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A new precursor for the synthesis of porphyrazine: 2,3-bis(4-methylphenyl)maleonitrile

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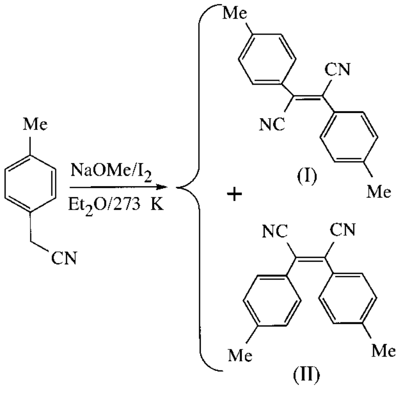
The structure of the title compound consists of discrete $C_{18}H_{14}N_2$ molecules in a *cis* configuration. The molecules are distorted from planarity.

Comment

It has been shown that both maleonitrile and fumaronitrile compounds can be cyclized into porphyrazine macrocycles, but in very low yields when using the fumaronitrile isomer (Fitzgerald *et al.*, 1991). The fumaronitriles must first be thermally isomerized to the maleonitrile *cis* isomer before cyclization can occur. It has been reported that dialkyl or alkyl/aryl-mixed fumaronitriles can be photoisomerized to the maleonitrile form (Fitzgerald *et al.*, 1991). Diarylfumaronitriles on the contrary have been shown to be unable to be photoisomerized (Sargent & Timmons, 1963). We had set out to prepare the porphyrazine precursor molecule 2,3-bis(4-methylphenyl)maleonitrile but in several reports, each using different synthetic conditions, only the fumaronitrile isomer was isolated (Chatterjea *et al.*, 1966; Ogata & Nagura, 1974; Pochat, 1978; Kurihara *et al.*, 1987). Using a previously reported procedure (Baumann *et al.*, 1997) for the oxidative coupling of *para*-substituted benzyl cyanides, we have isolated not only the *trans*, (I), but also the *cis* isomer, 2,3-bis(4-methylphenyl)maleonitrile, (II), and characterized them by several methods including X-ray crystallography. Due to the relative high yields of their syntheses, these latter compounds are therefore of interest for the preparation of porphyrazines.



Although the structure of the *trans* isomer, (I), has been determined, it will not be presented in this article because of its low quality, mainly due to the thin, needle-shaped crystals and the poor diffracting power of the samples. The molecule of the title compound, (II), is not planar: it is distorted from planarity along the C=C bond. This is evident as shown by the torsion angles along the C=C bond (Table 1) and with the values of the angles between the planes defined by C1, C3, C5 and C2, C4, C12 [10.6 (1)°] and those defined by C1, C2, C5, C12 and C1, C2, C3, C4 [7.43 (2)°]. A view of the molecule can be seen in Fig. 1.

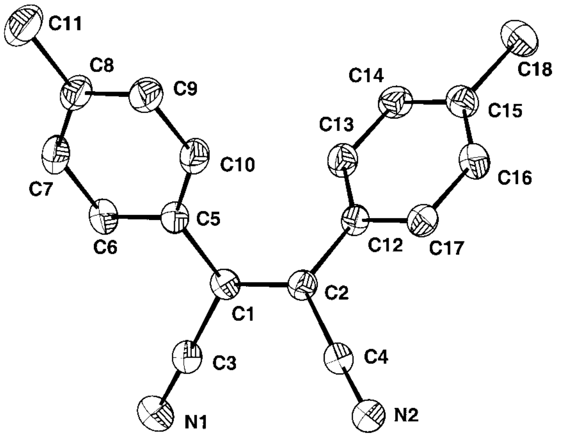


Figure 1
The molecular structure of (II), showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

Such non-planarity was also observed in the *trans*-α,β-dicyanostilbene (Wallwork, 1961), which is the only aryl-containing disubstituted dinitrile compound reported so far in the Cambridge Structural Database. Since the accuracy of its structural determination is not comparable to the present one, no comparison will be undertaken. The *p*-methylphenyl groups are twisted about the C5–C8 and C12–C15 axes and form an angle of 37.54 (6) and 43.88 (6)° with the mean plane built around the C=C bond (least-square plane through atoms C1, C2, C3, C4, C5 and C12). The angle between the two *p*-methylphenyl group planes is 56.95 (6)°.

