

2,2'-{2-[(*E*)-3-Phenylprop-2-enyl]-2,3-dihydro-1*H*-isoindol-1,3-diylidene}dimalononitrile, a π -deficient system for $\pi \cdots \pi$ (1:1) stacking investigationsColm Crean, John F. Gallagher*
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Key indicators

Single-crystal X-ray study

 $T = 296$ KMean $\sigma(\text{C}-\text{C}) = 0.003$ Å R factor = 0.042 wR factor = 0.112

Data-to-parameter ratio = 13.3

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

The title compound, $\text{C}_{23}\text{H}_{13}\text{N}_5$, derived from cinnamyl alcohol and 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile, is a heterocyclic TCNQ analogue of interest as an electron-deficient component in charge-transfer complexes. A small perturbation of the four $\text{C}-\text{C}\equiv\text{N}$ angles from linearity is observed, which are in the range $173.41(18)$ – $176.3(2)^\circ$; the $\text{C}\equiv\text{N}$ bond lengths are in the range $1.144(2)$ – $1.146(2)$ Å. The terminal phenyl group is oriented at an angle of $77.17(6)^\circ$ to the C_4N ring and the $\text{C}=\text{C}$ bond is short, $1.319(2)$ Å. There are no classical hydrogen bonds, although intramolecular $\text{C}-\text{H}\cdots\text{N}$ and intermolecular $\text{C}-\text{H}\cdots\pi(\text{arene})$ interactions influence the crystal-structure packing.

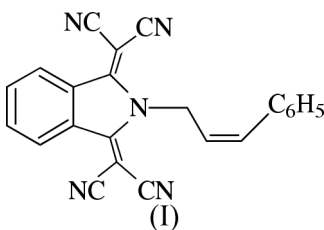
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Comment

Organic conductors are currently an important research area in materials chemistry (Martin *et al.*, 1997; Yamashita & Tomura, 1998), with special interest in the interaction of π -deficient and π -excessive materials in 1:1 complexes, *e.g.* TCNQ/TTF, where TCNQ is tetracyanoquinodimethane and TTF is tetrathiafulvalene.



The bond lengths and angles in the heterocyclic ring of the title compound, (I) (Fig. 1), are similar to those reported previously in related systems (McNab *et al.*, 1997; Brady *et al.*, 1998; Gallagher & Murphy, 1999; Brady & Gallagher, 2000). For TCNQ (tetracyanoquinodimethane) systems (280 examples), the average exocyclic $\text{Csp}^2=\text{Csp}^2$ and $\text{Csp}^2-\text{Csp}^1$ bond lengths are $1.392(17)$ and $1.427(10)$ Å, respectively; thus, in (I), the $\text{C6A}-\text{C7A}$, $\text{C6A}-\text{C8A}$, and $\text{C6B}-\text{C7B}$ and $\text{C6B}-\text{C8B}$ bond lengths in the range $1.425(3)$ – $1.436(3)$ Å are normal (Orpen *et al.*, 1994). The four nitrile $\text{C}\equiv\text{N}$ values are from $1.144(2)$ to $1.146(2)$ Å, which compare with the average $\text{C}\equiv\text{N}$ dimension from the literature, $1.144(8)$ Å (Orpen *et al.*, 1994). The exocyclic indolinyl ring $\text{C}=\text{C}$ bond lengths are $1.372(2)$ and $1.374(2)$ Å, which are longer than typical double bonds. The four remaining exocyclic indolinyl cyano $\text{C}-\text{C}$ bond lengths are in the range $1.425(3)$ – $1.436(3)$ Å and similar

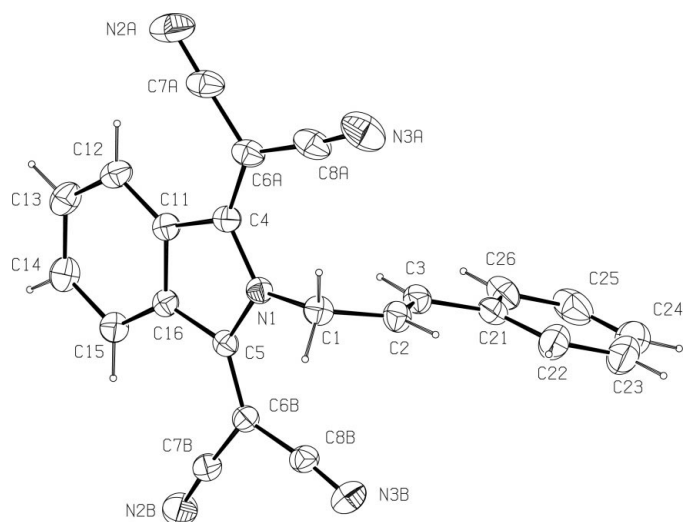


Figure 1
A view of (I) with the atomic numbering scheme. Displacement ellipsoids are depicted at the 30% probability level.

to previously reported values. The angles which the $C(\equiv N)_2$ groups make with the C_4N ring are $7.01(10)$ ($C6A$) and $2.33(10)^\circ$ ($C6B$), demonstrating a small twist from planarity about the $C4-C6(A/B)$ bonds.

The hydrogen bonding in (I) is dominated by intramolecular $C-H \cdots N$ interactions and close contacts (details in Table 2). There are two intramolecular $C(\text{arene})-H \cdots \pi(C \equiv N)$ interactions with $C12-H12 \cdots N2A$ and $C15-H15 \cdots N2B$. $C \cdots N$ distances of $3.390(3)$ and $3.390(2)$ Å, respectively. A $C1-H1B \cdots N3A$ intramolecular contact is present [$C1 \cdots N3A$ $3.401(2)$ Å and $C-H \cdots N$ 139°]. A $C-H \cdots \pi(\text{arene})$ interaction is also present, $C14-H14 \cdots Cg1$, where $Cg1$ is the centroid of $\{C21-C26\}^i$ [symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; details in Table 2]. The closest $C14 \cdots C26^i$ contact distance is $3.696(2)$ Å with a $C14-H14 \cdots Cg1$ angle of 121° .

