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4-(Phenothiazin-10-yl)benzene-1,2-dicarbonitrile

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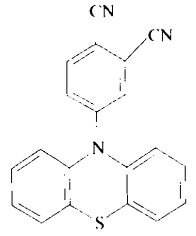
Abstract

The title compound, $C_{20}H_{11}N_3S$, crystallizes with two molecules in the asymmetric unit. The molecules are non-planar, with a central ring in a boat conformation. The dihedral angle between the least-squares planes of the benzo rings fused to the central ring is 44.6 (1)° in one molecule, and 50.1 (1)° in the other.

Comment

The title compound, (I), was isolated as a reaction intermediate in the preparation of a phthalocyanine (Şaşmaz & Ağar, 1999). For many years, phthalocyanines have attracted great interest in various research fields such as chemical sensors, electrochromism, batteries, photodynamic therapy, semiconductive materials, liquid crystals and nonlinear optics (Moser & Thomas, 1983; Leznoff & Lever, 1989–1993).



(I)

In compound (I) there are two independent molecules in the asymmetric unit. In both molecules the bond lengths and angles show normal values and are comparable to 1-isopropyl-10-methylphenothiazine (Shirley *et al.*, 1984). The benzo and phenyl rings are nearly planar in each case, with a maximum deviation of −0.021 (2) Å for C19*A*. In molecule *A*, the folding angle between the least-squares planes of the two benzo

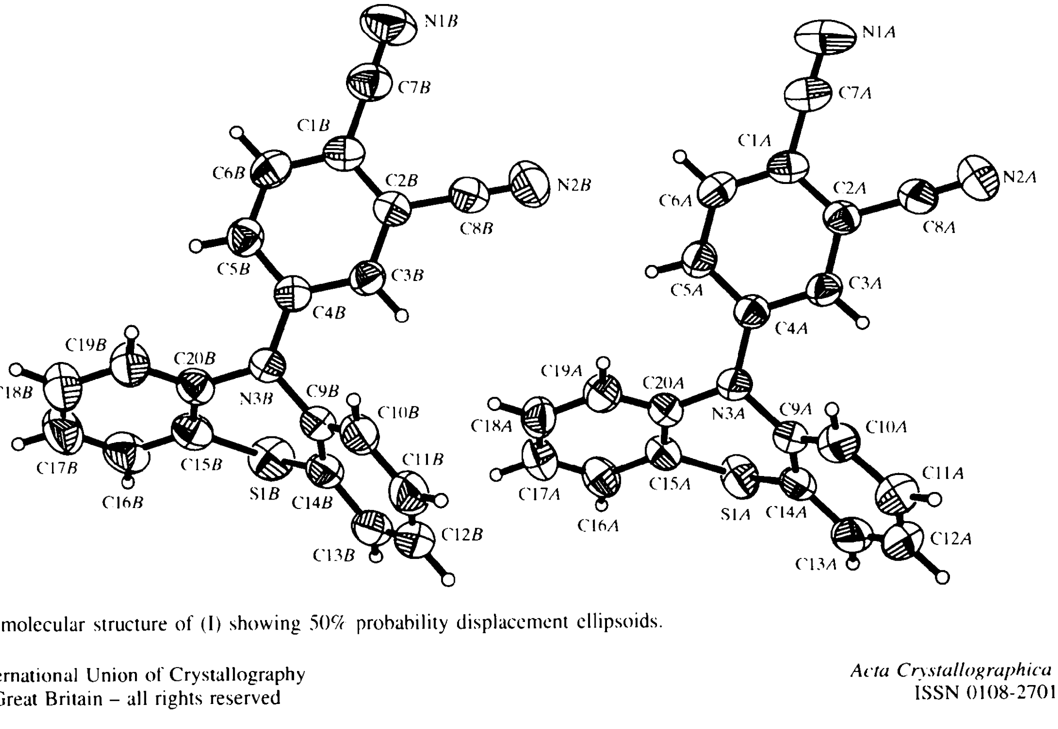


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids.