Experimental

Compound (I) (pale yellow needles) was synthesized in 43% yield using procedures similar to that found for the coupling of related benzyl cyanide compounds (Baumann *et al.*, 1997). Elemental and melting-point analyses were in agreement with those previously reported for this compound (Pochat, 1978; Chatterjea *et al.*, 1966). Compound (II) was obtained in 15% yield from the filtrate of (I) after the filtrate was placed in a freezer at 253 K for 3 d. Well formed yellow hexagonal plates crystallized, were filtered, washed with MeOH and dried under vacuum (m.p. 432–433 K, uncorrected).

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Elemental analysis: found C 83.31, H 5.30, N 10.68%; calculated for $C_{18}H_{14}N_2$ C 83.69, H 5.46, N 10.84%. IR (KBr): 3033, 2923 (CH), 2216 (CN), 1654 (C=C) cm^{-1}.

Crystal data

$C_{18}H_{14}N_2$
$M_r = 258.31$
Monoclinic, $P2_1/c$
$a = 8.5424$ (8) Å
$b = 18.089$ (2) Å
$c = 9.3202$ (9) Å
$\beta = 90.898$ (11)°
$V = 1440.0$ (3) Å^3
$Z = 4$

$D_x = 1.192$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5000 reflections
$\theta = 2.20$–26.06°
$\mu = 0.071$ mm^{-1}
$T = 160$ (2) K
Plate, yellow
0.40 × 0.23 × 0.08 mm

Data collection

Stoe IPDS diffractometer
φ scans
11 258 measured reflections
2795 independent reflections
1754 reflections with $I > 2\sigma(I)$
$R_{int} = 0.054$

$\theta_{max} = 26.06°$
$h = -10 \rightarrow 10$
$k = -22 \rightarrow 22$
$l = -11 \rightarrow 11$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.100$
$S = 0.953$
2795 reflections
185 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0551P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.013$
$\Delta\rho_{max} = 0.15$ e Å^{-3}
$\Delta\rho_{min} = -0.15$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.362 (2)	C3—N1	1.145 (2)
C1—C3	1.446 (2)	C4—N2	1.146 (2)
C1—C5	1.474 (2)	C8—C11	1.504 (2)
C2—C4	1.440 (2)	C15—C18	1.505 (2)
C2—C12	1.479 (2)		
C2—C1—C3	117.26 (13)	C1—C2—C12	128.27 (14)
C2—C1—C5	127.47 (14)	C4—C2—C12	114.91 (12)
C3—C1—C5	115.20 (12)	N1—C3—C1	178.93 (17)
C1—C2—C4	116.81 (13)	N2—C4—C2	178.16 (16)
C3—C1—C2—C4	−9.1 (2)	C3—C1—C2—C12	171.1 (2)
C5—C1—C2—C4	167.7 (2)	C5—C1—C2—C12	−12.1 (3)

H atoms on the phenyl groups were placed geometrically at 0.95 Å and riding the adjacent C atom with an isotropic displacement parameter 20% higher than the one of the adjacent C atom. H atoms of the methyl groups were treated as idealized disordered (two positions rotated 60° from each other) with an isotropic displacement parameter 20% higher than that of the adjacent C atom and the C—H distance free to vary [C—H 1.00 (2) to 1.00 (3) Å].

Data collection: *IPDS Software* (Stoe & Cie, 1996*a*); cell refinement: *IPDS Software*; data reduction: *XRED* (Stoe & Cie, 1996*b*); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *SHELXL*97 (Sheldrick, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1070). Services for accessing these data are described at the back of the journal.

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