Acta Cryst. (1996). C**52**, 3225–3227

Trinitrophloroglucinol

J. Jens Wolff,[a] Frank Gredel,[a] Hermann Irngartinger[a] and Thomas Dreier[b]

[a]*Organisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany, and* [b]*Physikalisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 253, D-69120 Heidelberg, Germany. E-mail: f60@ix.urz.uni-heidelberg.de*

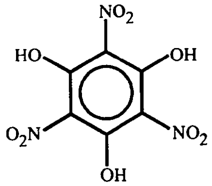
(*Received 2 May 1996; accepted 15 July 1996*)

Abstract

In contrast to the previously investigated hydrated form, anhydrous 2,4,6-trinitro-1,3,5-benzenetriol, $C_6H_3N_3O_9$, crystallizes in a non-centrosymmetric space group and shows non-linear optical activity in solution and in the solid state. The nitro groups are rotated out of the plane of the ring, the degree of twist being related to the number of intramolecular hydrogen bonds.

Comment

2,4,6-Trinitro-1,3,5-benzenetriol [(1), trinitrophloroglucinol] shows an unusually high second-order polarizability (high values of tensor β) in solution (Verbiest *et al.*, 1994). Anhydrous (1) also shows detectable second-harmonic generation efficiency (0.05 × urea) in the solid state. This activity is incompatible with the centrosymmetric space group $P\bar{3}c1$ which has been reported as a result of an X-ray crystal structure analysis of (1).2/3H_2O (Pierce-Butler, 1982; Hertel & Schneider, 1931). We have, therefore, determined the crystal structure of anhydrous (1) and found that it crystallizes in the non-centrosymmetric space group $P2_1$. The molecular structure of (1) is shown in Fig. 1.



(1)

The average C—O bond length [1.319 (3) Å] is a little shorter than that found in unconjugated phenols [normally about 1.364 (15) Å; Orpen *et al.*, 1994]. The average C—C bond distances of the six-membered ring are the same for both forms [1.405 (3) Å] and are slightly larger than those found in benzene derivatives [1.397 (9) Å; Orpen *et al.*, 1994]. This larger value is reasonable owing to the increased substitution and increased probability of conjugation. In both forms of (1), with and without crystal water, the shortest C—C bonds [(1) 1.384 (3), 1.390 (3) Å; (1).2/3H_2O 1.386 (3) Å] are adjacent to C6 bonded to the nitro group which is twisted most out of the plane of the ring.

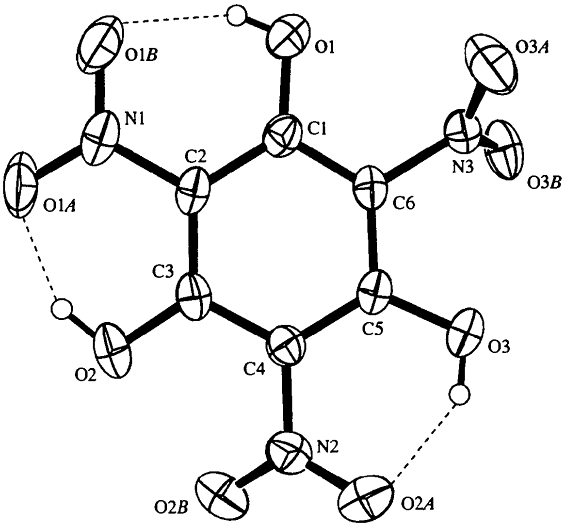


Fig. 1. View of 2,4,6-trinitro-1,3,5-benzenetriol (1) with atomic labelling. Displacement ellipsoids are shown at the 50% probability level.