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rings is 44.6 (1)° and they make dihedral angles of 115.0 (1) and 121.6 (1)° with the substituted phenyl ring; in molecule *B*, these values are 50.1 (1), 112.7 (1) and 119.3 (1)°, respectively. The central ring is in a boat conformation and the asymmetry parameters defined by Nardelli (1983) are q_2 = 0.610 (1), q_3 = 0.031 (2), Q = 0.611 (1) Å, φ_2 = −180.0 (2), θ = 87.2 (2)° for molecule *A* and q_2 = 0.651 (2), q_3 = 0.040 (2), Q = 0.652 (2) Å, φ_2 = −178.9 (2), θ = 86.5 (2)° for molecule *B*. The two independent molecules have almost identical orientations and their centroids are separated by the vector [0.4597, −0.2581, 0.2808].

Experimental

Thiodiphenylamine (11.95 g, 60.0 mmol) was dissolved in dry Me_2SO (100 ml) under nitrogen and 4-nitrophthalonitrile (10.38 g, 60.0 mmol) was added. After stirring for 15 min, finely ground anhydrous K_2CO_3 (12.42 g, 90.0 mmol) was added portionwise over 2 h with efficient stirring. The reaction mixture was stirred under nitrogen at room temperature for 24 h. Water (500 ml) was then added and the product filtered off, washed with water until the filtrate became neutral, and then washed with cold ethanol and diethyl ether. The yellowish precipitate was crystallized from ethanol by cooling: m.p. 472–473 K, yield 56.38%, satisfactory analyses. IR: 3080–3000 (aromatic C—H), 2220 cm^{-1} (C≡N); ^{1}H NMR ($CDCl_3$): 7.57–7.12 (11H, *m*, aromatic H).

Crystal data

$C_{20}H_{11}N_3S$
M_r = 325.38
Monoclinic
$P2_1/c$
a = 16.5433 (4) Å
b = 16.4583 (5) Å
c = 12.3847 (2) Å
β = 103.965 (1)°
V = 3272.36 (14) Å^3
Z = 8
D_x = 1.321 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 5702 reflections
θ = 1.5–33.0°
μ = 0.202 mm^{-1}
T = 293 (2) K
Prismatic
0.96 × 0.72 × 0.24 mm
Pale yellow

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan using *SADABS* (Sheldrick, 1996*a*)
T_{min} = 0.158, T_{max} = 0.950 (effective values, see text)
17 082 measured reflections

5739 independent reflections
4471 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 25°
$h = -23 \rightarrow 25$
$k = -25 \rightarrow 23$
$l = -17 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.095

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.156 e Å^{-3}
$\Delta\rho_{min}$ = −0.214 e Å^{-3}

S = 1.034
5739 reflections
522 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0333P)^2 + 0.7447P]$ where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: *SHELXTL96* (Sheldrick, 1996*b*)
Extinction coefficient: 0.0111 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S1A—C15A	1.761 (2)	S1B—C14B	1.764 (2)
S1A—C14A	1.767 (2)	S1B—C15B	1.768 (2)
N1A—C7A	1.141 (2)	N1B—C7B	1.147 (2)
N2A—C8A	1.141 (2)	N2B—C8B	1.144 (2)
N3A—C4A	1.401 (2)	N3B—C4B	1.404 (2)
N3A—C9A	1.435 (2)	N3B—C9B	1.435 (2)
N3A—C20A	1.439 (2)	N3B—C20B	1.441 (2)
C15A—S1A—C14A	98.63 (8)	C14B—S1B—C15B	97.79 (8)
C4A—N3A—C9A	120.37 (13)	C4B—N3B—C9B	120.58 (13)
C4A—N3A—C20A	121.37 (13)	C4B—N3B—C20B	121.56 (13)

C20A—N3A—C9A—C14A	47.0 (2)
N3A—C9A—C14A—S1A	−1.3 (2)
C15A—S1A—C14A—C9A	−34.7 (2)
C14A—S1A—C15A—C20A	34.9 (2)
S1A—C15A—C20A—N3A	1.0 (2)
C9A—N3A—C20A—C15A	−46.9 (2)
C20B—N3B—C9B—C14B	49.7 (2)
N3B—C9B—C14B—S1B	−1.7 (2)
C15B—S1B—C14B—C9B	−36.8 (2)
C14B—S1B—C15B—C20B	38.1 (2)
S1B—C15B—C20B—N3B	−0.8 (2)
C9B—N3B—C20B—C15B	−48.2 (2)

Crystals were very brittle and shattered with degradation of quality on attempted cutting, so a large crystal had to be used which exceeded the size of the X-ray beam (0.8 mm collimator) and led to variation of the effective scattering volume during data collection. The *SADABS* program corrects for this effect at the same time as for absorption and other frame-scaling factors, and hence generates effective relative transmission factors that do not refer to absorption effects alone. Transmission factors for absorption alone are estimated as 0.83–0.95.

