

## 4,5-Bis(3-methoxyphenylsulfanyl)phthalonitrile

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## Key indicators

Single-crystal X-ray study

T = 293 K

Mean  $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$ 

R factor = 0.051

wR factor = 0.151

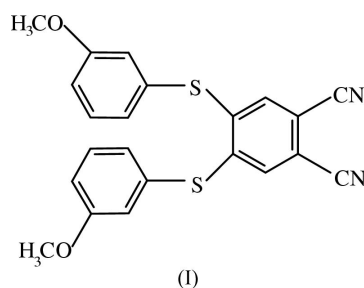
Data-to-parameter ratio = 19.7

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

In the title compound,  $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_2\text{S}_2$ , two benzene rings are connected by a phthalonitrile moiety, the dihedral angle between them being  $47.9(2)^\circ$ . The crystal structure is stabilized by intermolecular  $\text{C}-\text{H}\cdots\text{N}$  contacts.

## Comment

Phthalonitriles are known precursors of phthalocyanines, an important class of molecules with wide applications (Leznoff & Lever, 1989–1996) ranging from catalysis to solid-state materials. Disubstituted phthalonitriles [e.g. 4,5-bis(3-methoxythiophenoxy)phthalonitrile] are generally used for synthesis of octasubstituted phthalocyanines (McKeown, 1998). For many years, phthalocyanines have attracted continued interest in various research fields, such as chemical sensors, electrochromism, batteries, photosensitizers for photodynamic cancer therapy, semiconductive materials, liquid crystals and non-linear optics (Leznoff & Lever, 1989–1996).



The average value of C–N bond distances in the title compound, (I), (Table 1) indicates triple-bond character and it is consistent with the values observed in 4-(2-allylphenoxy)-phthalohalonitrile (Köysal *et al.*, 2003a) and 4-(8-quinolinoxy)phthalohalonitrile (Köysal *et al.*, 2003b). The O–C bond distances correspond to those in 4,4'-(*N*-phenyl-

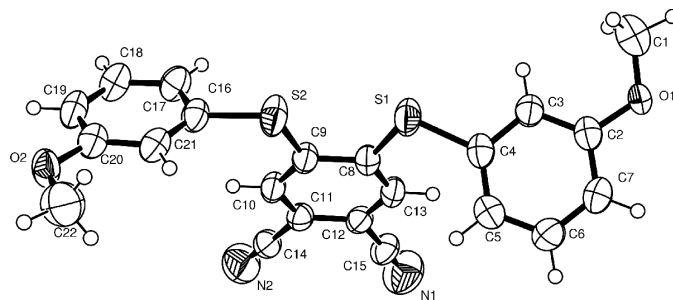


Figure 1

The structure of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

2,2'-iminodiethoxy)-diphthalonitrile (Ocak *et al.*, 2003). The three aromatic rings in the molecule are not coplanar. The dihedral angle between the C2–C7 and C16–C21 rings is 47.9 (2)°. These rings make dihedral angles of 61.61 (8)° and 70.76 (9)°, respectively with the central aromatic ring. The two methoxy groups are in an *anti*-orientation with respect to the central aromatic ring.

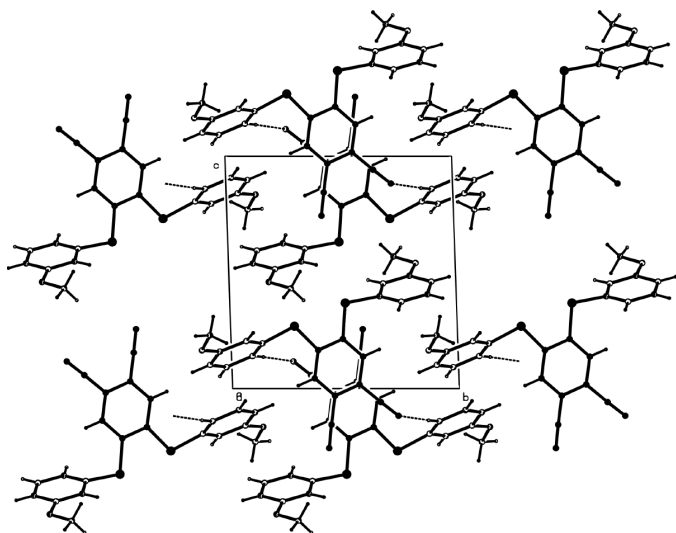
The crystal structure (Fig. 2) is stabilized by an intermolecular contact C5–H5···N2<sup>i</sup> (*i* = –*x*, –*y* + 1, –*z*).

