

4,4'-[2,2-Methylenebis(4-chlorophenoxy)]
diphthalonitrile

Ufuk Çoruh,^{a*} Şamil Işık,^a
Nesuhi Akdemir,^a Erbil Açar,^a
Ezequiel M. Vázquez-López^b and
Ahmet Erdönmez^a

^aOndokuz Mayıs University, Faculty of Art and Science, Department of Physics, 55139 Samsun, Turkey, and ^bDepartamento de Química Inorgánica, Facultad de Ciencias—Química, Universidade de Vigo, 36200-Vigo, Galicia, Spain

Correspondence e-mail: ucoruh@hotmail.com

Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

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

R factor = 0.047

wR factor = 0.104

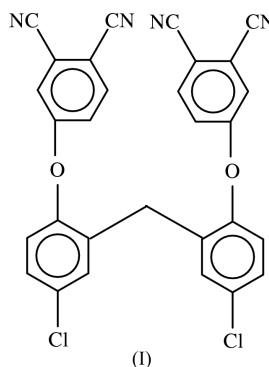
Data-to-parameter ratio = 14.9

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

The title compound, $\text{C}_{29}\text{H}_{14}\text{Cl}_2\text{N}_4\text{O}_2$, (I), contains four phenyl rings. Two of these carry two cyano groups each, whereas the other two carry one Cl atom each. The structure involves four planar phenyl rings. The structure of (I) is stabilized by C—H \cdots N-type intermolecular close contacts.

Comment

As part of an investigation of the synthesis of polymeric phthalocyanines, the title compound, (I), was obtained and its structure analysed by standard analytical techniques (elemental analysis, NMR and IR). For many years, phthalocyanines have attracted much interest in various research fields, such as chemical sensors, electrochromism, batteries, photodynamic therapy, semiconductive materials, liquid crystals and non-linear optics (Moser & Thomas, 1983; Leznoff & Lever, 1989–1996).



Comparison of the IR spectral data clearly indicated the formation of 4,4'-[2,2-methylenebis(4-chlorophenoxy)]-diphthalonitrile by the disappearance of the O—H bond of 2,2'-methylenebis(4-chlorophenoxy) at $3650\text{--}3590\text{ cm}^{-1}$, and the appearance of a new absorption at 2220 cm^{-1} ($\text{C}\equiv\text{N}$). The spectrum of 4,4'-[2,2-methylenebis(4-chlorophenoxy)]-diphthalonitrile also indicates the presence of aromatic rings and $\text{C}\equiv\text{N}$ groups by the intense stretching bonds of $3090\text{--}2820$ ($\text{C}-\text{H}$) and 2220 cm^{-1} ($\text{C}\equiv\text{N}$). In the ^1H NMR spectrum of (I), the bridging methylene H atoms are observed at 3.98 p.p.m. and the aromatic H atoms of the phenyl rings at 7.22–8.02 p.p.m.

An ORTEP drawing of the molecule, with the atomic numbering scheme, is shown in Fig. 1. The C—C bond distances and C—C—C angles in the four phenyl rings are in good agreement with the expected values for aromatic rings. The average $\text{N}\equiv\text{C}$ bond length, $1.142(3)\text{ \AA}$, is short enough to indicate its triple-bond character. This value shows good agreement with 4-(phenothiazin-10-yl)benzene-1,2-dicarbonitrile (Öztürk *et al.*, 1999). The C—O bond lengths between

Received 23 July 2002

Accepted 25 July 2002

Online 31 July 2002

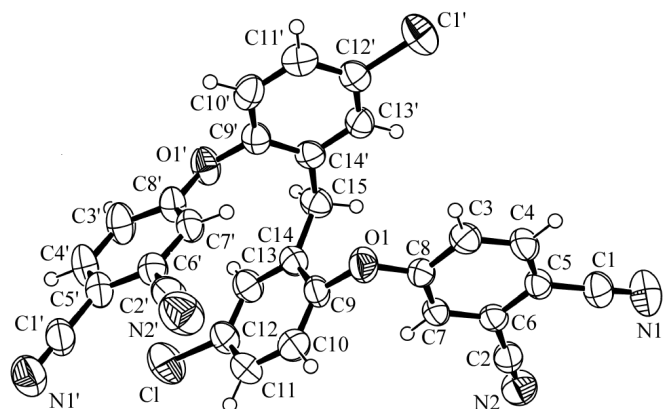


Figure 1

A view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

the aromatic rings and the bond angles at O are very close to those reported by Öztürk *et al.* (2000). The C1—C bond lengths are very close to those found by Pandi *et al.* (2002). The four phenyl rings in the molecule are essentially planar. The dihedral angle between the C3—C8 and C9—C14 planes is 88.52 (6)°, while the dihedral angle between the C3'—C8' and C9'—C14' planes is 76.84 (6)°. The angle between the C3—C8 and C9'—C14' planes is 3.26 (7)°.

As can be seen from the packing diagram (Fig. 2), the crystal structure of (I) is stabilized by the close contact C15—H15A...N1ⁱ (see Table 2 for details and symmetry code).

