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Monoclinic form of 2-{5,5-dimethyl-3-[2-(2,4,6-trimethoxyphenyl)vinyl]cyclohex-2-enylidene}malononitrile

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On slow evaporation of an ethyl acetate solution, the title compound, $C_{22}H_{24}N_2O_3$, crystallizes simultaneously in two crystalline forms, differing in colour, size and shape. The molecule in the violet plate-like monoclinic crystal reported here is almost planar with the exception of the dimethylcyclohexene moiety, which has a twisted conformation. The red triclinic crystals [see Kolev *et al.* (2001*a*), *Acta Cryst.* E**57**, o966–o967] are built of the same molecules with similar geometry; however, the cyclohexene fragment in the triclinic crystal has a more symmetric sofa conformation. Another difference between the structures is the existence of a non-classical hydrogen bond involving one of the nitrile groups in the triclinic form. The molecules in the monoclinic form are held together by van der Waals interactions.

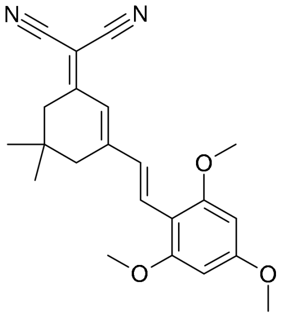
Key indicators

Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.003 Å
R factor = 0.054
wR factor = 0.136
Data-to-parameter ratio = 14.7

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

Comment

Due to their solvatochromic behaviour (Lemke, 1970), the derivatives of 2-(5,5-dimethyl-3-styrylcyclohex-2-enylidene)-malononitrile are supposed to be good candidates for nonlinear optical (NLO) and electrooptical applications. In the course of our investigations on this class of substances, we studied the crystal structures of the title compound, (I).



(I)

The mean molecular plane orientations in the monoclinic crystal of the title compound alternate between (113) and $(\bar{1}1\bar{3})$. The least-squares plane through atoms C1/C2/C3/C4/C6 in the cyclohexene ring indicates a better planarity for the plane in the triclinic crystal (Kolev *et al.*, 2001*a*) [χ^2 = 44, maximum deviation from planarity = 0.0090 (19) Å] than in the monoclinic crystal [χ^2 = 676, maximum deviation from planarity = 0.035 (3) Å]. The dihedral angle between this plane and the least-squares plane of the C14–C19 phenyl ring is 4.69 (5)° in the triclinic and 8.87 (8)° in the monoclinic crystal, which means that the deviations from the overall planarity of the molecule are also smaller in the triclinic

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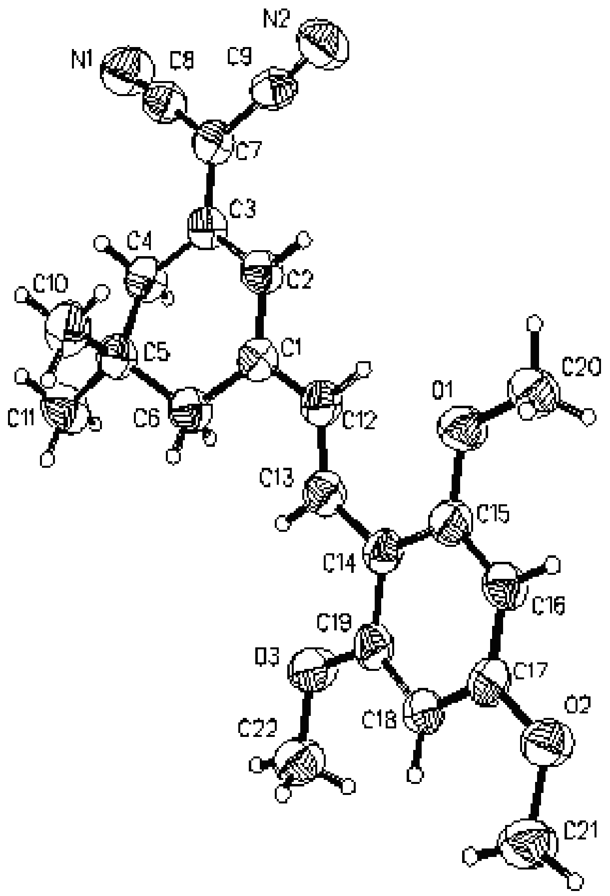

