Crystal structure of 4-[(4-*N,N*-dimethylaminophenyl)amino]-3-ethoxy-3-cyclobutene-1,2-dione, C₁₄H₁₆N₂O₃

T. Kolev^I, D. Yancheva^{II}, M. Schürmann^I, D.-Chr. Kleb^I, 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 October 9, 2000, CCDC-No. 1267/538

Abstract

C₁₄H₁₆N₂O₃, triclinic, *P* $\bar{1}$ (No. 2), *a* = 6.3066(1) Å, *b* = 7.5559(2) Å, *c* = 14.7551(4) Å, α = 88.5449(9)°, β = 82.533(1)°, γ = 69.205(1)°, *V* = 651.6 Å³, *Z* = 2, *R*_{gt}(*F*) = 0.046, *wR*_{ref}(*F*²) = 0.134, *T* = 291 K.

Source of material

The title compound was prepared according to the general procedure described by Tietze et al. [1]. Diethylester of squaric acid (3,4-diethoxy-3-cyclobutene-1,2-dione, 1.21 g, 7.1 mmol) was dissolved in 10 ml ethanol. 4-Amino-*N,N*-dimethylaniline (0.97 g, 7.1 mmol) was dissolved in 50 ml ethanol and added to the first solution at continuous stirring at room temperature. The reaction mixture was stirred for 6 hours. The obtained yellow precipitate was filtered off, dried in vacuo and recrystallized from ethanol (mp 413 K–415 K). Crystals were grown by slow evaporation from ethyl acetate.

Discussion

In the course of our investigations on organic nonlinear optical (NLO) materials we now determined the crystal structure of the title compound. The asymmetric unit of the crystal contains one formula unit C₁₄H₁₆N₂O₃. The molecule except the ethoxy group is nearly planar. The molecules are linked by a N—H...O hydrogen bond (*d*(N1—H1...O3) = 3.007(2) Å, $\angle$ (N—H...O) = 171°). A short intramolecular H...O contact (2.21 Å) indicates a intramolecular hydrogen bond (*d*(C2—H2...O3) = 3.130(2) Å, $\angle$ (C—H...O) = 155°).

Table 1. Data collection and handling.

Crystal:	yellow plate, size 0.1 × 0.4 × 0.5 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.94 cm ⁻¹
Diffractometer, scan mode:	Nonius KappaCCD, 410 frames, $\Delta\omega$ = 1°
2 θ _{max} :	54.86°
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} :	8182, 2910
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ (<i>I</i> _{obs}), 1957
<i>N</i> (<i>param</i>) _{refined} :	236
Programs:	SHELXS-97 [2], SHELXTL-Plus [3], SHELXL-97 [4], PARST95 [5]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1)	2i	0.788(3)	0.314(2)	0.368(1)	0.056(5)
H(2)	2i	0.270(3)	0.295(3)	0.479(1)	0.078(6)
H(3)	2i	0.211(4)	0.216(3)	0.634(1)	0.078(6)
H(5)	2i	0.869(3)	0.133(2)	0.658(1)	0.069(5)
H(6)	2i	0.924(3)	0.220(3)	0.506(1)	0.073(5)
H(7A)	2i	0.734(4)	0.176(3)	0.816(2)	0.095(7)
H(7B)	2i	0.817(4)	−0.037(3)	0.783(1)	0.090(6)
H(7C)	2i	0.625(3)	0.038(3)	0.868(2)	0.082(6)
H(8A)	2i	0.278(3)	0.101(3)	0.858(2)	0.085(6)
H(8B)	2i	0.212(3)	0.044(3)	0.765(1)	0.082(6)
H(8C)	2i	0.167(3)	0.258(3)	0.790(1)	0.069(5)
H(13A)	2i	0.875(4)	0.493(3)	0.079(1)	0.093(7)
H(13B)	2i	0.610(3)	0.521(2)	0.078(1)	0.069(5)
H(14A)	2i	0.988(5)	0.168(4)	0.050(2)	0.14(1)
H(14B)	2i	0.717(5)	0.197(4)	0.051(2)	0.14(1)
H(14C)	2i	0.850(3)	0.279(3)	−0.029(2)	0.081(6)

