Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

4,4′-[2,2′-(Piperidine-1,4-diyldiethylene)di(tosylimino)]diphthalonitrile

Ufuk Çoruh,[a]* Nesuhi Akdemir,[a] Erbil Ağar,[a] Ezequiel M. Vázquez-López[b] and Ahmet Erdönmez[a]

[a]Ondokuz Mayıs University, Art and Science Faculty, Department of Physics, 55139 Samsun, Turkey, and [b]Departamento de Química Inorgánica, Facultade 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 K
Mean σ(C–C) = 0.007 Å
R factor = 0.046
wR factor = 0.154
Data-to-parameter ratio = 17.5

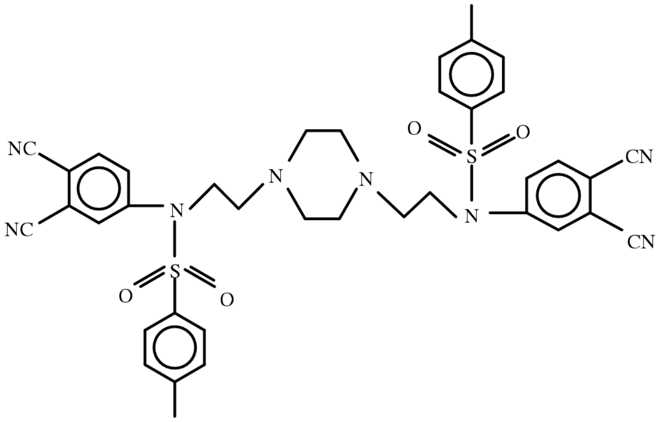
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 8 July 2002
Accepted 10 July 2002
Online 19 July 2002

The title compound, $C_{38}H_{36}N_8O_4S_2$, has a center of symmetry and the central six-membered ring shows a chair conformation. The dihedral angle between the ring carrying the tosyl group and the phthalonitrile ring is 36.98 (11)°. The crystal structure is stabilized by an intramolecular C—H···N and two intermolecular C—H···O close contacts.

Comment

The title compound, (I), is a precursor in the synthesis of network phthalocynine polymers (Ağar *et al.*, 1995). 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; McKeown, 1998).



(I)

The atom-numbering scheme and a displacement ellipsoid plot of (I) are shown in Fig. 1. The geometry of the S atoms is distorted from the tetrahedral configuration, with the largest deviation in the O—S—O angle [O1—S1—O2 = 120.41 (18)°] and the angles O1—S1—N3 and O2—S1—N3 [107.37 (18) and 106.16 (18)°, respectively]. The S1—N3 distance is 1.628 (3) Å, very close to those in the literature (Işık *et al.* 1999) and in contrast with the previously observed range of 1.63–1.69 Å (Kálmán *et al.*, 1981; Öztürk *et al.*, 2000). This shortening is due to the electron-withdrawing character of the diphthalonitrile group, as in 10,11-dibromo-3,6-ditosyl-3,6-diazabicyclo-[6.4.0]dodeca-1(8),9,11-triene (Işık *et al.*, 1999).

The S1—C13 bond distance and average S═O bond length are 1.765 (4) and 1.433 (3) Å, respectively. The bond lengths in the literature (Öztürk *et al.*, 2000) are 1.742 (6) and 1.430 (5) Å, respectively. The C1≡N1 and C2≡N2 bond distances are 1.130 (5) and 1.142 (5) Å, respectively, and show N≡C triple-bond character. The ring composed of atoms C18,

DOI: 10.1107/S1600536802012308

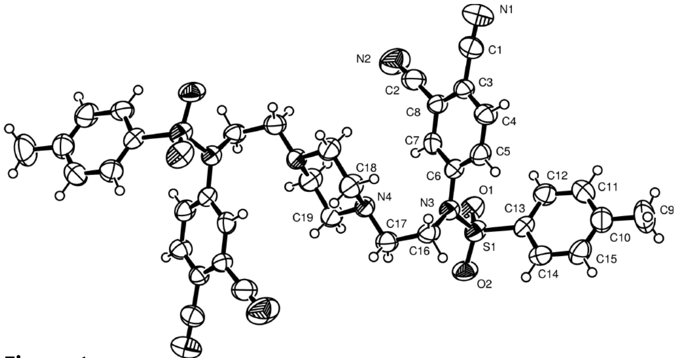


Figure 1
A view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

C19 and N4 and their symmetry equivalents is almost in a chair conformation. The crystal structure of (I) is stabilized by the intramolecular C7—H7···N4 interaction, and the intermolecular C15—H15···O1^{i} and C18—H18*A*···O2^{ii} close contacts (see Table 2 for details and symmetry code).

