

2-{3-[2-(4-Hydroxyphenyl)vinyl]-5,5-dimethylcyclohex-2-en-1-ylidene}malononitrile

Tsonko Kolev,^a Zornitza Glavcheva,^b Denitsa Yancheva,^b Markus Schürmann,^a Dirk-Christian Kleb,^a Hans Preut^{a*} and Paul Bleckmann^a

^aFachbereich Chemie, Universität Dortmund, Otto-Hahn-Straße 6, 44221 Dortmund, Germany, and ^bBulgarian Academy of Sciences, Institute of Organic Chemistry, 1113 Sofia, Bulgaria

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

Key indicators

Single-crystal X-ray study

$T = 291\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ Å}$

R factor = 0.039

wR factor = 0.095

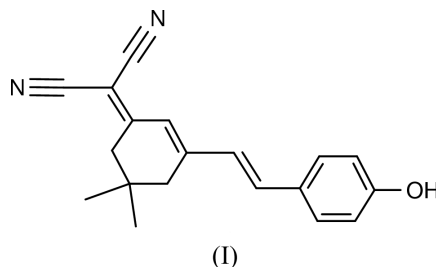
Data-to-parameter ratio = 9.5

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

The structure of the title compound, $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}$, was studied in the course of our investigations on organic non-linear optical (NLO) materials. Its molecule with the exception of the $\text{C}(\text{CH}_3)_2$ group is nearly planar.

Comment

The structure of the title compound, (I) (Fig. 1), was studied in the course of our investigations on organic non-linear optical (NLO) materials. Its molecule with the exception of the $\text{C}(\text{CH}_3)_2$ group is nearly planar; the disubstituted C atom is displaced by 0.624 (2) Å from the mean plane of the remaining atoms of the cyclohexene ring. The hydrogen bond formed by the hydroxy group with the N atom of one of the cyano groups [$\text{O}-\text{H}\cdots\text{N}$: $\text{O}\cdots\text{N}$ 2.958 (3) Å and $\text{O}-\text{H}\cdots\text{N}$ 173°] links the molecules in the crystal into infinite chains stretching along the [013] direction.



Experimental

The starting compound, 3,5,5-trimethyl(cyclohex-2-enylidene)-malonodinitrile, $\text{C}_{12}\text{H}_{14}\text{N}_2$, was prepared by means of Knoevenagel condensation of malonodinitrile (660 mg, 10 mmol, Fluka) and isophorone (1.382 g, 10 mmol, Fluka). Both compounds were dissolved in *N,N*-dimethylformamide (50 ml). The solution was stirred for eight hours at room temperature. Piperidinium acetate (600 mg) was used as a catalyst. A yellow precipitate was obtained from the resulting dark-yellow solution after evaporation of half of the solvent. The product was filtered and recrystallized from 95% ethanol. Yield 70%, m.p. 346–347 K. The title compound was prepared according to a published procedure (Lemke, 1970) from 3,5,5-trimethyl(cyclohex-2-enylidene)malonodinitrile (1.86 g, 10 mmol) and 4-hydroxybenzaldehyde (1.22 g, 10 mmol) in a 150 ml trichloromethane solution with continuous stirring for two days at room temperature. Piperidinium acetate was used as a catalyst. The orange–red solution was purified by column chromatography on silica gel. The orange precipitate ($\lambda_{\text{max}} = 421\text{ nm}$ in MeOH) was recrystallized from glacial acetic acid [Yield 65% m.p. 478–479 K; literature m.p. 483–484 K (Lemke, 1970)]. Crystals were grown by slow (several days) evaporation from ethyl acetate.

Received 4 May 2001

Accepted 21 May 2001

Online 31 May 2001

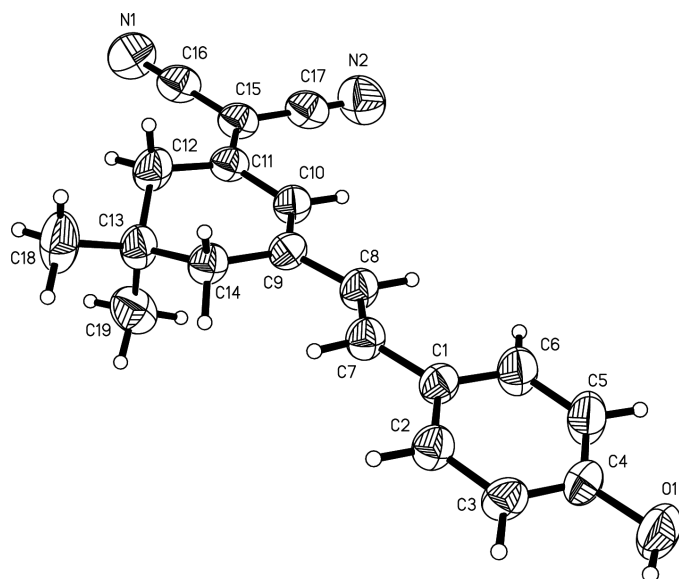


Figure 1
View of the title compound showing the labelling of all non-H atoms. Displacement ellipsoids are shown at 50% probability levels. H atoms are drawn as circles of arbitrary radii.

Crystal data

$C_{19}H_{18}N_2O$
 $M_r = 290.35$
 Orthorhombic, $Pna2_1$
 $a = 15.4413(3) \text{ \AA}$
 $b = 10.9988(3) \text{ \AA}$
 $c = 9.5699(2) \text{ \AA}$
 $V = 1625.31(6) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.187 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 10060 reflections
 $\theta = 3.1\text{--}27.4^\circ$
 $\mu = 0.07 \text{ mm}^{-1}$
 $T = 291(1) \text{ K}$
 Block, red
 $0.25 \times 0.23 \times 0.23 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer
 201 frames via ω rotation ($\Delta\omega = 1^\circ$) and two times 20 s per frame (two sets at different κ angles)
 1921 measured reflections
 1921 independent reflections

1302 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$
 $\theta_{\text{max}} = 27.4^\circ$
 $h = -19 \rightarrow 19$
 $k = -14 \rightarrow 14$
 $l = -12 \rightarrow 12$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.095$
 $S = 0.99$
 1921 reflections
 203 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0555P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.12 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.11 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.017 (3)

Table 1

Hydrogen-bonding geometry ($\text{\AA}, ^\circ$).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1\cdots H1\cdots N1^i$	0.82	2.14	2.958 (3)	173.3

Symmetry code: (i) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} + z$.

H atoms were placed in calculated positions with U_{iso} 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.

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* and *PARST95* (Nardelli, 1995).

We thank the 'Internationales Büro bei der DLR' (Germany) for the support of our project BUL-006-99. One of us (TK) thanks the Alexander von Humboldt-Stiftung for financial support.

References

- 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 Enzymol.* **276**, 307–326.
- Sheldrick, G. M. (1990). *Acta Cryst. A* **46**, 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.