

Table 1. Selected geometric parameters (Å, °)

B1—O1	1.363 (2)	N3—C4	1.287 (2)
C6—O6	1.368 (2)	C4a—C8a	1.399 (2)
N2—N3	1.3930 (19)	C4—C4a	1.449 (2)
N2—C9	1.422 (2)	C8a—B1	1.529 (3)
B1—N2	1.455 (2)		
N3—N2—C9	111.99 (13)	C8—C8a—B1	124.45 (14)
N3—N2—B1	122.73 (14)	C4a—C8a—B1	117.93 (14)
C9—N2—B1	125.26 (14)	O1—B1—N2	121.79 (16)
C4—N3—N2	118.01 (13)	C8a—B1—O1	122.04 (15)
N3—C4—C4a	127.65 (15)	N2—B1—C8a	116.17 (14)
C8a—C4a—C4	117.49 (15)		
C9—N2—N3—C4	-177.96 (15)	C14—O13—C13—N14	-2.2 (3)
B1—N2—N3—C4	0.5 (2)	O1—B1—N2—C9	-0.8 (3)
N2—N3—C4—C4a	-0.7 (3)	C8—C8a—B1—O1	-2.4 (3)
N3—C4—C4a—C8a	-0.4 (3)	C4a—C8a—B1—O1	178.11 (16)
C4—C4a—C8a—B1	1.4 (2)	C8—C8a—B1—N2	177.99 (15)
N3—N2—C9—N14	-179.52 (13)	C4a—C8a—B1—N2	-1.5 (2)
B1 N2 C9 N14	2.1 (2)		

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O1—H1...N14	0.82	1.89	2.599 (2)	144
O6—H6A...O6 ⁱ	0.82 (2)	1.90 (5)	2.699 (2)	163 (5)
O6—H6B...O15 ⁱⁱ	0.84 (2)	1.92 (4)	2.754 (3)	167 (5)
O15—H15A...O1	0.82 (3)	2.02 (3)	2.833 (3)	171 (3)
O15—H15B...O15 ⁱⁱⁱ	0.78 (3)	2.57 (4)	2.751 (3)	95 (3)

Symmetry codes: (i) 2 - x, -y, -1 - z; (ii) 2 - x, 1 - y, -1 - z; (iii) 2 - x, 2 - y, -z.

Fourier maps and the circular Fourier hydrogen-locating method available in *SHELXL97* (Sheldrick, 1997) both strongly indicated that the H(O6) atom was split over two sites. The two positions, designated H6A and H6B, were refined with fixed isotropic displacement factors and restrained O—H distances. In addition, the sum of their site occupancies was constrained to equal 1.0 resulting in occupancy values of 0.52 (3) and 0.48 (3), respectively. Sites H15A and H15B were refined in a similar manner although no site occupancy refinement was required. All other H atoms are riding. The rotational orientation of the methyl group was refined by the circular Fourier method available in *SHELXL97* (Sheldrick, 1997).

Data collection: *MSCI/AFD Diffractometer Control Software* (Molecular Structure Corporation, 1996). Cell refinement: *MSCI/AFD Diffractometer Control Software*. Data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1997). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *LS* in *TEXSAN* and *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEP* (Johnson, 1965) in *TEXSAN*. Software used to prepare material for publication: *TEXSAN*, *SHELXL97* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1557). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). **C55**, 1704–1706

A zwitterionic Meisenheimer complex of 2,4,6-trinitrobenzene

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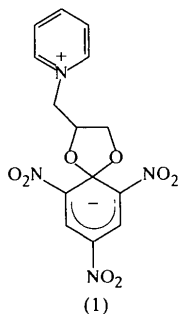
Abstract

In molecules of the zwitterionic Meisenheimer complex 4-(*N*-pyridiniummethyl)-1,3-dioxolane-2-spiro-1'-2',4',6'-trinitrocyclohexadienide (C₁₄H₁₂N₄O₈), the nitro groups do not possess equivalent geometries. The C—N bond to the nitro group *para* to the saturated C atom is shorter than those of the others, and bond lengths vary

considerably between the two unsaturated sections of the six-membered ring. These observations indicate a significant contribution from a resonance form in which the six-membered ring has a 2,5-diene geometry and the *para* nitro adopts the *aci* resonance form.

