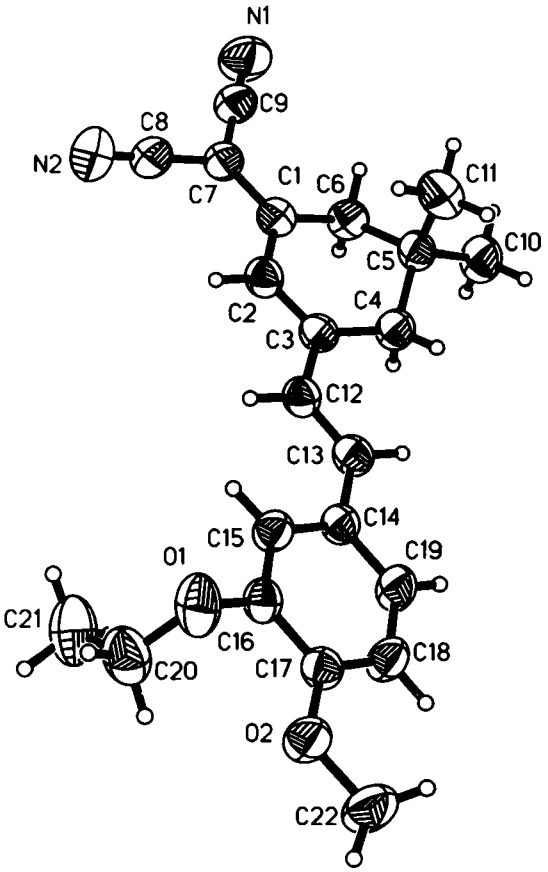
Crystal structure of 2-{3-[2-(3-ethoxy-4-methoxy-phenyl)-vinyl]-5,5-dimethyl-cyclohex-2-enylidene}-malononitrile, $C_{22}H_{24}N_2O_2$

T. Kolev[I], D. Yancheva[II], D.-Chr. Kleb[I], M. Schürmann[I], Z. Glavcheva[II], H. Preut*[,I] and P. Bleckmann[I]

[I] Universität Dortmund, Fachbereich Chemie, Otto-Hahn-Str. 6, D-44221 Dortmund, Germany
[II] Bulgarian Academy of Sciences, Institute of Organic Chemistry, 1113 Sofia, Bulgaria

Received August 16, 2000, CCDC-No. 1267/507



Abstract

$C_{22}H_{24}N_2O_2$, monoclinic, $P12_1/n1$ (No. 14), $a = 7.559(1)$ Å, $b = 19.943(2)$ Å, $c = 12.990(2)$ Å, $\beta = 93.62(2)°$, $V = 1954.3$ Å^3, $Z = 4$, $R_{gt}(F) = 0.044$, $wR_{ref}(F^2) = 0.119$, $T = 291$ K.

Source of material

The title compound was synthesized according the procedure described by Lemke [1]. 3-methyl-5,5-dimethyl-(cyclohex-2-enylidene)-malonodinitrile (5 mmol) was dissolved in 60 ml ethanol by continuous stirring for 30 minutes at moderate temperature. 3-ethoxy-4-methoxy-benzaldehyde (5 mmol) was dissolved in 30 ml ethanol and added dropwise to the solution. Some drops of triethylamine were used as a catalyst. The solution became red after a few minutes and the resulting compound precipitated. After 30 min reaction time the solution was cooled and the resulting 2-{3-[2-(3-ethoxy-4-methoxy-phenyl)-vinyl]-5,5-dimethyl-cyclohex-2-enylidene}-malononitrile was isolated and recrystallized twice from ethanol (mp 467 K – 468 K). Red transparent crystals were grown from toluene solution by slow evaporation over a period of a week. The purity of the compound was confirmed by elemental analysis, IR, UV-vis and mass spectrometry.

* Correspondence author
(e-mail: uch002@uxp1h.hrz.uni-dortmund.de)

Discussion

Organic nonlinear optical (NLO) materials have attracted much attention in the past years due to potential applications in various fields such as telecommunication, optical data storage and optical information processing. Because of their notable chemical flexibility that allows for molecular engineering of the nonlinear optical responses and their fast electronic responses, organic materials are particularly interesting candidates for the elaboration of optimized NLO materials [2,3,4]. The conversion of 3-methyl-5,5-dimethyl-(cyclohex-2-enilidene)-malonodinitrile into the corresponding 2-{3-[2-(3-ethoxy-4-methoxy-phenyl)vinyl]-5,5-dimethyl-cyclohex-2-enylidene}-malononitrile is a way to enhance the charge transfer transition on the molecular level - a requirement for a design of efficient second- and third-order nonlinear optical materials.

Table 1. Data collection and handling.

