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Acta Cryst. (1999). **C55**, 1918–1920

4-Triethylammoniomethyl-1,3-dioxolane-2-spiro-1′-2′,4′,6′-trinitrocyclohexadienide

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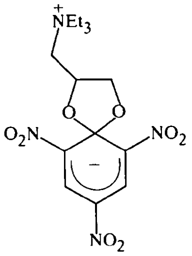
(*Received 24 May 1999; accepted 5 July 1999*)

Abstract

In molecules of the title compound, $C_{15}H_{22}N_4O_8$, the geometry of the six-membered ring is typical for Meisenheimer complexes of 2,4,6-trinitrobenzene. However, the difference between the C—N bond lengths to the nitro groups in *para* and *ortho* positions with respect to the saturated C atom is less pronounced than in related compounds.

Comment

Recently, it was demonstrated that dipolar spirocyclic Meisenheimer complexes play an important role in the chemistry of heterocyclic compounds (Knyazev & Drozd, 1995). Special attention is paid to compounds containing tropylium as an intramolecular cation due to their potential for acylotropic tautomerism (Kurbatov *et al.*, 1997). The structures of a few such σ complexes of derivatives of 2,4,6-trinitrobenzene were previously determined using X-ray diffraction (Furmanova *et al.*, 1980; Olekhnovich *et al.*, 1982). Now we report the result of the X-ray investigation of another type of zwitterionic Meisenheimer complex (1).



(1)

The six-membered ring C1–C6 is planar to within 0.019 Å. The C4—C5 [1.377 (7) Å] and C5—C6 [1.369 (7) Å] bond lengths are equal within one standard deviation. The C2—C3 [1.353 (7) Å] and C3—C4 [1.402 (7) Å] distances are approximately 0.02 Å shorter and longer, respectively, than the mean of the C4—C5 and C5—C6 distances. This bond length distribution within the six-membered ring of (1) differs from those previously in other dipolar and intermolecular Meisenheimer complexes of 2,4,6-trinitrobenzene (Furmanova *et al.*, 1980; Olekhnovich *et al.*, 1982; Borbulevych *et al.*, 1998) in which the C2—C3 and C5—C6 bonds are considerably shorter than C3—C4 and C4—C5.

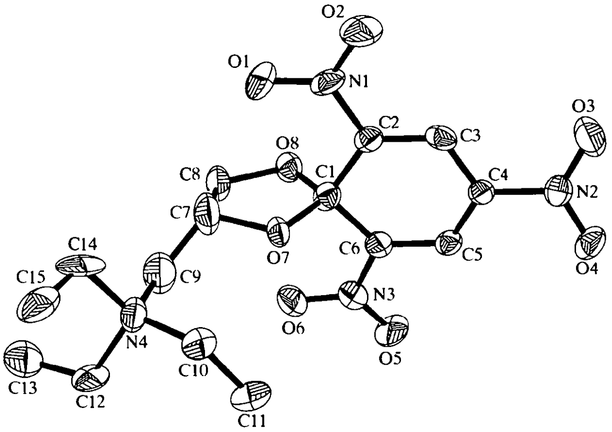


Fig. 1. View of the title compound. The non-H atoms are shown with displacement ellipsoids drawn at the 50% probability level and the H atoms have been omitted for clarity.

In (1) the C—N bond lengths to the nitro groups are equal within two standard deviations (Table 1), while in the Meisenheimer complex of 2,4,6-trinitrobenzene with potassium as the cation (Borbulevych *et al.*, 1998), considerable shortening of the C—N bond [1.418 (2) Å] *para* to the saturated C atom [compared with 1.438 (2) and 1.434 (2) Å for the two other bonds] was observed. On the other hand, in some dipolar σ-complexes with tropylium cations (Furmanova *et al.*, 1980; Olekhnovich *et al.*, 1982) the difference between the C—N bond lengths is less pronounced.