Comment

The formation of Meisenheimer complexes is a key stage in nucleophilic aromatic substitution (S_NAr) reactions (Artamkina *et al.*, 1982; Buncl *et al.*, 1995). Such intermediates are converted to various products depending on the structure and electron-density distribution of the organic anion (Artamkina *et al.*, 1990; Buncl *et al.*, 1995; Knyazev & Drozd, 1995; Knyazev *et al.*, 1999*a,b*; Terrier, 1982). This has led to continuing interest in the molecular structure of Meisenheimer complexes. The majority of previous structural studies concerned compounds where the cation was an alkali metal ion. However, zwitterionic Meisenheimer complexes have been shown to play an important role in the chemistry of heterocyclic compounds (Knyazev & Drozd, 1995) and only a few structures of such compounds have been determined using X-ray diffraction methods. These contain tropylium as the intramolecular cation (Furmanova *et al.*, 1980; Olekhovich *et al.*, 1982). Now we report the result of an X-ray investigation of a zwitterionic Meisenheimer complex with pyridinium, (1).



The six-membered ring C1–C6 in (1) adopts a sofa conformation; the deviation of C1 from the plane of the rest of the atoms of the ring is 0.096 (2) Å. The C3–C4 [1.399 (2) Å] and C4–C5 [1.396 (2) Å] bond lengths are significantly longer than the C2–C3 [1.357 (2) Å] and C5–C6 [1.365 (2) Å] distances.

The nitro groups in molecule (1) are significantly different. The C4–N2 bond [1.424 (2) Å] is slightly shorter than the C–N bonds of the nitro groups lying *ortho* to the saturated C atom C1 [C2–N1 1.444 (2), C6–N3 1.435 (2) Å]. Moreover, C–C bond lengths vary considerably between the two unsaturated sections of the six-membered ring; the C1–C2 [1.510 (2) Å] and C1–C6 [1.514 (2) Å] distances being far longer than

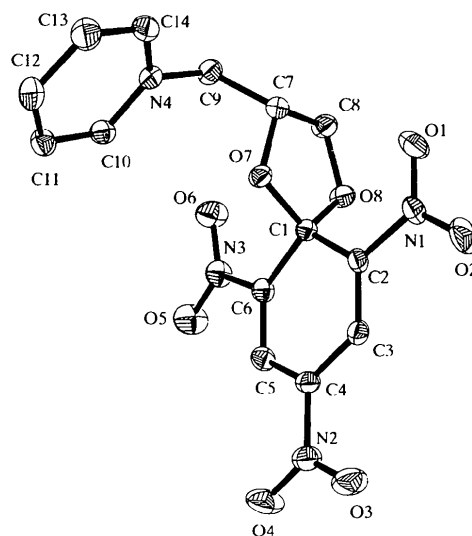
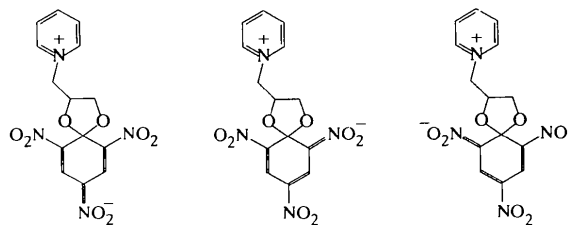


Fig. 1. View of the title compound. The non-H atoms are shown with displacement ellipsoids drawn at the 50% probability level and H atoms have been omitted for clarity.

the C3–C4 [1.399 (2) Å] and C4–C5 [1.396 (2) Å] distances. These observations indicate that the resonance form (see below) in which the six-membered ring has a 2,5-diene geometry and the *para* nitro adopts the *aci* resonance form makes a major contribution to the overall structure of the molecule. Similar results were obtained for other Meisenheimer complexes of 2,4,6-trinitrobenzene (Borbulevych *et al.*, 1998; Furmanova *et al.*, 1980).



The nitro groups in (1) are nearly coplanar with the C1–C6 ring [the O1–N1–C2–C1, O3–N2–C4–C3 and O6–N3–C6–C1 torsion angles are 1.4 (2), 3.1 (2) and –6.8 (2)°, respectively] in spite of the presence of short intramolecular contacts: O1···C7 2.868 (2) (van der Waals radii sum is 3.00 Å; Zefirov & Zorky, 1989), O1–C8 2.926 (2), O6–C8 2.949 (2), O2···H3 2.33 (2) (2.45), O3···H3 2.38 (2) and O5···H5 2.34 (2) Å.

The dioxolane ring in (1) adopts an envelope conformation with C7 displaced from the plane of the remaining ring atoms by –0.191 (2) Å. The dihedral angle between the least-squares mean planes of the five- and six-membered rings is 87.40 (5)°.