Figure 1

View of the title compound showing the labelling of non-H atoms. Displacement ellipsoids are shown at the 50% probability level. H atoms are drawn as circles of arbitrary radii.

crystal. The six torsion angles in the cyclohexene ring [triclinic: −0.8 (3), 1.7 (3), −28.6 (3), 51.7 (2), 27.2 (3) and −51.4 (2)°; monoclinic: −3.0 (4), −2.7 (4), 32.0 (3), −52.8 (3), −21.2 (3) and 47.8 (3)°; both sequences correspond to endocyclic torsion angles associated with the bonds C1—C2 through C6—C1 in the ring] indicate a higher symmetry of the conformation of the cyclohexene ring in the triclinic crystal.

In the triclinic crystal, the intermolecular contact of 2.60 Å between the H10*C* and N2(*x* + 1, *y*, *z*) atoms indicates a non-classical hydrogen bond [with the C10—H10*C*···N2(*x* + 1, *y*, *z*) angle equal to 160°], whereas the molecules in the monoclinic crystal are held together by pure van der Waals interactions.

Experimental

The title compound was synthesized using a general procedure described by Lemke (1970). The preparation of the starting compound, 3,5,5-trimethyl(cyclohex-2-enylidene)malonodinitrile, $C_{12}H_{14}N_2$, is described in one of our previous papers (Kolev *et al.* 2001*b*). The starting compound (5 mmol) was dissolved in 60 ml of dry toluene by continuous stirring. 2,4,6-Trimethoxybenzaldehyde (5 mmol) was added to the solution, and nearly 1 ml of triethylamine was used as a catalyst. The solution became red after a few minutes and the resulting compound precipitated. After 6 h reaction time, the solution was cooled and 2-{5,5-dimethyl-3-[2-(2,4,6-trimethoxyphenyl)vinyl]cyclohex-2-enylidene}malononitrile was isolated and recrystallized twice from ethyl acetate with an excellent yield of 92% (m.p. 477–478 K). The purity of the compound was confirmed by elemental analysis, IR, UV–vis and mass spectrometry. Two types of crystals, different in colour, size and shape, were grown simultaneously from an ethyl acetate solution by slow evaporation over a period of several days. They were separated manually.

Crystal data

$C_{22}H_{24}N_2O_3$
$M_r = 364.43$
Monoclinic, $P2_1/n$
$a = 10.7130$ (3) Å
$b = 9.0471$ (3) Å
$c = 20.6565$ (7) Å
$\beta = 90.1565$ (13)°
$V = 2002.05$ (11) Å^3
$Z = 4$

$D_x = 1.209$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 30702 reflections
$\theta = 3.1$–25.4°
$\mu = 0.08$ mm^{-1}
$T = 291$ (1) K
Plate, violet
0.50 × 0.30 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
277 frames *via* ω-rotation ($\Delta\omega = 1°$) and two times 5 s per frame with 3 sets at different κ-angles
30 702 measured reflections
3595 independent reflections

1654 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.063$
$\theta_{\rm max} = 25.4°$
$h = -12 \rightarrow 12$
$k = -10 \rightarrow 10$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.136$
$S = 0.95$
3595 reflections
244 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0589P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.15$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.16$ e Å^{-3}

H atoms were placed in calculated positions with $U_{\rm iso}$ constrained to be $1.5U_{\rm eq}$ of the carrier atom for the methyl–H and $1.2U_{\rm eq}$ for the remaining H atoms.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL*97, *PARST*95 (Nardelli, 1995) and *PLATON* (Spek, 2001).

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