Triclinic
$P\bar{1}$
$a = 12.984\ (7)$ Å
$b = 13.034\ (5)$ Å
$c = 16.749\ (8)$ Å
$\alpha = 82.04\ (3)^\circ$
$\beta = 72.31\ (4)^\circ$
$\gamma = 87.45\ (4)^\circ$
$V = 2674\ (2)$ Å^3
$Z = 4$
$D_x = 1.494$ Mg m^{-3}
D_m not measured

Cell parameters from 22 reflections
$\theta = 10\text{–}11^\circ$
$\mu = 0.121$ mm^{-1}
$T = 213\ (2)$ K
Parallelepiped
0.30 × 0.30 × 0.20 mm
Yellow

Data collection

Syntex $P2_1$/PC diffractometer
ω scans
Absorption correction: none
9781 measured reflections
9325 independent reflections
4276 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.074$
$\theta_{\rm max} = 25^\circ$
$h = 0 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = -18 \rightarrow 19$
2 standard reflections every 98 reflections intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.178$
$S = 1.154$
9322 reflections
793 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.092P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.027$
$\Delta\rho_{\rm max} = 0.81$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.45$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	H···*A*	*D*—H···*A*
O1*W*—H1*WA*···O1*A*$^{\rm i}$	1.90	158
O1*W*—H1*WB*···O1*B*$^{\rm i}$	1.86	159
O2*W*—H2*WA*···O1*C*	1.76	173
O2*W*—H2*WB*···O2*D*	1.95	168
O2*SA*—H2*SA*···O1*W*	1.74	176
O2*SB*—H2*SB*···O2*W*	1.68	172

Symmetry code: (i) $1 - x, 1 - y, -z$.

Data collection: *P*3 (Siemens, 1989*a*). Cell refinement: *P*3. Data reduction: *XDISK* (Siemens, 1989*b*). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1342). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1915–1918

2,3-Dihydro-3-methyl-2′,4′,6′-trinitrospiro[1,3-thiazolotropylium-2,1′-cyclohexadienide]

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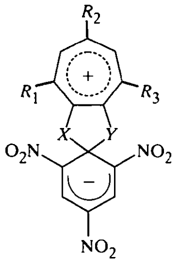
Abstract

In molecules of the title compound, $C_{14}H_{10}N_4O_6S$, 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 of the nitro groups *para* and *ortho* to the saturated C atom is less pronounced than in related compounds. There is significant conjugation between the seven-membered

ring and the heteroatoms of the five-membered ring, which gives rise to considerable shortening of the S—C and N—C bond lengths to the tropylium cation. In addition, *ab initio* calculations show that the S atom has a greater positive charge (0.48) than the total charge of the tropylium cation (0.34).

Comment

Meisenheimer complexes are important intermediates in nucleophilic aromatic substitution (SNAr) reactions (Artamkina *et al.*, 1982; Buncel *et al.*, 1995) because the products of such reactions depend strongly on the structure and electron-density distribution of the organic anion (Artamkina *et al.*, 1990; Buncel *et al.*, 1995; Knyazev & Drozd, 1995; Knyazev *et al.*, 1999; Terrier, 1982). The molecular structures of Meisenheimer complexes have accordingly attracted continuing attention. Whereas the majority of previous structural studies concerned compounds having alkali metal cations, dipolar spirocyclic Meisenheimer complexes containing tropylium as an intramolecular cation are shown to play an important role in the chemistry of heterocyclic compounds because of their ability to undergo acylotropic tautomerism (Knyazev & Drozd, 1995; Kurbatov *et al.*, 1997). However, the structures of only a few such σ-bonded complexes derived from 2,4,6-trinitrobenzene have been determined by X-ray diffraction (Furmanova *et al.*, 1980; Olekhnovich *et al.*, 1982). Compounds of this series have different combinations of heteroatoms [O,O (2), N,O (3) and N,N (4)] bonded to the spiro-C atom. Herein we report the result of the X-ray investigation of a dipolar Meisenheimer complex, (1), having N and S atoms as part of the five-membered ring.