The nitro groups in (1) are almost coplanar with the plane of the C1–C6 ring: the O1—N1—C2—C1, O3—N2—C4—C3 and O6—N3—C6—C1 torsion angles are −2.7 (7), −9.8 (7) and −3.9 (8)°, respectively, in spite of the presence of intramolecular short contacts O1···C8 2.971 (8), O1···C7 2.803 (9), O1···H7 2.28, O2···H3 2.33, O3···H3 2.43, O4···H5 2.44, O5···H5 2.33, O6···C8 2.904 (8) Å, where the sum of the corresponding van der Waals radii (Zefirov & Zorky, 1989) is 3.00 Å for O and C, and 2.45 Å for O and H.

The five-membered ring in (1) has an envelope conformation: the deviation of the flap atom C7 from the plane of the other atoms of this ring is 0.25 (1) Å. The angle between the least-squares planes of the six- and five-membered rings is 87.5 (2)°. The substituent on C7 has an equatorial orientation and the N4—C9 bond is synclinal with respect to the C7—O7 bond.

The presence of the bulky cation gives rise to short intramolecular contacts between its atoms and those of dioxolane ring: O7···C10 2.914 (7), O7···H10*B* 2.36, C7···H10*B* 2.78 and C14···H7 2.84 Å, where the sum of the corresponding van der Waals radii is 3.00 Å for O and C, and 2.87 Å for C and H.

Experimental

Compound (1) was prepared according to a known procedure (Knyazev & Drozd, 1996). Crystals of (1) were obtained by isothermal evaporation of a solution of (1) in acetonitrile.

Crystal data

$C_{15}H_{22}N_4O_8$
$M_r = 386.37$
Monoclinic
$P2_1/c$
$a = 7.879\ (3)$ Å
$b = 10.971\ (6)$ Å
$c = 19.831\ (9)$ Å
$\beta = 91.20\ (3)°$
$V = 1713.9\ (13)$ Å^3
$Z = 4$
$D_x = 1.497$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 10–11°$
$\mu = 0.122$ mm^{-1}
$T = 193\ (2)$ K
Needle
0.55 × 0.25 × 0.20 mm
Red

Data collection

Syntex $P2_1$/PC diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3223 measured reflections
2996 independent reflections
1256 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.079$
$\theta_{\max} = 25.05°$
$h = -3 \rightarrow 9$
$k = -12 \rightarrow 13$
$l = -23 \rightarrow 23$
2 standard reflections every 98 reflections intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.077$
$wR(F^2) = 0.172$
$S = 1.177$
2940 reflections
247 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1024P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.55$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—C2	1.428 (7)	N4—C14	1.548 (8)
N2—C4	1.444 (7)	O7—C1	1.429 (6)
N3—C6	1.430 (7)	O7—C7	1.456 (7)
N4—C9	1.537 (8)	O8—C1	1.414 (6)
N4—C10	1.518 (7)	O8—C8	1.444 (6)
N4—C12	1.516 (7)		
C1—O7—C7	109.0 (4)	C5—C4—C3	120.9 (5)
C1—O8—C8	109.9 (4)	C6—C5—C4	120.3 (5)
O8—C1—O7	108.0 (4)	C5—C6—C1	125.9 (5)
C6—C1—C2	107.3 (4)	O7—C7—C8	104.9 (4)
C3—C2—C1	125.1 (5)	O8—C8—C7	105.6 (4)
C2—C3—C4	120.4 (5)		
C8—O8—C1—O7	−1.9 (6)	C2—C1—C6—C5	4.6 (7)
C7—O7—C1—O8	−8.9 (6)	C2—C3—C4—C5	3.9 (8)
C1—O7—C7—C8	15.4 (7)	C3—C4—C5—C6	−2.7 (8)
C1—O8—C8—C7	11.3 (6)	C4—C5—C6—C1	−2.0 (8)
C6—C1—C2—C3	−3.4 (7)	O7—C7—C8—O8	−16.1 (7)

The high value of *R* is attributed to the relatively poor quality of the crystal resulting in a weak set of data.