Experimental

1,4-Bis[*N*-(2-tosylaminoethyl)]-1,4-diazacyclohexane (13.16 g, 27.42 mmol; Hancock *et al.*, 1990) was dissolved in dry dimethyl sulfoxide (150 ml) under nitrogen and 4-nitrophthalonitrile (10.11 g, 58.43 mmol) was added. After stirring for 30 min, finely ground anhydrous K_2CO_3 (19.73 g, 142.97 mmol) was added portionwise over a period of 2 h with efficient stirring. The reaction mixture was stirred under nitrogen at room temperature for 24 h. Water was then added and the product filtered off and washed with water until the filtrate was neutral. The product was then refluxed in methanol, filtered and dried. The title compound, (I), was crystallized from dimethylformamide *via* slow evaporation at room temperature (yield 8.13 g, 40.51%). Analysis calculated for $C_{38}H_{36}N_8O_4S_2$: C 62.28, H 4.95, N 15.29%; found: C 62.65, H 4.93, N 15.44%. Full IR, ^{1}H and ^{13}C NMR spectral data have been deposited elsewhere (Çelebi, 2002).

Crystal data

$C_{38}H_{36}N_8O_4S_2$
$M_r = 732.89$
Monoclinic, $P2_1/c$
$a = 8.4238$ (11) Å
$b = 29.217$ (4) Å
$c = 7.7120$ (11) Å
$\beta = 98.052$ (3)°
$V = 1879.4$ (5) Å^3
$Z = 2$

$D_x = 1.295$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 9948 reflections
$\theta = 1.4$–28.0°
$\mu = 0.19$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.21 × 0.19 × 0.06 mm

Data collection

Bruker CCD area-detector diffractometer
φ and ω scans
Absorption correction: none
9948 measured reflections
4124 independent reflections

1241 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.078$
$\theta_{\rm max} = 28.0°$
$h = -10 \rightarrow 11$
$k = -33 \rightarrow 38$
$l = -10 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.154$
$S = 0.72$
4124 reflections
235 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0613P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.22$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N3—C6	1.440 (5)	C10—C9	1.499 (6)
N3—C16	1.465 (5)	N4—C19	1.453 (4)
N3—S1	1.628 (3)	N4—C17	1.456 (4)
S1—O1	1.429 (3)	N4—C18	1.456 (5)
S1—O2	1.438 (3)	C1—N1	1.130 (5)
S1—C13	1.765 (4)	N2—C2	1.142 (5)
C16—C17	1.523 (5)		
C6—N3—C16	118.3 (3)	O2—S1—N3	106.16 (18)
C6—N3—S1	119.0 (3)	O1—S1—C13	106.8 (2)
C16—N3—S1	120.8 (3)	O2—S1—C13	109.1 (2)
O1—S1—O2	120.41 (18)	N3—S1—C13	106.16 (17)
O1—S1—N3	107.37 (18)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7···N4	0.93	2.95	3.319 (5)	105
C15—H15···O1^{i}	0.93	2.69	3.559 (5)	155
C18—H18*A*···O2^{ii}	0.97	2.60	3.248 (5)	123

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

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 methyl-group C—H distance at 0.96 Å.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: SAINT; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1995).

The authors thank Ezequiel M. Vázquez-López for data collection and collaboration.

References

Ağar, E., Şaşmaz, S., Batı, B. & Özdemir, M. (1995). *Synth. React. Inorg. Met. Org. Chem.* **25**, 1165–1167.
Bruker (1998). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Çelebi, T. (2002). MSc Thesis, Ondokuz Mayıs University, The Institute of Science, 55139 Samsun, Turkey.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Hancock, R. N., Ngwenya, M. P., Evers, A., Wade, P. W., Boeyens, J. C. A. & Dobsan, S. M. (1990). *Anorg. Chem.* **29**, 264–270.
Işık, Ş., Öztürk, S., Fun, H.-K., Ağar, E. & Şaşmaz, S. (1999). *Acta Cryst.* C**55**, 1850–1852.
Kálmán, A., Czugler, M. & Argay, G. (1981). *Acta Cryst.* B**37**, 868–877.
Leznoff, C. C. & Lever, A. B. P. (1989–1996). *Phthalocyanines: Properties & Applications*, Vols. 1, 2, 3 and 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.
Öztürk, S., Işık, Ş., Ağar, E., Şaşmaz, S., Fun, H.-K. & Erdönmez, A. (2000). *Spectrosc. Lett.* **33**, 245–254.
Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.