Experimental

The title compound was prepared by the 5 d reaction under argon of DIAD (diisopropylazodicarboxylate) (0.37 g, 1.9 mmol), triphenylphosphine (0.49 g, 1.9 mmol), 2,2'-(isoindolylidene)bispropanedinitrile (0.25 g, 1.9 mmol) (Farbenfabriken Bayer Aktiengesellschaft, 1968), cinnamyl alcohol (0.25 g, 1.9 mmol) in 40 ml tetrahydrofuran. 2,2'-(Cinnamylisoindolylidene)bispropanedinitrile, (I), was isolated as an orange crystalline material after column chromatography (m.p. 469–471 K uncorrected). IR (KBr, cm^{-1}): 3049, 2372, 2335, 2224, 1563, 1465, 1407, 1228, 1146, 1109, 983, 775, 723; UV-Vis (CH_3CN) $\lambda_{\text{max}}(\epsilon)$: 552 (5250), 459 (6667), 414 (38333), 392 (39167), 249 (47083) nm; ^1H NMR (400 MHz, δ , CDCl_3): 8.75 (*m*, 2H, aromatic), 7.85 (*m*, 2H, aromatic), 7.37 (*m*, 2H, aromatic), 7.30 (*m*, 3H, aromatic), 6.50 (*d*, $J = 16$ Hz, 1H), 6.25 (*m*, 1H), 5.50 (*m*, 2H); ^{13}C NMR (δC , CDCl_3): 156.8, 135.0, 134.8, 134.0, 130.9, 128.8, 128.7, 126.9, 126.0, 120.5, 113.1, 112.3, 62.1, 47.8.

Crystal data

$\text{C}_{23}\text{H}_{13}\text{N}_5$
 $M_r = 359.38$
Monoclinic, $P2_1/n$
 $a = 14.3872(18)$ Å
 $b = 8.2696(10)$ Å
 $c = 16.1442(15)$ Å
 $\beta = 108.327(7)^\circ$
 $V = 1823.4(4)$ Å³
 $Z = 4$

$D_x = 1.309$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 33 reflections
 $\theta = 7.1-20.5^\circ$
 $\mu = 0.08$ mm⁻¹
 $T = 296(1)$ K
Block, orange
 $0.43 \times 0.38 \times 0.28$ mm

Data collection

Bruker P4 diffractometer
 $\omega-2\theta$ scans
4331 measured reflections
3367 independent reflections
2630 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.012$
 $\theta_{\text{max}} = 25.5^\circ$

$h = -1 \rightarrow 17$
 $k = -1 \rightarrow 10$
 $l = -19 \rightarrow 18$
3 standard reflections
every 197 reflections
intensity decay: 2%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.112$
 $S = 1.06$
3367 reflections
253 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0529P)^2 + 0.3178P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.25$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.16$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

N1—C1	1.469 (2)	C1—C2	1.495 (2)
N1—C4	1.386 (2)	C2—C3	1.319 (2)
N1—C5	1.388 (2)	C3—C21	1.471 (2)
N2A—C7A	1.145 (2)	C4—C6A	1.374 (2)
N3A—C8A	1.146 (2)	C4—C11	1.460 (2)
N2B—C7B	1.144 (2)	C5—C6B	1.372 (2)
N3B—C8B	1.145 (2)	C5—C16	1.461 (2)
C1—N1—C4	125.99 (12)	N1—C5—C6B	125.80 (14)
C1—N1—C5	123.11 (12)	N1—C4—C11	107.12 (12)
C4—N1—C5	110.82 (12)	N1—C5—C16	106.81 (12)
N1—C1—C2	113.84 (13)	N2A—C7A—C6A	176.3 (2)
C1—C2—C3	126.34 (15)	N3A—C8A—C6A	175.3 (2)
C2—C3—C21	126.82 (16)	N2B—C7B—C6B	175.81 (18)
N1—C4—C6A	126.02 (15)	N3B—C8B—C6B	173.41 (18)
C4—N1—C1—C2	−102.16 (17)	C1—C2—C3—C21	−174.28 (16)
C5—N1—C1—C2	81.50 (18)	C2—C3—C21—C22	−1.5 (3)
N1—C1—C2—C3	6.6 (2)	C2—C3—C21—C26	176.66 (17)

Table 2

Hydrogen-bonding geometry (Å, °).

$Cg1$ is the centroid of $\{C21-C26\}^i$.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C1—H1B \cdots N3A	0.97	2.61	3.401 (2)	139
C12—H12 \cdots N2A	0.93	2.59	3.390 (3)	145
C12—H12 \cdots C7A	0.93	2.45	3.019 (3)	119
C15—H15 \cdots N2B	0.93	2.59	3.390 (2)	145
C15—H15 \cdots C7B	0.93	2.46	3.015 (2)	119
C14—H14 \cdots Cg1 ⁱ	0.93	3.20	3.984 (2)	143

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

In (I), all H atoms bound to C atoms were treated as riding, with *SHELXL97* (Sheldrick, 1997) defaults for C–H lengths and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methylene H atoms and $1.2U_{\text{eq}}(\text{C})$ for the remainder. Examination of the structure with *PLATON* (Spek, 1998) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *XSCANS* (Bruker, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *NRCVAX96* (Gabe *et al.*, 1989) and *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *PLATON* (Spek, 1998); software used to prepare material for publication: *NRCVAX96*, *SHELXL97* and *WordPerfect* macro *PREP8* (Ferguson, 1998).

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