y*, *z*) stacks with ring *A* at ($\frac{1}{2}-x$, $\frac{1}{2}-y$, $-z$), with a distance of 3.926 (2) Å between the ring centroids. There is similar π–π stacking involving ring *B* at (*x*, *y*, *z*) and ring *B* at ($-x$, $1-y$, $-z$), with a distance of 3.848 (2) Å between the ring centroids.

Experimental

4,5-Bis(4-methylthiophenoxy)phthalonitrile was synthesized according to the procedure reported by Rey *et al.* (1998) with minor modifications. Single crystals were obtained from ethanol at room temperature *via* slow evaporation.

Crystal data

$C_{22}H_{16}N_2S_2$
$M_r = 372.49$
Monoclinic, $C2/c$
$a = 27.347$ (3) Å
$b = 15.4675$ (10) Å
$c = 15.5745$ (17) Å
$\beta = 119.093$ (7)°
$V = 5756.7$ (9) Å^3
$Z = 12$

$D_x = 1.289$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 7445 reflections
$\theta = 1.6$–24.6°
$\mu = 0.29$ mm^{-1}
$T = 293$ (2) K
Tablet, colourless
0.38 × 0.28 × 0.17 mm

Data collection

Stoe IPDS-II diffractometer
φ scans
Absorption correction: by integration (*X-RED*32; Stoe & Cie, 2002)
$T_{\min} = 0.917$, $T_{\max} = 0.952$
20 063 measured reflections

5661 independent reflections
2308 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.089$
$\theta_{\max} = 26.0°$
$h = -33 \rightarrow 33$
$k = -19 \rightarrow 19$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.060$
$S = 0.73$
5661 reflections
355 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0153P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.12$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C6	1.756 (2)	S2—C16	1.773 (3)
S1—C9	1.774 (3)	C1—N1	1.131 (3)
S2—C5	1.766 (2)	N2—C2	1.138 (3)
C4—C5—S2	122.5 (2)	C7—C6—S1	122.40 (19)
C6—C5—S2	117.97 (18)	C5—C6—S1	118.43 (17)

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

*Cg*2 is the centroid ring *C* (C9–C14).

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
C7—H7$\cdots$N3^{i}	0.93	2.62	3.491 (3)	156
C28—H28$\cdots$*Cg*2^{ii}	0.93	2.63	3.519 (4)	161

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

H atoms were positioned geometrically and treated using a riding model, with aromatic C—H distances of 0.93 Å and methyl-group C—H distances of 0.96 Å. $U_{\rm iso}$(H) values were calculated as $1.5U_{\rm eq}$(methyl group) or the parent atom. The methyl groups are disordered and were refined in two sets of positions rotated from each other by 60°, with equal occupancy.

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, 1997) and *PARST* (Nardelli, 1995).

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