organic papers

2-[3-Dicyanomethylene-2-(3-methoxybenzylidene)indan-1-ylidene]malononitrile

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The title compound, $C_{23}H_{12}N_4O$, has potential application in non-linear optics; it has a chiral crystal structure despite the lack of a stereogenic centre. The crystal structure involves two intermolecular C—H$\cdots$N hydrogen bonds.

Comment

The title compound, (I), was synthesized as part of a research project based on new non-linear optical chromophores. It has been reported that organometallic derivatives of indane show second harmonic generation properties (Janowska *et al.*, 2003, 2006)

(I)
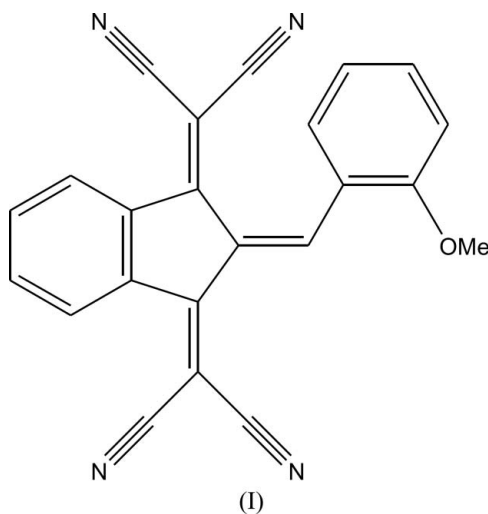
The molecular structure of (I) is shown in Fig. 1. The indan unit has an essentially planar geometry, with atom C1 displaced by 0.184 (3) Å from the plane formed by atoms C2–C9. The dihedral angle between the mean planes of the five-membered ring (C1–C5) and the fused benzene (C3/C4/C6–C9) ring is 3.37 (15)°. The dicyanomethylene substituents are tilted from the attached ring. These substituents form angles of 12.82 (11) and 15.02 (11)° for C20–C22/N21/N22 and C50–C52/N51/N52, respectively, with the planar indane ring system. The planes of the benzene rings form a dihedral angle of 43.85 (14) Å. As expected, the non-H atoms of the methoxy group do not deviate significantly from the plane of the attached ring, the maximum deviation being 0.303 (3) Å for atom C120.

In the crystal structure, because of the lack of typical proton donors, classical hydrogen bonds are absent. There are, however, two C—H$\cdots$N contacts which are slightly shorter than the corresponding sum of van der Waals radii (Table 1). In addition, there are short CN$\cdots$CN contacts, which probably

compete with hydrogen bonds (Hori *et al.*,2000; Shabatina *et al.*, 1997; Kuribayashi *et al.*, 1999): N52···C52^i = 3.064 (7) Å and N52···C51^{ii} = 3.236 (7) Å [symmetry codes: (i) $\frac{1}{2} - x, -y, \frac{1}{2} + z$; (ii) $x, y, 1 + z$].

Interestingly, (I) crystallizes in a non-centrosymmetric space group despite the absence of any stereogenic centres. However, the molecule itself is chiral; steric hindrance precludes rotation about the formally single C10—C11 bond, and the formal double bond prevents any rotation about C1—C10. A chiral crystal structure is particularly important in the case of compounds having potential applications in non-linear optics.

Experimental

Compound (I) was obtained by refluxing equimolar amounts of 2-methoxybenzaldehyde and 1,3-bis(dicyanomethylene)indan in acetic anhydride for 1 h, followed by evaporation to dryness and chromatography (silica gel/chloroform). Crystals were obtained by slow diffusion of hexane into a chloroform solution of (I) at room temperature.

Crystal data

C$_{23}$H$_{12}$N$_4$O
M_r = 360.37
Orthorhombic, $P2_12_12_1$
a = 16.023 (7) Å
b = 20.624 (5) Å
c = 5.493 (8) Å
V = 1815 (3) Å^3

Z = 4
D_x = 1.319 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 293 (2) K
Needle, orange
0.5 × 0.1 × 0.1 mm

Data collection

Rigaku AFC-5S diffractometer
ω scans
Absorption correction: none
8817 measured reflections
1873 independent reflections
962 reflections with $I > 2\sigma(I)$

R_{int} = 0.130
θ_{max} = 25°
3 standard reflections
every 150 reflections
intensity decay: 0.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.065
S = 1.04
1873 reflections
254 parameters
H-atom parameters constrained

$w = [\exp\{5(\sin\theta/\lambda)^2\}]/[\sigma^2(F_o^2) + (0.01P)^2]$ where $P = 0.33333F_o^2 + 0.66667F_c^2$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.10 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C16—H16···N22^{iii}	0.93	2.73	3.646 (6)	170
C8—H8···N21^{iv}	0.93	2.64	3.345 (6)	133

Symmetry codes: (iii) $x, y, z - 1$; (iv) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$.

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances in the
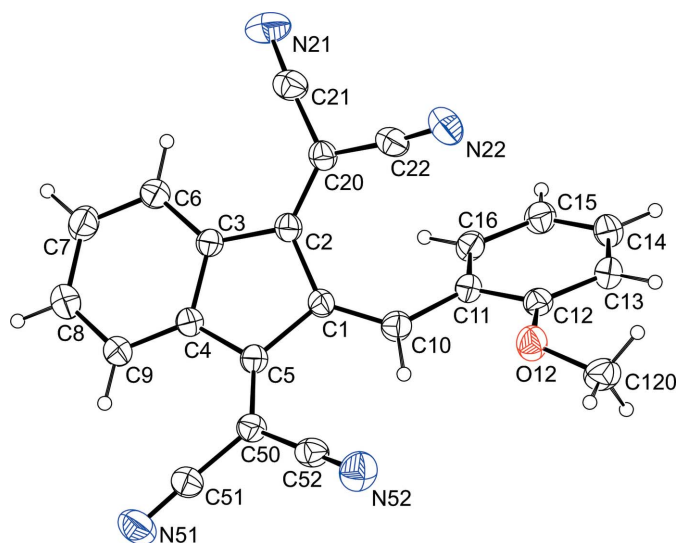

Figure 1
View of the molecular structure of (I) (50% probability displacement ellipsoids)

range 0.93–0.98 Å. For methyl H atoms, U_{iso}(H) = 1.5U_{eq}(C); for all other H atoms, U_{iso}(H) = 1.2U_{eq}(C). In the absence of significant anomalous dispersion effects the Friedel pairs were merged. The higher than normal R_{int} value of 0.13 may be related to the fact that many of the data have weak intensity and the data/refined parameter ratio is lower than normal.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1989); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON* and *WinGX* (Farrugia, 1999).

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