Data collection: *P*3 (Siemens, 1989). Cell refinement: *P*3 (Siemens, 1989). Data reduction: *XDISK* (Siemens, 1991). Program(s) used to solve structure: *SHELXTL-Plus/PC*. Program(s) used to refine structure: *SHELXTL-Plus/PC*. Molecular graphics: *SHELXTL-Plus/PC*. Software used to prepare material for publication: *SHELXTL-Plus/PC*.

This work was supported by the Russian Foundation for Basic Research (grant Nos. 97–03–33783 and 96–15–97367) and International Fund 'Vidrodzhennya' (grant No. YSU 083067)

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1348). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1920–1921

2-(3,5-Dinitropyridyl-2-oxy)-3,5,7-trimethylcyclohepta-2,4,6-trien-1-one

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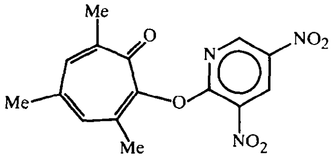
(*Received 24 May 1999; accepted 5 July 1999*)

Abstract

The molecules of the title compound, $C_{15}H_{13}N_3O_6$, exist in the ring-opened form. The seven-membered ring is considerably twisted with respect to the pyridine ring, the angle between the least-squares planes of these rings being 66.51 (8)°.

Comment

Compounds such as the title compound, (I), are of great interest because of their ability to undergo acylotropic tautomerism (Knyazev & Drozd, 1995; Kurbatov *et al.*, 1997). For example, in solution, (I) exhibits fast and reversible migration of the heteroaryl group (Olekhnovich *et al.*, 1985). The intermediate in this nucleophilic rearrangement is a dipolar spirocyclic Meisenheimer complex containing tropylium (cycloheptatrienylium) as an intramolecular cation. Such a situation gives rise to an equilibrium between the ring-opened and ring-closed isomers in solution and their interrelation is determined by many factors (Olekhnovich *et al.*, 1994). In several cases in the literature, the ring-closed form of such zwitterionic Meisenheimer complexes was observed in the crystal phase (Furmanova *et al.*, 1980; Olekhnovich *et al.*, 1982). The aim of the present X-ray study is to establish the structural isomer of (I) in the crystal.



(I)

In the crystal phase, molecules of (I) exist in the ring-opened form. The seven-membered ring is considerably twisted with respect to the pyridine ring, probably due to the presence of short intramolecular contacts: N1···C7 = 2.947 (3) and O6···C1 = 2.722 (3) Å (the corresponding sums of the van der Waals radii are 3.21 and 3.00 Å, respectively; Zefirov & Zorky, 1989). The angle between the least-squares planes of these rings is 66.51 (8)°.

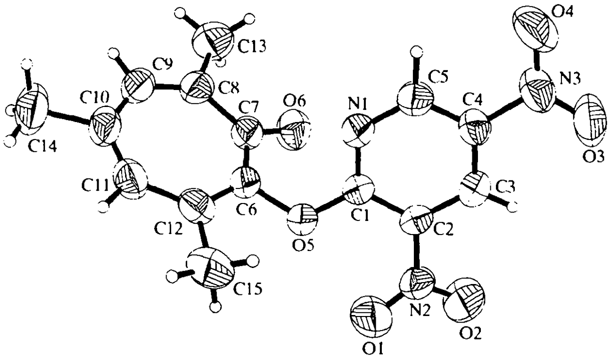


Fig. 1. View of the title compound, with displacement ellipsoids drawn at the 50% probability level and H atoms shown as small circles of arbitrary radius.

The nitro groups in (I) are somewhat twisted with respect to the plane of the pyridine ring: the O1—N2—C2—C1 and O4—N3—C4—C5 torsion angles are −16.3 (4) and −14.1 (4)°, respectively.

According to the bond-length distribution, no conjugation is present within the seven-membered ring. The C8—C9 [1.356 (4)], C10—C11 [1.349 (4)] and C6—C12 [1.359 (3) Å] distances are considerably shorter than the other bonds of the ring, indicating that the double bonds are localized.

Experimental

Compound (I) was prepared according to the procedure of Olekhnovich *et al.* (1985), and crystals suitable for X-ray analysis were obtained by isothermal evaporation from a solution of (I) in nitromethane.