The nitro groups are twisted differently with respect to the ring plane: in anhydrous (1), the nitro group bonded to C6 is rotated by 61 (3)° [63° for (1).2/3H_2O], the one at C4 is twisted by 23 (3)° [7° for (1).2/3H_2O] and the one at C2 remains coplanar. The larger the rotation angle, the longer the corresponding C—N bond

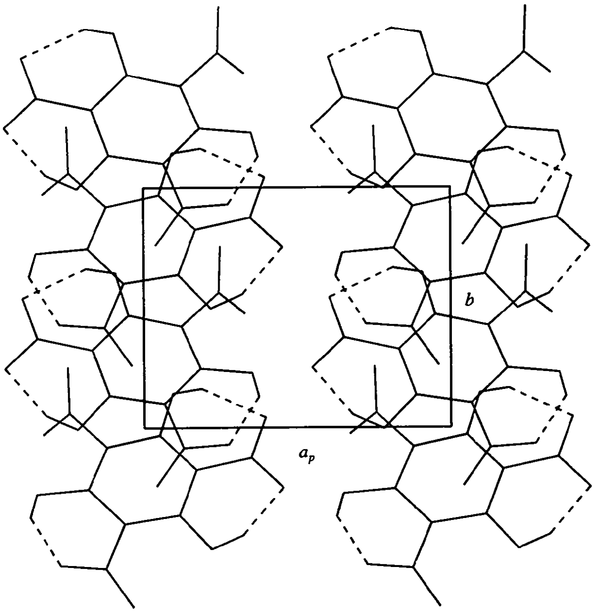


Fig. 2. Crystal-packing arrangement of compound (1) viewed along the *c* axis (a_p = a.cosβ).

(Table 2) as a result of diminished conjugation. The amount of twist is also related to the number of intramolecular hydrogen bonds (Table 3). In contrast to the nitro group at C6, the remaining two nitro groups form intramolecular hydrogen bonds. They are forced towards coplanarity by one (O3—H3···O2*A*) and two (O1—H1···O1*B*, O2—H2···O1*A*) hydrogen bonds, respectively.

The benzene ring deviates slightly from planarity with a sum of absolute torsion angles of 16.6 (3)°. The degree of twisting is twice as large as in the corresponding ring of (1).2/3H_2O (8.4°). The increase in C—C—C bond angles (Table 2) at acceptor-substituted C atoms and the decrease at donor-substituted C atoms is consistent with previous observations (Domenicano, 1992).

Fig. 2 illustrates the packing arrangement within the unit cell of (1). The molecules are arranged in a nearly centrosymmetrical manner. This explains why the non-linear optical activity of (1) in the solid state is only moderate.

Experimental

Crystals of (1) were obtained by sublimation [403 K/0.1 Torr (1×10^2 Pa); Wolff & Limbach, 1991]. **Caution:** impure (1) may explode under these conditions. Only samples of (1) prepurified by crystallization from water may be used.

Crystal data

$C_6H_3N_3O_9$
$M_r = 261.11$
Monoclinic
$P2_1$
$a = 8.397$ (1) Å
$b = 6.083$ (1) Å
$c = 9.671$ (1) Å
$\beta = 111.53$ (1)°
$V = 459.5$ (2) Å^3
$Z = 2$
$D_x = 1.89$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 75 reflections
$\theta = 10$–16°
$\mu = 0.172$ mm^{-1}
$T = 293$ K
Prism
0.45 × 0.45 × 0.35 mm
Light yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1276 measured reflections
1202 independent reflections
1071 observed reflections [$I > 2.5\sigma(I)$]

$R_{\rm int} = 0.029$
$\theta_{\rm max} = 27.97°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 8$
$l = -12 \rightarrow 11$
3 standard reflections monitored every 100 reflections intensity decay: 0.74%

Refinement

Refinement on F^2
$R(F) = 0.037$
$wR(F^2) = 0.047$
$S = 2.3$
1071 reflections
174 parameters
H atoms refined isotropically
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0009F_o^4]$

