Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

2-{3-[(*E*)-(3,4-Dimethoxyphenyl)ethenyl]-5,5-dimethylcyclohex-2-enylidene}malononitrile

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Key indicators

Single-crystal X-ray study
T = 290 K
Mean σ(C–C) = 0.004 Å
R factor = 0.058
wR factor = 0.124
Data-to-parameter ratio = 16.2

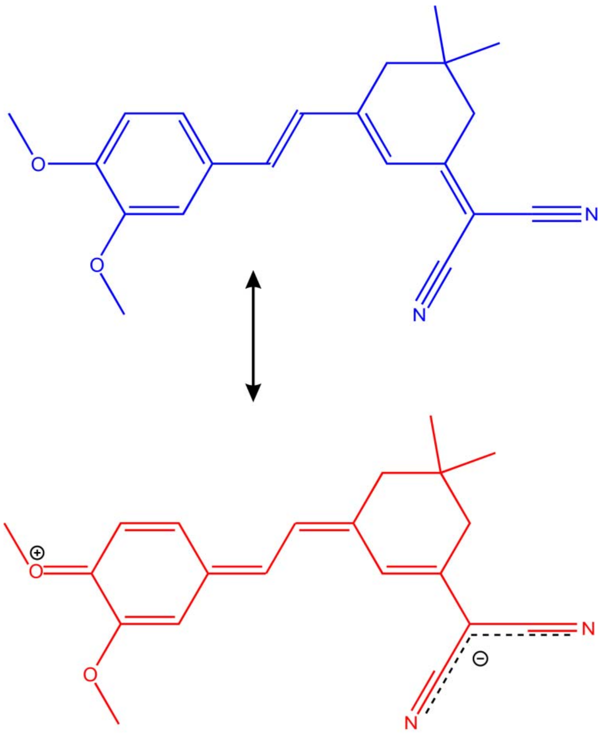
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 4 January 2005
Accepted 27 January 2005
Online 5 February 2005

The molecule of the title compound, $C_{21}H_{22}N_2O_2$, is nearly planar, except for the $C(CH_3)_2$ group on the cyclohexene ring. Molecules are connected *via* electrostatic C···O contacts, forming zigzag pseudo-chains along the *c* axis.

Comment

Organic non-linear optical (NLO) materials have attracted much attention in the past 20 years owing to their potential applications in various fields such as telecommunications, optical data storage and optical information processing. Organic molecules possess notable chemical flexibility for the molecular engineering of enhanced and fast electronic responses, which makes them particularly interesting candidates for elaboration of optimized non-linear optical materials (Chemla & Zyss, 1987; Nalwa *et al.*, 1997; Wolff & Wortmann, 1999). As a result of their solvatochromic behaviour, derivatives of 2-(3,5,5-trimethylcyclohex-2-enylidene)malononitrile are supposed to be good candidates for NLO, electro-optical and photorefractive applications (Steenwinckel *et al.*, 2000; Strutz & Hayden, 1999; Wortmann *et al.*, 1996).



(I)

In the course of our spectroscopic and structural investigation of this class of substances, we studied the crystal structure of the title compound, (I). The UV–vis spectrum of

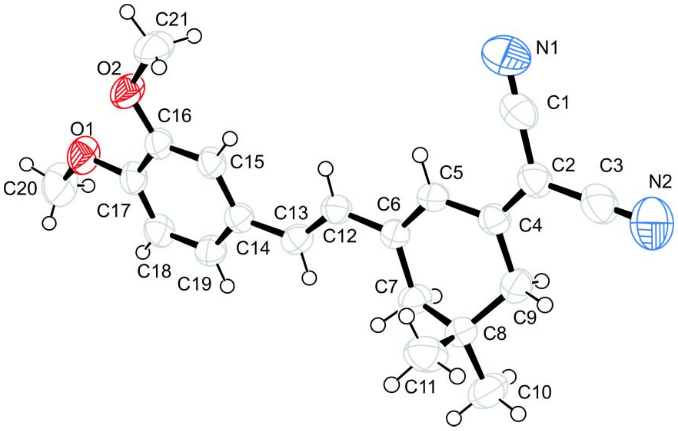


Figure 1
The molecular structure of (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids.

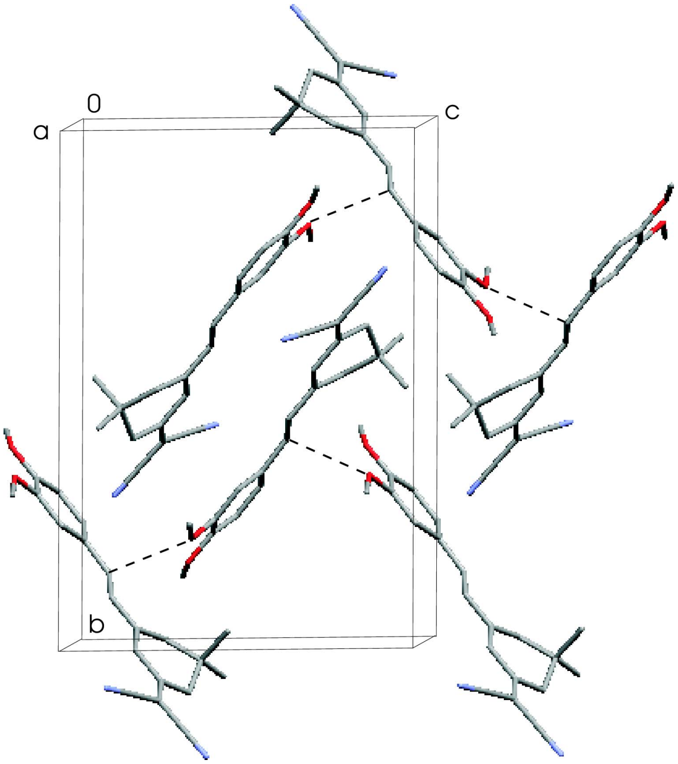


Figure 2
Projection of the crystal structure of (I), showing the short contacts (dashed lines) within the pseudo-chains. H atoms have been omitted for clarity.