Experimental

2,2'-Methylenebis(4-chlorophenol) (6.73 g, 25 mmol) was dissolved in dry DMF (100 ml) under a nitrogen atmosphere. 4-Nitrophthalonitrile (8.65 g, 50 mmol) was then added. After stirring for 13 min, finely ground anhydrous potassium carbonate (8 g, 50 mmol) was added portionwise over a period of 2 h with efficient stirring. The reaction mixture was stirred under nitrogen at 333 K for 24 h. Water was then added and the product was filtered off, washed with water until neutral, and then refluxed in ethanol, filtered and dried. Yield: 7.11 g (54.6%). The single crystals were obtained in DMF at room temperature *via* slow evaporation. m.p: 447–448 K, IR ($\nu_{\max}/\text{cm}^{-1}$): 3090–2820 (C—H), 2220 (C≡N), 1590, 1485, 1460, 1440, 1400, 1330, 1265, 1160, 1100, 1040, 930, 910, 810, 760, 690, 650 and 560. ¹H NMR (CDCl₃): 8.02–7.22 (12H, *M*), 3.98 (2H, *s*). Analysis calculated for C₂₉H₁₄Cl₂N₄O₂: C 66.80, H 2.69, N 10.75%; found: C 66.79, H 2.71, N 10.77%.

Crystal data

C₂₉H₁₄Cl₂N₄O₂
M_r = 521.34
 Triclinic, *P* $\bar{1}$
a = 8.3572 (9) Å
b = 12.1209 (13) Å
c = 12.5925 (13) Å
 α = 76.912 (2)°
 β = 84.302 (2)°
 γ = 85.681 (2)°
V = 1234.5 (2) Å³

Z = 2
D_x = 1.403 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 7156 reflections
 θ = 1.7–26.1°
 μ = 0.30 mm⁻¹
T = 293 (2) K
 Prism, colourless
 0.26 × 0.18 × 0.10 mm

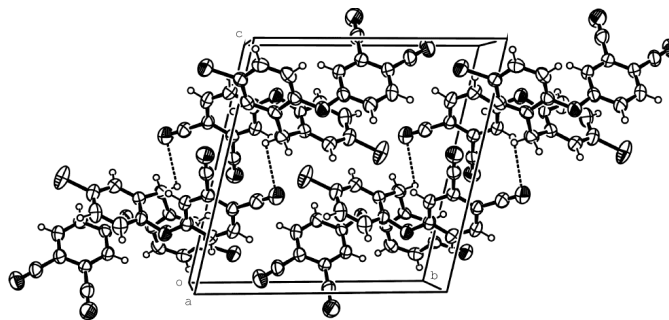


Figure 2

A packing diagram of (I), illustrating the close contact. The view direction is approximately parallel to the *a* axis.

Data collection

Bruker CCD area-detector diffractometer	2451 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.027$
Absorption correction: none	$\theta_{\text{max}} = 26.0^\circ$
7156 measured reflections	$h = -11 \rightarrow 10$
4969 independent reflections	$k = -15 \rightarrow 15$
	$l = -12 \rightarrow 16$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.047$	$w = 1/[\sigma^2(F_o^2) + (0.0416P)^2]$
$wR(F^2) = 0.104$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.83$	$(\Delta/\sigma)_{\text{max}} < 0.001$
4969 reflections	$\Delta\rho_{\text{max}} = 0.20 \text{ e } \text{Å}^{-3}$
334 parameters	$\Delta\rho_{\text{min}} = -0.21 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

C1'—C12'	1.736 (2)	O1—C9	1.411 (3)
C1—C12	1.738 (3)	C2'—N2'	1.150 (3)
O1'—C8'	1.373 (3)	C1—N1	1.133 (3)
O1'—C9'	1.411 (3)	C1'—N1'	1.145 (3)
O1—C8	1.376 (3)	C2—N2	1.141 (3)
C8'—O1'—C9'	118.94 (19)	C14'—C15—C14	114.0 (2)
C8—O1—C9	118.8 (2)		

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>
C15—H15A...N1 ⁱ	0.97	2.83	3.246 (4)	107

Symmetry code: (i) $-1 - x, 2 - y, 1 - z$.

All H atoms were positioned geometrically and refined using a riding model, fixing the aromatic C—H distance at 0.93 Å, the methylene C—H distance at 0.97 Å and the H—C—H angle at 107.65°.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 1998); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Farrugia, 1997); software used to prepare material for publication: *PARST* (Nardelli, 1995).

References

- Bruker (1998). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Leznoff, C. C. & Lever, A. B. P. (1989–1996). *Phthalocyanines: Properties and Applications*, Vols. 1, 2, 3 & 4. Weinheim & New York: VHC Publishers Inc.
- Moser, F. H. & Thomas, A. L. (1983). *The Phthalocyanines*, Vols. 1 and 2. Boca Raton, Florida: CRC Press.
- Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
- Öztürk, S., Işık, Ş., Fun, H. K., Kendi, E., Açar, E., Şaşmaz, S. & İbrahim, A. R. (1999). *Acta Cryst.* **C55**, 395–397.
- Öztürk, S., Işık, Ş., Akkurt, M., Açar, E., Şaşmaz, S. & Fun, H.-K. (2000). *Anal. Sci.* **16**, 663–664.
- Pandi, A. S., Rajakannan, V., Velmurugan, D., Parvez, M., Kim, M. J., Senthilvelan, A. & Rao, S. N. (2002). *Acta Cryst.* **C58**, o164–o167.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.