The substituent on C7 has an equatorial orientation [the C9—C7—O7—C1 torsion angle is 134.1 (1)°]. The pyridinium ring is rotated about the C7—C9 bond as shown by the C10—N4—C9—C7 torsion angle of -97.0 (1)°. The N4—C9 bond has +*sc* orientation with respect to the C7—O7 bond [the N4—C9—C7—O7 torsion angle is 43.5 (1)°].

Experimental

Crystals of (1) were obtained by evaporation of solvent from a solution of (1) in acetonitrile at ambient temperature.

Crystal data

C₁₄H₁₂N₄O₈

M_r = 364.28

Monoclinic

*C*2/*c*

a = 13.336 (3) Å

b = 13.837 (3) Å

c = 16.059 (4) Å

β = 98.51 (2)°

V = 2930.8 (12) Å³

Z = 8

D_x = 1.651 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 24 reflections

θ = 10–11°

μ = 0.138 mm⁻¹

T = 193 (2) K

Square prism

0.60 × 0.40 × 0.40 mm

Red

Data collection

Syntax *P2/PC* diffractometer

θ/2θ scans

Absorption correction: none

4456 measured reflections

4289 independent reflections

3202 reflections with

I > 2σ(*I*)

R_{int} = 0.041

θ_{max} = 30.06°

h = 0 → 18

k = 0 → 19

l = -22 → 22

2 standard reflections

every 98 reflections

intensity decay: 5%

Refinement

Refinement on *F*²

R [*F*² > 2σ(*F*²)] = 0.044

wR (*F*²) = 0.118

S = 1.103

4212 reflections

283 parameters

All H-atom parameters

refined

w = 1/[σ²(*F_o*²) + (0.0871*P*)²]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.001

Δρ_{max} = 0.42 e Å⁻³

Δρ_{min} = -0.25 e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

O1—N1—O2	121.81 (11)	C1—O8—C8	111.04 (9)
O1—N1—C2	119.30 (11)	C2—C1—C6	107.91 (9)
O2—N1—C2	118.90 (11)	C3—C2—C1	125.57 (11)
O3—N2—O4	121.92 (12)	C2—C3—C4	120.33 (11)
O3—N2—C4	118.99 (11)	C5—C4—C3	120.25 (11)
O4—N2—C4	119.08 (11)	C6—C5—C4	120.25 (11)
O5—N3—O6	122.02 (11)	C5—C6—C1	125.25 (11)
O5—N3—C6	118.99 (11)	O7—C7—C9	109.11 (10)
O6—N3—C6	118.99 (11)	O7—C7—C8	104.57 (10)
C10—N4—C9	118.75 (11)	C9—C7—C8	113.12 (11)
C14—N4—C9	120.42 (11)	O8—C8—C7	105.48 (10)
C7—O7—C1	110.67 (9)		
C8—O8—C1—O7	1.2 (1)	C4—C5—C6—C1	-1.3 (2)
C7—O7—C1—O8	-9.2 (1)	C2—C1—C6—C5	6.1 (2)
C6—C1—C2—C3	-7.0 (2)	C1—O7—C7—C8	12.8 (1)
C1—C2—C3—C4	3.1 (2)	C1—O8—C8—C7	6.4 (1)
C2—C3—C4—C5	2.8 (2)	O7—C7—C8—O8	-11.5 (1)
C3—C4—C5—C6	-3.7 (2)		

Data collection: *P3* (Siemens, 1989). Cell refinement: *P3*. Data reduction: *XDISK* (Siemens, 1991). Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

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Table 1. Selected geometric parameters (Å, °)

N1—O1	1.2336 (15)	O7—C7	1.4318 (14)
N1—O2	1.2395 (15)	O7—C1	1.4413 (14)
N1—C2	1.444 (2)	O8—C1	1.4247 (14)
N2—O3	1.237 (2)	O8—C8	1.430 (2)
N2—O4	1.244 (2)	C1—C2	1.510 (2)
N2—C4	1.424 (2)	C1—C6	1.514 (2)
N3—O5	1.239 (2)	C2—C3	1.357 (2)
N3—O6	1.240 (2)	C3—C4	1.399 (2)
N3—C6	1.435 (2)	C4—C5	1.396 (2)
N4—C10	1.349 (2)	C5—C6	1.365 (2)
N4—C14	1.352 (2)	C7—C8	1.540 (2)
N4—C9	1.486 (2)		