The data collection covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle for the crystal and each exposure of 10 s covered 0.3° in ω. The crystal-to-detector distance was 4 cm and the detector swing angle was −35°. Coverage of the unique set is over 99% complete. Crystal decay was monitored by repeating 30 initial frames at the end of data collection and analysing the duplicate reflections, and was found to be negligible. Data with $\theta > 25°$ were of very low intensity and were discarded.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1996*b*). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1257). Services for accessing these data are described at the back of the journal.

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7,8,10,11,12,13-Hexahydro-4-methylnaphtho[2,3-*c*]acridine

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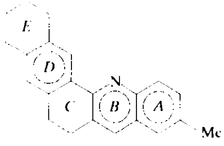
Abstract

In the title molecule, $C_{22}H_{21}N$, one of the two cyclohexane rings shows conformational disorder, with both major and minor conformers in half-chair conformations; the other cyclohexane ring adopts a conformation intermediate between sofa and half-chair.

Comment

The synthesis and biological evaluation of polycyclic azaarenes (PAA) with bay regions (Pullman & Pullman, 1955) have acquired great importance, due to their presence in the biosphere as serious environmental pollutants (Dong *et al.*, 1977; Schmeltz & Hoffman, 1977). These compounds reach the environment mainly from energy industries, automobile exhausts, cigarette smoke and the incomplete combustion of fossil fuels. Such PAA's and their oxidative metabolites have been reported to possess mutagenic and/or carcinogenic properties (Jerina, 1986; Wood *et al.*, 1989; Ray & Kar, 1993). Isolation of such compounds in sufficient amounts and in pure form from environmental sediments is difficult. In order to prepare sufficient material, Ray and his group have been working towards the synthesis and characterization of such compounds (Kar, Karmakar & Ray, 1989; Kar, Sami & Ray, 1992; Ray *et al.*, 1996). As a part of this programme, the crystal structure of the title compound, (I), was determined.



(I)

Bond lengths and angles in the title compound agree with those observed in a chloro-derivative of this structure (Ray *et al.*, 1995). One of the cyclohexane rings (*C*) present in the structure shows conformational disorder; both the major and minor conformers adopt half-chair conformations, but in opposite orientations. The conformation of the other cyclohexane ring (*E*) lies between sofa and half-chair, with asymmetry parameters $\Delta C_s(\mathrm{C10}) = 0.050(2)$ and $\Delta C_2(\mathrm{C10—C15}) = 0.054(1)$ (Nardelli, 1983). The mean plane through the major conformer of ring *C* forms dihedral angles of 6.60 (7) and 4.82 (7)°, respectively, with the planes through the rings *A*, *B* and *D*; the dihedral angle between rings *D* and

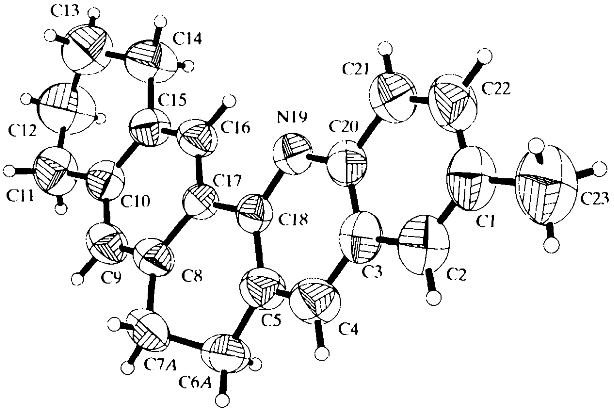


Fig. 1. The structure of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme. For clarity, only the major (80%) conformer of ring *C* is shown.

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