(1) $X=S$, $Y=NMe$, $R_1=R_2=R_3=H$
(2) $X=Y=O$, $R_1=R_2=R_3=Me$
(3) $X=NH$, $Y=O$, $R_1=R_2=R_3=H$
(4) $X=Y=NH$, $R_1=R_2=R_3=H$

The six-membered C1–C6 ring in (1) adopts a sofa conformation, with C1 displaced from the plane of the remaining five atoms by 0.114 (5) Å (Fig. 1). The C3—C4 [1.401 (5) Å] and C4—C5 [1.380 (5) Å] bond lengths are longer than the C2—C3 [1.351 (5) Å] and C5—C6 [1.349 (5) Å] distances. Similar bond-length distributions within the six-membered ring were observed in molecules (2)–(4) (Furmanova *et al.*, 1980; Olekhnovich *et al.*, 1982) and in intermolecular σ complexes of 2,4,6-trinitrobenzene (Borbulevych *et al.*, 1998).

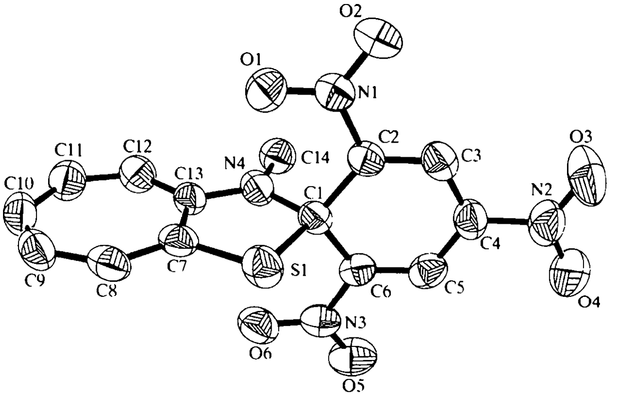


Fig. 1. View of the title compound. The non-H atoms are shown with displacement ellipsoids drawn at the 50% probability level and H atoms have been omitted for clarity.

In molecule (1), the difference between the C—N bond lengths of the nitro groups *para* [C4—N2 1.432 (5) Å] and *ortho* [C2—N1 1.450 (4) and C6—N3 1.442 (4) Å] to the saturated C atom is less pronounced than in Meisenheimer complexes of 2,4,6-trinitrobenzene with K^+ as the cation (Borbulevych *et al.*, 1998); a similar situation was found for molecules (2) and (3). However, in (4), the C—N bond in the *para* position is very short [1.407 (5) Å; Olekhnovich *et al.*, 1982], while those of the nitro groups in the *ortho* positions have the same lengths as in (1).

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 2.1 (4), 0.4 (5) and −3.6 (5)°, respectively], in spite of the presence of short intramolecular contacts (all in Å): O1···S1 = 3.078 (3) (van der Waals radii sum = 3.13; Zefirov & Zorky, 1989), O6···S1 = 3.090 (3), O1···N4 = 2.751 (4) (2.79), O6···N4 = 2.727 (4), O2···H3 = 2.322 (5) (2.45), O3···H3 = 2.429 (5), O5···H5 = 2.318 (5), O4···H5 = 2.425 (5) and O6···C13 = 2.920 (4) (3.00).

The five-membered ring in (1) adopts a very flattened envelope conformation, with the largest deviation from the least-squares mean plane of 0.012 (4) Å for N4. The molecule possesses a non-crystallographic mirror plane which passes through atoms N2, C4, C1, S1, C7–C13, N4 and C14; the dihedral angle between the five- and six-membered rings is 89.6 (1)°.

The S1—C7 bond [1.718 (4) Å] is considerably shorter than the average value of 1.773 Å for C_{aryl}—S and is very close to the C—S bond length of 1.712 Å in thiophene (Allen *et al.*, 1987). The N4—C13 bond length of 1.336 (4) Å is also shortened compared with the average value of 1.371 Å (Allen *et al.*, 1987).

These observations indicate strong conjugation between the π systems of the seven-membered ring and the lone pairs of the heteroatoms. This, in turn, should considerably influence positive charge distribution within the cationic part of the molecule, and this assumption was confirmed by non-empirical quantum-chemical calculations at the HF/6-31+G* level of theory using the *GAMESS* program (Schmidt *et al.*, 1993) and using the frozen geometry of (1) taken from the present X-ray diffraction study. The calculations demonstrate that the N4 and S1 atoms possess significant negative (−0.23) and positive (0.48) charges, respectively.

Within the seven-membered ring, the C—C bond distances are not equivalent. The C7—C8 [1.386 (5) Å], C8—C9 [1.384 (5) Å], C10—C11 [1.406 (6) Å] and C12—C13 [1.397 (5) Å] bond lengths are close to the typical value for C_{aryl}—C_{aryl}, while C9—C10 [1.341 (6) Å] and C11—C12 [1.352 (5) Å] are considerably shorter and C7—C13 [1.448 (5) Å] is longer. A similar bond distribution was found in the unsubstituted tropylium cation (Bruce *et al.*, 1986). Therefore, we can assume that this effect is an intrinsic property of the tropylium fragment rather than being induced by the influence of the heteroatoms.