$(\Delta/\sigma)_{\rm max} = 0.024$
$\Delta\rho_{\rm max} = 0.242$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.270$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1*A*	−0.4520 (2)	0.2493 (5)	0.5854 (2)	0.0622 (6)
O1*B*	−0.3954 (2)	−0.0422 (4)	0.7197 (2)	0.0585 (6)
O1	−0.0934 (2)	−0.1445 (3)	0.8838 (2)	0.0467 (4)
O2*A*	0.2754 (2)	0.5690	0.6506 (2)	0.0647 (6)
O2*B*	0.0390 (2)	0.7419 (4)	0.6053 (2)	0.0542 (5)
O2	−0.2175 (2)	0.5044 (4)	0.5759 (2)	0.0486 (5)
O3*A*	0.2490 (2)	−0.2561 (4)	0.9582 (2)	0.0588 (6)
O3*B*	0.3301 (2)	0.0257 (4)	1.0983 (2)	0.0481 (5)
O3	0.3523 (2)	0.2726 (4)	0.8545 (2)	0.0473 (5)
N1	−0.3476 (2)	0.1250 (4)	0.6733 (2)	0.0416 (5)
N2	0.1278 (2)	0.5827 (4)	0.6519 (2)	0.0405 (5)
N3	0.2441 (2)	−0.0618 (4)	0.9813 (2)	0.0341 (4)
C1	−0.0503 (2)	0.0303 (4)	0.8240 (2)	0.0319 (5)
C2	−0.1685 (2)	0.1745 (4)	0.7220 (2)	0.0327 (5)
C3	−0.1125 (2)	0.3637 (4)	0.6676 (2)	0.0321 (5)
C4	0.0660 (2)	0.3989 (4)	0.7118 (2)	0.0307 (5)
C5	0.1839 (2)	0.2537 (4)	0.8099 (2)	0.0313 (5)
C6	0.1224 (2)	0.0780 (4)	0.8675 (2)	0.0306 (5)

Table 2. *Selected geometric parameters (Å, °)*

O1*A*—N1	1.231 (3)	N1—C2	1.433 (2)
O1*B*—N1	1.237 (3)	N2—C4	1.441 (3)
O1—C1	1.323 (3)	N3—C6	1.467 (2)
O2*A*—N2	1.247 (3)	C1—C2	1.418 (3)
O2*B*—N2	1.204 (3)	C1—C6	1.384 (3)
O2—C3	1.312 (3)	C2—C3	1.415 (3)
O3*A*—N3	1.206 (3)	C3—C4	1.416 (3)
O3*B*—N3	1.219 (2)	C4—C5	1.404 (3)
O3—C5	1.323 (2)	C5—C6	1.390 (3)
C2—C1—C6	118.0 (2)	C3—C4—C5	121.0 (2)
C1—C2—C3	121.2 (2)	C4—C5—C6	118.7 (2)
C2—C3—C4	118.0 (2)	C1—C6—C5	122.8 (2)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O1*B*	0.75 (2)	1.87 (2)	2.527 (2)	146 (3)
O2—H2···O1*A*	0.88 (4)	1.75 (5)	2.535 (3)	148 (4)
O3—H3···O2*A*	0.83 (4)	1.86 (4)	2.574 (2)	144 (3)

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1988). Cell refinement: *CAD*-4 *Software*. Data reduction: *PROCESS MolEN* (Fair, 1990). Program(s) used to solve structure: direct methods (*SIR*; Burla *et al.*, 1989). Program(s) used to refine structure: *LSFM MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

We thank the Deutsche Forschungsgemeinschaft for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1389). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.
Domenicano, A. (1992). *Accurate Molecular Structures*, edited by A. Domenicano & I. Hargittai, p. 437. New York: Oxford University Press.
Enraf–Nonius (1988). *CAD*-4 *Operations Manual*. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Hertel, E. & Schneider, K. (1931). *Z. Phys. Chem. Abt. B*, **12**, 139–150.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1994). *Structure Correlation*, Vol. 2, edited by H.-B. Bürgi & J. D. Dunitz, Appendix *A*. Weinheim: VCH.
Pierce-Butler, M. A. (1982). *Acta Cryst.* B**38**, 3097–3100.
Verbiest, T., Clays, K., Samyn, C., Wolff, J. J., Reinhoudt, D. & Persoons, A. (1994). *J. Am. Chem. Soc.* **116**, 9320–9323.
Wolff, J. J. & Limbach, H.-H. (1991). *Liebigs Ann. Chem.* pp. 691–693.