* Correspondence author

(e-mail: uch002@uxpl.hrz.uni-dortmund.de)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
O(1)	2i	0.7564(2)	0.3975(2)	0.1866(1)	0.0455(6)	0.0931(8)	0.0379(6)	-0.0384(6)	-0.0022(4)	0.0066(5)
O(2)	2i	0.2471(2)	0.4309(2)	0.1376(2)	0.0582(7)	0.143(1)	0.0621(8)	-0.0505(8)	-0.0272(6)	0.0428(8)
O(3)	2i	0.1186(2)	0.3383(2)	0.3499(7)	0.0371(6)	0.0937(9)	0.0564(7)	-0.0311(6)	-0.0032(5)	0.0152(6)
N(1)	2i	0.6538(2)	0.3054(2)	0.3856(8)	0.0359(7)	0.0629(8)	0.0382(7)	-0.0261(6)	-0.0006(5)	0.0026(5)
N(2)	2i	0.5009(2)	0.1128(2)	0.7525(9)	0.0480(8)	0.105(1)	0.0464(8)	-0.0306(8)	-0.0050(6)	0.0229(7)
C(1)	2i	0.6077(2)	0.2600(2)	0.4782(9)	0.0379(7)	0.0471(8)	0.0392(8)	-0.0191(6)	-0.0007(6)	-0.0002(6)
C(2)	2i	0.3960(3)	0.2619(3)	0.5170(1)	0.0427(9)	0.090(1)	0.0467(9)	-0.0349(8)	-0.0090(7)	0.0113(8)
C(3)	2i	0.3615(3)	0.2148(3)	0.6071(1)	0.0413(9)	0.089(1)	0.0501(9)	-0.0335(8)	-0.0035(7)	0.0118(8)
C(4)	2i	0.5365(2)	0.1638(2)	0.6622(1)	0.0411(8)	0.0545(8)	0.0421(8)	-0.0192(7)	-0.0030(6)	0.0062(6)
C(5)	2i	0.7475(3)	0.1655(2)	0.6221(1)	0.0380(8)	0.077(1)	0.0493(9)	-0.0229(7)	-0.0088(7)	0.0113(8)
C(6)	2i	0.7817(3)	0.2131(2)	0.5320(1)	0.0333(8)	0.069(1)	0.0472(9)	-0.0218(7)	-0.0013(6)	0.0074(7)
C(7)	2i	0.6814(4)	0.0692(3)	0.8087(1)	0.067(1)	0.083(1)	0.049(1)	-0.033(1)	-0.0149(9)	0.0125(9)
C(8)	2i	0.2748(3)	0.1321(3)	0.7935(1)	0.054(1)	0.072(1)	0.048(1)	-0.0253(9)	0.0043(8)	0.0095(9)
C(9)	2i	0.5199(2)	0.3416(2)	0.3200(8)	0.0357(7)	0.0426(7)	0.0412(8)	-0.0169(6)	-0.0017(6)	-0.0011(6)
C(10)	2i	0.5659(2)	0.3829(2)	0.2286(7)	0.0382(7)	0.0504(8)	0.0392(8)	-0.0215(6)	-0.0002(6)	0.0029(6)
C(11)	2i	0.3443(3)	0.3981(2)	0.2059(1)	0.0412(8)	0.065(1)	0.0533(9)	-0.0243(7)	-0.0091(7)	0.0133(7)
C(12)	2i	0.2854(2)	0.3542(2)	0.3046(1)	0.0346(7)	0.0544(9)	0.0488(9)	-0.0181(6)	-0.0046(6)	0.0068(6)
C(13)	2i	0.7632(3)	0.4328(3)	0.0884(1)	0.052(1)	0.075(1)	0.0365(8)	-0.0306(9)	-0.0034(7)	0.0119(7)
C(14)	2i	0.8329(6)	0.2542(3)	0.0359(2)	0.122(2)	0.082(1)	0.043(1)	-0.029(2)	-0.007(1)	0.004(1)

References

1. Tietze, L. F.; Arlt, M.; Beller, M.; Glüsenkamp, K.-H.; Jähde, E.; Rajewsky, M. F.: Squaric Acid Diethyl Ester: A New Coupling Reagent for the Formation of Drug Biopolymer Conjugates. Synthesis of Squaric Acid Ester Amides and Diamides. *Chem. Ber.* **124** (1991) 1215-1221.
2. Sheldrick, G. M.: Phase Annealing in SHELX-90: Direct Methods for Larger Structures. *Acta Crystallogr. A* **46**, (1990) 467-473.
3. Sheldrick, G. M.: SHELXTL-Plus. Release 4.1 Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA 1991.
4. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures, University of Göttingen, Germany 1997.
5. Nardelli, M.: PARST95 – an update to PARST: A system of Fortran routines for calculating molecular structure parameters from the results of crystal structure analyses. *J. Appl. Crystallogr.* **28** (1995) 659.