Experimental

Compound (1) was prepared according to the procedure of Olekhnovich *et al.* (1982). Crystals were obtained by isothermal evaporation from a solution of (1) in nitromethane.

Crystal data

$C_{14}H_{10}N_4O_6S$
$M_r = 362.32$
Triclinic
$P\bar{1}$
$a = 7.250 (3)$ Å
$b = 9.938 (5)$ Å
$c = 11.169 (6)$ Å
$\alpha = 72.88 (4)°$
$\beta = 82.74 (4)°$
$\gamma = 83.40 (4)°$
$V = 760.3 (6)$ Å^3
$Z = 2$
$D_x = 1.583$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 10–11°$
$\mu = 0.256$ mm^{-1}
$T = 293 (2)$ K
Square prism
0.40 × 0.20 × 0.20 mm
Black

Data collection

Siemens *P*3 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3586 measured reflections
3314 independent reflections
1743 reflections with $I > 2\sigma(I)$
$R_{int} = 0.072$

$\theta_{max} = 27.06°$
$h = -4 \rightarrow 9$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 14$
2 standard reflections every 98 reflections intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.072$
$wR(F^2) = 0.163$
$S = 1.158$
3256 reflections
227 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1143P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.64$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S1—C1	1.890 (3)	N4—C1	1.485 (4)
S1—C7	1.718 (4)	N4—C13	1.336 (4)
N1—O1	1.220 (4)	C1—C6	1.500 (5)
N1—O2	1.229 (3)	C1—C2	1.507 (4)
N1—C2	1.450 (4)	C2—C3	1.351 (5)
N2—O3	1.218 (5)	C3—C4	1.401 (5)
N2—O4	1.243 (4)	C4—C5	1.380 (5)
N2—C4	1.432 (5)	C5—C6	1.349 (5)
N3—O5	1.238 (4)	C7—C8	1.386 (5)
N3—O6	1.230 (4)	C7—C13	1.448 (5)
N3—C6	1.442 (4)		
C7—S1—C1	93.3 (2)	C5—C4—C3	120.5 (3)
C13—N4—C1	119.8 (3)	C6—C5—C4	120.3 (3)
C6—C1—C2	108.3 (3)	C5—C6—C1	125.4 (3)
N4—C1—S1	102.0 (2)	C13—C7—S1	112.4 (2)
C3—C2—C1	124.9 (3)	N4—C13—C7	112.4 (3)
C2—C3—C4	120.1 (3)		
C6—C1—C2—C3	−8.3 (4)	C3—C4—C5—C6	−2.6 (5)
C1—C2—C3—C4	3.6 (5)	C4—C5—C6—C1	−3.5 (5)
C2—C3—C4—C5	2.5 (5)	C2—C1—C6—C5	8.3 (5)

The slightly elevated R_1 value of 0.072 is due to the rather poor crystal quality typical of Meisenheimer complexes.

Data collection: *P*3 (Siemens, 1989). Cell refinement: *P*3. 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*.

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: BM1341). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1918–1920

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

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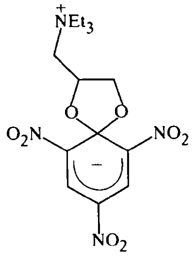
(*Received 24 May 1999; accepted 5 July 1999*)

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.

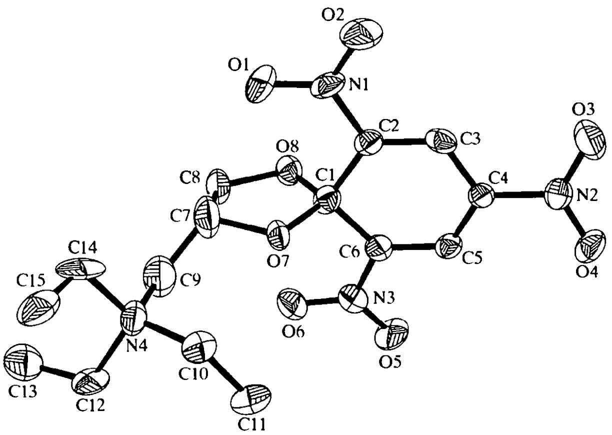


Fig. 1. View of the title compound. The non-H atoms are shown with displacement ellipsoids drawn at the 50% probability level and the H atoms have been omitted for clarity.