Acta Cryst. (1996). C**52**, 3227–3229

(*S*),(*E*)-5-Methoxycarbonyl-2-triphenylmethylaminohex-4-en-4-olide†

Vassilios Nastopoulos,[a] Constantinos Athanassopoulos,[a] Dionissios Papaioannou[a] and Enrico Gavuzzo[b]

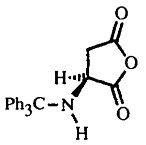
[a]*Department of Chemistry, University of Patras, Gr 265 00 Patras, Greece, and* [b]*Istituto di Strutturistica Chimica, CNR, CP no. 10, 00016 Monterotondo Stazione, Roma, Italy. E-mail: nastopoulos@upatras.gr*

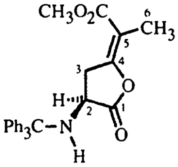
(*Received 19 June 1996; accepted 10 September 1996*)

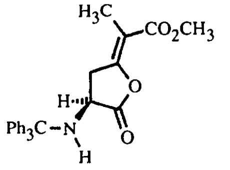
Abstract

The title compound, $C_{27}H_{25}NO_4$, is the major product of the Wittig reaction of (*S*)-*N*-triphenylmethylaspartic anhydride with the stabilized ylide $Ph_3P{=}C(Me)CO_2Me$. The crystal structure determination unambiguously confirms the *E* configuration of the C4═C5 double bond and shows that the molecule, with the exception of the triphenylmethylamino moiety, adopts an overall planar conformation.

Comment


(1)


(2)


(3)

We have recently shown that the readily available (*S*)-*N*-triphenylmethylaspartic anhydride, (1), can be applied in the asymmetric synthesis of amino acid and peptide derivatives through its reactions with a variety of nucleophiles (Athanassopoulos, Tzavara, Papaioannou, Sindona & Maia, 1995). In particular, Wittig reaction of the anhydride (1) with the stabilized ylide $Ph_3P{=}C(Me)CO_2Me$ produces a mixture of the isomeric enollactones (2) and (3) in the ratio 6:1.7. The assignment of the configuration of their C═C double bond was based solely on the magnitude of the homoallylic couplings between the H(C3) and H(C6) protons. In this paper, we describe the crystal structure of the title enollactone, (2), which shows unambiguously that the C4═C5 double bond of the major product of the above-mentioned Wittig reaction has the *E* configura-

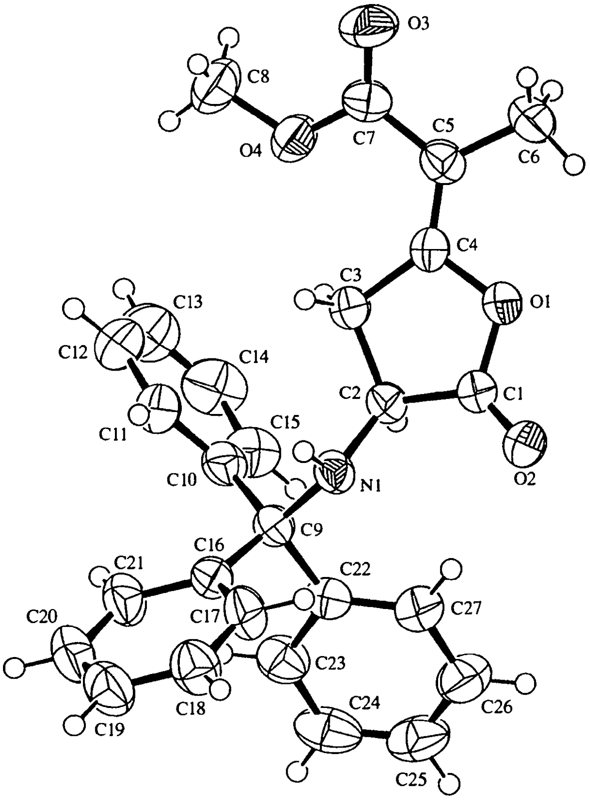


Fig. 1. Molecular structure with atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary size.

---

† Alternative nomenclature: methyl 2-[2-oxo-3-(triphenylmethylamino)-tetrahydrofuran-5-ylidene]propanoate.