Crystal:	red plate, size 0.12 × 0.30 × 0.50 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.76 cm^{-1}
Diffractometer, scan mode:	Nonius Mach3 Argus, ω/2θ
$2\theta_{max}$:	50.16°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7345, 3456
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2007
$N(param)_{refined}$:	253
Programs:	CORINC [5], SHELXS-97 [6], SHELXTL-PLUS [7], SHELXL-97 [8]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
H(2)	4e		0.2232	0.4693	–0.0711	0.057
H(4A)	4e		–0.2575	0.4186	–0.1090	0.063
H(4B)	4e		–0.1822	0.3457	–0.1142	0.063
H(6A)	4e		–0.0644	0.4728	–0.3432	0.061
H(6B)	4e		–0.1672	0.5019	–0.2521	0.061
H(10A)	4e		–0.4126	0.4233	–0.2738	0.104
H(10B)	4e		–0.3781	0.3462	–0.2848	0.104
H(10C)	4e		–0.3289	0.3955	–0.3726	0.104
H(11A)	4e		0.0913	0.3516	–0.2550	0.099

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(11B)	4e		-0.0195	0.3520	-0.3612	0.099
H(11C)	4e		-0.0693	0.3024	-0.2740	0.099
H(12)	4e		0.1439	0.4060	0.0716	0.054
H(13)	4e		-0.1605	0.3318	0.0467	0.059
H(15)	4e		0.2263	0.3496	0.2186	0.055
H(18)	4e		-0.2322	0.2346	0.3557	0.066
H(19)	4e		-0.2683	0.2779	0.1925	0.067
H(20A)	4e	0.50	0.4826	0.3248	0.5040	0.086
H(20B)	4e	0.50	0.2831	0.3244	0.5301	0.086
H(21A)	4e	0.50	0.3807	0.4348	0.5186	0.121

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(21B)	4e	0.50	0.2337	0.4218	0.4302	0.121
H(21C)	4e	0.50	0.4340	0.4224	0.4055	0.121
H(20C)	4e	0.50	0.4291	0.3787	0.3478	0.083
H(20D)	4e	0.50	0.5329	0.3449	0.4430	0.083
H(21D)	4e	0.50	0.3680	0.4411	0.5041	0.182
H(21E)	4e	0.50	0.2932	0.3757	0.5524	0.182
H(21F)	4e	0.50	0.1904	0.4096	0.4576	0.182
H(22A)	4e		-0.0433	0.1842	0.5904	0.122
H(22B)	4e		-0.1143	0.1627	0.4793	0.122
H(22C)	4e		-0.1840	0.2286	0.5283	0.122