### Experimental

3-methoxythiophenol (1.43 g, 10.20 mmol) and 4,5-dichlorophthalonitrile (1.00 g, 5.08 mmol) were dissolved in dry DMF (50 ml) with stirring under N<sub>2</sub>. Dry fine-powdered potassium carbonate (2.1 g, 15.21 mmol) was added in portions (10 × 1 mmol) every 10 min. The reaction mixture was stirred for 48 h at room temperature and poured into ice–water (150 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 1.08 g (52.68%). Single crystals were obtained from ethyl acetate by slow evaporation at room temperature (m.p. 421 K); elemental analysis, calculated for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C 65.32, H 3.99, N 6.92%; found: C 65.28 H 3.90 N 6.96%. <sup>1</sup>H NMR (CDCl<sub>3</sub>) 3.86 p.p.m. (*s*, 3H, OCH<sub>3</sub>), 7.03–7.48 p.p.m. (*m*, 5H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>) 55.50 (OCH<sub>3</sub>), 111.74, 115.36, 116.28, 120.23, 127.68, 129.68, 129.42, 130.12, 131.40, 144.03, 160.88.

### Crystal data

C <sub>22</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub>	Z = 2
M <sub>r</sub> = 404.49	D <sub>x</sub> = 1.378 Mg m <sup>–3</sup>
Triclinic, P1	Mo Kα radiation
a = 7.8208 (11) Å	Cell parameters from 16920 reflections
b = 11.0356 (14) Å	θ = 2.5–28.6°
c = 11.5767 (15) Å	μ = 0.29 mm <sup>–1</sup>
α = 91.531 (10)°	T = 293 (2) K
β = 102.391 (11)°	Prism, yellow
γ = 91.567 (11)°	0.30 × 0.22 × 0.12 mm
V = 975.0 (2) Å <sup>3</sup>	



**Figure 2**  
The packing of (I).

### Data collection

Stoe IPDS 2 diffractometer	4979 independent reflections
ω scans	2390 reflections with <i>I</i> > 2σ( <i>I</i> )
Absorption correction: by integration ( <i>X-RED32</i> ; Stoe, 2002)	<i>R</i> <sub>int</sub> = 0.084
<i>T</i> <sub>min</sub> = 0.926, <i>T</i> <sub>max</sub> = 0.970	θ <sub>max</sub> = 28.7°
25939 measured reflections	<i>h</i> = –10 → 10
	<i>k</i> = –14 → 14
	<i>l</i> = –14 → 15

### Refinement

Refinement on <i>F</i> <sup>2</sup>	H-atom parameters constrained
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.051	<i>w</i> = 1/[σ <sup>2</sup> ( <i>F</i> <sub>o</sub> <sup>2</sup> ) + (0.0861 <i>P</i> ) <sup>2</sup> ]
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.151	where <i>P</i> = ( <i>F</i> <sub>o</sub> <sup>2</sup> + 2 <i>F</i> <sub>c</sub> <sup>2</sup> )/3
<i>S</i> = 0.85	(Δ/σ) <sub>max</sub> < 0.001
4979 reflections	Δρ <sub>max</sub> = 0.37 e Å <sup>–3</sup>
253 parameters	Δρ <sub>min</sub> = –0.37 e Å <sup>–3</sup>

**Table 1**

Selected geometric parameters (Å, °).

C1–O1	1.406 (4)	C14–N2	1.141 (4)
C2–O1	1.361 (3)	C15–N1	1.146 (4)
C4–S1	1.775 (3)	C16–S2	1.780 (3)
C8–S1	1.759 (3)	C20–O2	1.360 (4)
C9–S2	1.755 (3)	C22–O2	1.422 (5)
C2–O1–C1	117.5 (2)	C8–S1–C4	105.00 (13)
C20–O2–C22	117.6 (3)	C9–S2–C16	104.28 (13)
C3–C2–O1–C1	6.0 (5)	C17–C16–S2–C9	–71.0 (3)
C5–C4–S1–C8	–51.8 (3)		

**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C5–H5···N2 <sup>i</sup>	0.93	2.56	3.493 (4)	177.9

Symmetry code: (i) –*x*, 1 – *y*, –*z*.

H atoms were positioned geometrically and refined using a riding model, with aromatic C–H = 0.93 Å, other C–H = 0.96–0.97 Å and *U*<sub>iso</sub>(H) = 1.2 or 1.5 times *U*<sub>eq</sub>(C).

Data collection: *X-AREA* (Stoe, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe, 2002); structure solution: *SHELXS97* (Sheldrick, 1997); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999), *PARST* (Nardelli, 1995).

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