

2-{3-[2-(2,4-Dimethoxyphenyl)vinyl]-5,5-dimethyl-cyclohex-2-enylidene}malononitrile

Tsonko Kolev,^a Markus Schürmann,^b Dirk-Christian Kleb,^b Hans Preut^{b*} and Michael Spittler^a^aInstitut für Umweltforschung, Universität Dortmund, Otto-Hahn-Straße 6, 44221 Dortmund, Germany, and ^bFachbereich Chemie, Universität Dortmund, Otto-Hahn-Straße 6, 44221 Dortmund, Germany

Correspondence e-mail: uch002@uxp1.hrz.uni-dortmund.de

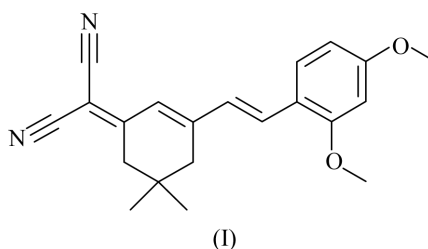
Key indicators

Single-crystal X-ray study
T = 291 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
R factor = 0.041
wR factor = 0.103
Data-to-parameter ratio = 18.0For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The molecule of the title compound, $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2$, is nearly planar, with the exception of the $\text{C}(\text{CH}_3)_2$ group; the disubstituted C atom is displaced by 0.602 (2) Å from the mean plane [maximum deviation from planarity 0.196 (2) Å] through the remaining non-H atoms of the molecule.

Comment

Owing to their solvatochromic behaviour (Lemke, 1970), derivatives of 2-(5,5-dimethyl-3-styrylcyclohexenylidene)-malononitrile are good candidates for non-linear optical (NLO), electro-optical (EO) and photorefractive (PR) applications. Some molecules of this class have been investigated by means of electric-field-induced second harmonic generation (EFISH) in chloroform. The dipole moments and molecular hyperpolarizabilities of these compounds are large enough for them to be used as active components of electro-optic and photorefractive polymers (Ermer *et al.*, 1997). The title compound, (I), crystallizes in a centrosymmetric space group and can be used only for third-order NLO applications.



Experimental

The title compound was synthesized according to the general procedure of Lemke (1970). (3,5,5-Trimethylcyclohex-2-enylidene)-malonodinitrile (0.93 g, 5 mmol; Kolev *et al.*, 2001) was dissolved in 60 ml anhydrous ethanol by continuous stirring for 3 h at moderate temperature. 2,4-Dimethoxybenzaldehyde (0.83 g, 5 mmol) was dissolved in 30 ml anhydrous ethanol and added dropwise to the solution. Nearly 2 ml of piperidine were used as a catalyst. The solution became red after a few minutes and the resulting compound precipitated. After a 3 h reaction time, the solution was cooled and the title compound, (I), isolated and recrystallized twice from ethanol. Purification was achieved *via* column chromatography on silica gel, using chloroform as eluent. Yield: 0.34 g (43%); m.p. 456–457 K. The purity of the compound was confirmed by elemental analysis, IR, UV–vis and mass spectrometry. Red transparent crystals were grown from a toluene solution by slow evaporation at room temperature over a period of one week.

Received 6 September 2002
Accepted 25 September 2002
Online 30 September 2002

Crystal data

$C_{21}H_{22}N_2O_2$
 $M_r = 334.41$
 Triclinic, $P\bar{1}$
 $a = 7.7607$ (2) Å
 $b = 8.9488$ (2) Å
 $c = 14.7723$ (4) Å
 $\alpha = 75.4549$ (10)°
 $\beta = 79.0465$ (11)°
 $\gamma = 69.9378$ (11)°
 $V = 926.68$ (4) Å³

$Z = 2$
 $D_x = 1.198$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 12122 reflections
 $\theta = 3.0$ – 27.5 °
 $\mu = 0.08$ mm⁻¹
 $T = 291$ (1) K
 Plate, dark red
 $0.25 \times 0.10 \times 0.05$ mm

Data collection

Nonius KappaCCD diffractometer
 ω scans, at different κ settings
 12 122 measured reflections
 4161 independent reflections
 1951 reflections with $I > 2\sigma(I)$

$R_{int} = 0.044$
 $\theta_{max} = 27.5$ °
 $h = -10 \rightarrow 10$
 $k = -10 \rightarrow 11$
 $l = -18 \rightarrow 19$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.103$
 $S = 0.87$
 4161 reflections
 231 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0475P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.14$ e Å⁻³
 $\Delta\rho_{min} = -0.13$ e Å⁻³
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.026 (3)

H atoms were placed in calculated positions, with U_{iso} values constrained to be 1.5 times U_{eq} of the carrier atom for the methyl-H atoms and 1.2 times U_{eq} for the remaining H atoms. The methyl groups were allowed to rotate but not to tip.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL97*, *PARST95* (Nardelli, 1995) and *PLATON* (Spek, 2001).

TK thanks the DAAD for a grant within the priority programme 'Stability Pack for South Eastern Europe' and the

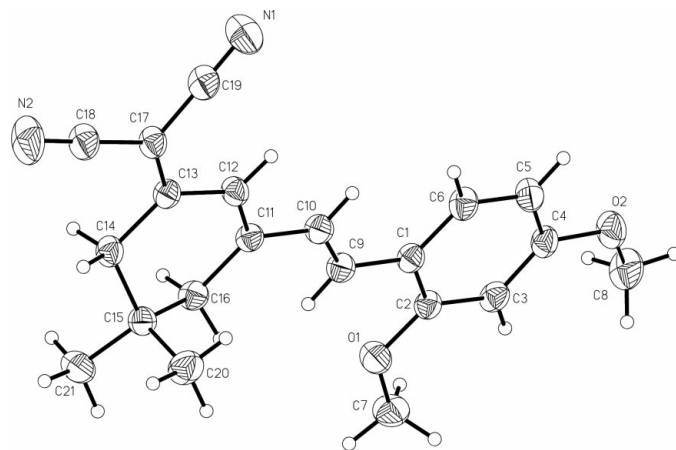


Figure 1

View of the title compound (*XP*; Sheldrick, 1991), showing the labelling of all non-H atoms. Displacement ellipsoids are shown at 30% probability levels. H atoms are drawn as circles of arbitrary radii.

Alexander von Humboldt-Stiftung Bonn, Bad Godesberg, Germany.

References

- Ermer, S., Lovejoy, S. M., Leung, D. S., Warren H., Moylan, C. R. & Twieg R. J. (1997). *Chem. Mater.* **9**, 1437–1442.
 Kolev, T., Glavcheva, Z., Yancheva, D., Schürmann, M., Kleb, D.-C., Preut, H. & Bleckmann, P. (2001). *Acta Cryst.* **E57**, o561–o562.
 Lemke, R. (1970). *Chem. Ber.* **103**, 1894–1898.
 Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
 Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
 Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
 Spek, A. L. (2001). *PLATON*. University of Utrecht, The Netherlands.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1 Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.