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	4e		0.3231(2)	0.29717(7)	0.3937(1)	0.0487(9)	0.071(1)	0.082(1)	-0.0028(7)	-0.0273(8)	0.0036(8)
C(1)	4e		0.0929(2)	0.48427(9)	-0.2115(1)	0.049(1)	0.043(1)	0.046(1)	0.0038(9)	0.0017(9)	-0.0004(8)
N(1)	4e		0.1691(3)	0.5733(1)	-0.4362(2)	0.095(2)	0.091(1)	0.063(1)	-0.009(1)	0.011(1)	0.021(1)
O(2)	4e		0.0564(2)	0.23707(7)	0.4802(1)	0.0549(9)	0.0704(9)	0.0484(8)	-0.0114(7)	-0.0070(6)	0.0173(7)
C(2)	4e		0.1212(3)	0.45701(9)	-0.1103(1)	0.047(1)	0.050(1)	0.044(1)	-0.0014(9)	-0.0042(8)	0.0002(9)
N(2)	4e		0.5119(3)	0.5528(1)	-0.1552(2)	0.066(1)	0.087(2)	0.091(2)	-0.020(1)	-0.001(1)	-0.007(1)
C(3)	4e		0.0066(2)	0.41397(9)	-0.0686(1)	0.045(1)	0.046(1)	0.0391(9)	0.0025(9)	-0.0012(8)	0.0004(8)
C(4)	4e		-0.1585(3)	0.3922(1)	-0.1303(1)	0.050(1)	0.061(1)	0.047(1)	-0.007(1)	-0.0027(9)	0.0050(9)
C(5)	4e		-0.1488(3)	0.39899(9)	-0.2468(1)	0.049(1)	0.052(1)	0.042(1)	-0.0038(9)	-0.0058(9)	0.0041(8)
C(6)	4e		-0.0798(2)	0.46898(9)	-0.2698(1)	0.049(1)	0.055(1)	0.047(1)	0.0023(9)	-0.0023(9)	0.0075(9)
C(7)	4e		0.2159(3)	0.52412(9)	-0.2538(1)	0.053(1)	0.047(1)	0.047(1)	-0.0027(9)	0.0048(9)	0.0016(9)
C(8)	4e		0.3802(3)	0.5404(1)	-0.1988(2)	0.060(1)	0.054(1)	0.058(1)	-0.009(1)	0.010(1)	0.003(1)
C(9)	4e		0.1896(3)	0.5518(1)	-0.3552(2)	0.064(1)	0.056(1)	0.056(1)	-0.006(1)	0.011(1)	0.005(1)
C(10)	4e		-0.3344(3)	0.3902(1)	-0.2994(2)	0.063(2)	0.087(2)	0.056(1)	-0.016(1)	-0.015(1)	0.007(1)
C(11)	4e		-0.0251(3)	0.3464(1)	-0.2881(2)	0.079(2)	0.061(1)	0.058(1)	0.003(1)	-0.004(1)	-0.005(1)
C(12)	4e		0.0426(2)	0.38996(9)	0.0353(1)	0.044(1)	0.047(1)	0.043(1)	-0.0014(9)	-0.0032(8)	-0.0010(8)
C(13)	4e		-0.0582(3)	0.34639(9)	0.0836(1)	0.049(1)	0.054(1)	0.043(1)	-0.0008(9)	-0.0054(9)	0.0017(9)
C(14)	4e		-0.0265(2)	0.31926(9)	0.1870(1)	0.043(1)	0.049(1)	0.0400(9)	-0.0039(9)	-0.0034(8)	0.0018(8)
C(15)	4e		0.1343(2)	0.32560(9)	0.2455(1)	0.040(1)	0.051(1)	0.047(1)	-0.0045(9)	0.0013(9)	0.0031(9)
C(16)	4e		0.1598(2)	0.29744(9)	0.3413(1)	0.038(1)	0.045(1)	0.047(1)	-0.0014(8)	-0.0059(8)	-0.0001(8)
C(17)	4e		0.0201(3)	0.26308(9)	0.3844(1)	0.050(1)	0.046(1)	0.041(1)	-0.0025(9)	-0.0038(9)	0.0033(8)
C(18)	4e		-0.1385(3)	0.2570(1)	0.3278(2)	0.044(1)	0.068(1)	0.053(1)	-0.016(1)	-0.0034(9)	0.013(1)
C(19)	4e		-0.1607(3)	0.2838(1)	0.2303(2)	0.046(1)	0.069(1)	0.051(1)	-0.014(1)	-0.0123(9)	0.011(1)
C(20)	4e	0.50	0.3633(8)	0.3355(3)	0.4772(4)	0.075(4)	0.073(3)	0.063(3)	-0.005(3)	-0.019(3)	0.001(3)
C(21)	4e	0.50	0.352(2)	0.4106(8)	0.456(1)	0.058(6)	0.070(5)	0.110(8)	0.006(5)	-0.028(5)	-0.007(5)
C(20')	4e	0.50	0.4158(7)	0.3549(3)	0.4119(4)	0.064(3)	0.083(4)	0.059(3)	-0.034(3)	-0.015(3)	0.021(3)
C(21')	4e	0.50	0.306(2)	0.400(1)	0.489(1)	0.083(8)	0.12(1)	0.16(1)	0.002(7)	-0.016(7)	-0.062(9)
C(22)	4e		-0.0826(3)	0.2001(1)	0.5230(2)	0.079(2)	0.104(2)	0.060(1)	-0.031(1)	-0.005(1)	0.032(1)

Acknowledgments. We thank the 'Internationales Büro bei der DLR' (Germany) for the support of our project BUL-006-99. One of us (T. K.) thanks the Alexander von Humboldt-Stiftung for financial support.

References

1. Lemke, R.: Solvatochromie von 80 mμ in verschiedenen Alkoholen bei Arylidenisophoron Abkömmlingen, Chem. Ber. **103** (1970) 1894-1898.
2. Nalwa, H. S.; Miyata, S. (Eds): Nonlinear Optics of Organic Molecules and Polymers. CRC Press, Boca Raton 1997.
3. Wolff, J. J.; Wortmann, R.: Organic Materials for Second-Order Non-Linear Optics, 121-217 in Advances in Physical Organic Chemistry, Vol. 32, Bethell, D. (Editor), 1999.
4. Bosshard, C.; Sutter, K.; Pretre, P.; Hulliger, J.; Flörsheimer, M.; Kaatz, P.; Günter, P.: Organic Nonlinear Optical Materials, Gordon & Breach, Amsterdam 1995.
5. Dräger, M.; Gattow, G.: CORINC. Acta Chimica Scandinavica **25** (1971) 761, revised version by Wiehl, L. and Schollmeyer, D. Universität Mainz, Germany 1994.
6. Sheldrick, G. M. Phase Annealing in SHELX-90: Direct Methods for Larger Structures. Acta Crystallogr. A**46** (1990) 467-473.
7. Sheldrick, G. M.: SHELXTL-Plus. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA 1991.
8. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures, University of Göttingen, Germany 1997.