(I) shows λ_{max} at 434 nm. This value illustrates a strong charge transfer (CT) through the molecule. The two most probable resonance structures of (I) are presented in the scheme; the locations of the partial positive and negative charges are shown.

In (I), the molecule has an extended structure (Fig. 1), as seen from the torsion angles of the backbone (Table 1). The cyclohexene and the aromatic rings are nearly coplanar, with a dihedral angle of 8.7 (2)°, while the $C(CH_3)_2$ group is displaced from the molecular plane. Neighboring molecules alternate in orientation along the *c* axis, with a dihedral angle between molecular planes of 76.8 (3)°. This arrangement is stabilized by one short contact of 3.099 (4) Å between atoms C13 and O2(x, $\frac{3}{2} - y$, $\frac{1}{2} + z$), which can be explained as an electrostatic atomic interaction due to charge alternation of non-H atoms within the molecule (Kolev *et al.*, 2003). Thus, zigzag pseudo-chains along *c* are observed. The chains are parallel to each other in the *a* direction and interdigitate in the *b* direction (Fig. 2).

Experimental

Compound (I) was synthesized in a manner similar to the general procedure described by Lemke (1970). The preparation of the starting compound 2-(3,5,5-trimethylcyclohex-2-enylidene)malononitrile was previously reported (Kolev *et al.*, 2001). The starting compound (1.86 g, 10 mmol) was dissolved in dry methanol (25 ml) with continuous stirring. (3,4-Dimethoxy)benzaldehyde (1.66 g, 10 mmol, Aldrich) was added to the solution and piperidine (nearly 2 ml) was used as a catalyst. After stirring for 3 h at room temperature, a red precipitate was formed. The solution was filtered and the crystalline product was recrystallized twice from ethyl acetate (yield 68%, m.p. 446–447 K). Elemental analysis calculated: C 75.42, H 6.63, N 8.38%; found: C 75.50, H 6.55, N 8.40%. UV–vis spectrum: λ_{max} = 434 nm (EtOH). The band assignment of the IR spectrum (KBr pellet) was performed by DFT/6-31G* calculations (Kolev *et al.*, 2003). The ν_{C-H} vibrations of the aromatic ring appear at 3076 (*w*), 3054 (*w*) and 3006 cm^{-1} (*w*). There are eight aliphatic ν_{C-H} strong bands between 2960 and 2830 cm^{-1}. The very strong band at 2213 cm^{-1} is assigned to the ν_{CN} vibration of the cyano groups. The bands at 1555 (*s*), 1504 (*s*) and 1613 cm^{-1} (*s*) are assigned to the vibrations of the three conjugated double bonds. The ν_{O-C} vibration of the methoxy groups give rise to two intense bands at 1164 and 1137 cm^{-1}.

Crystal data

$C_{21}H_{22}N_2O_2$
$M_r = 334.41$
Monoclinic, $P2_1/c$
$a = 8.711$ (2) Å
$b = 18.005$ (3) Å
$c = 12.5175$ (18) Å
$\beta = 107.66$ (2)°
$V = 1870.8$ (6) Å^3
$Z = 4$
$D_x = 1.187$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 22 reflections
$\theta = 16.6$–17.5°
$\mu = 0.08$ mm^{-1}
$T = 290$ (2) K
Prism, red
0.26 × 0.20 × 0.14 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled $\omega/2\theta$ scans
Absorption correction: none
7703 measured reflections
3674 independent reflections
1433 reflections with $I > 2\sigma(I)$
$R_{int} = 0.101$
$\theta_{max} = 26.0°$
$h = 0 \rightarrow 10$
$k = -22 \rightarrow 22$
$l = -15 \rightarrow 14$
3 standard reflections every 500 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.124$
$S = 0.96$
3674 reflections
227 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0338P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.15$ e Å^{-3}
$\Delta\rho_{min} = -0.14$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0076 (9)

Acta Cryst. (2005). E**61**, o550–o552 Tsonko Kolev *et al.* • $C_{21}H_{22}N_2O_2$ **o551**

Table 1
Selected torsion angles (°).

C3—C2—C4—C5	178.5 (3)	C13—C14—C15—C16	178.3 (2)
C4—C5—C6—C12	177.9 (2)	C15—C16—C17—O1	−180.0 (3)
C6—C12—C13—C14	177.8 (3)	C16—C17—O1—C20	175.9 (3)

H atoms were placed in idealized positions (C—H = 0.93–0.96 Å) and constrained to ride on their parent atoms, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) or 1.5$U_{\rm eq}$($C_{\rm Me}$).

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

TK, DY and RW thank the DAAD and the Alexander von Humboldt Foundation for a grant within the priority programme (Stability Pact for South-Eastern Europe). This work has been supported by the Bulgarian National Fund of Scientific Research (contracts X-1213 and F-1212).

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o552 Tsonko Kolev *et al.* • $C_{21}H_{22}N_2O_2$ *Acta Cryst.* (2005). E**61**, o550–o552