C7B—H6B···O2A	1.00	2.32	3.288 (2)	164
O1C—H1C···O1D	0.85	2.07	2.895 (2)	169
O1D—H1D···O2A	0.85	1.87	2.700 (2)	172
O1E—H1E···O3B	0.85	2.10	2.911 (12)	159
O1E—H2E···O1B'	0.85	2.13	2.933 (10)	159

Symmetry codes: (i) $1-x$, $\frac{1}{2}+y$, $1-z$; (ii) $-x$, $\frac{1}{2}+y$, $1-z$; (iii) $x-1,y,z$; (iv) $1+x,y,z$; (v) $1-x, y-\frac{1}{2}, 1-z$.

The structures of AF2p (α-form) and LF2p (β-form) were solved directly using *SHELXTL* (Sheldrick, 1997b). The cell dimensions are rather similar to those of LVe (a = 11.01, b = 23.52, c = 12.26 Å and β = 90.01°; Görbitz & Torgersen, 1999) and the unorthodox systematic absences are the same: $h00$, h = $4n$ + 2 absent; $0k0$, k = $2n$ + 1 absent; $00l$, l = $2n$ + 1 absent. The two structures proved to be isomorphous, and the structure of VF2p was solved in the same indirect manner as described previously for LVe (Görbitz & Torgersen, 1999). As observed for LVe (Görbitz & Torgersen, 1999), the VF2p crystal used for data collection was a TLQS (twin-lattice quasi-symmetry) twin (Giacovazzo *et al.*, 1992), which was effectively treated as TLS (twin-lattice symmetry) since all reflections contained intensity from both twin components. Crystal twinning for a monoclinic system emulating orthorhombic was handled by the *SHELXTL* command *TWIN* 1 0 0 0 −1 0 0 0 −1. The fractions of the two components are 0.576 (2) and 0.424 (2). Pairs of peptide molecules related by non-crystallographic screw axes were connected by tight *SAME* 0.0002 0.0004 commands, constraining equivalent bond lengths and bond angles (but not torsion angles) to be almost similar. This procedure was tested and discussed for refinement of LVe (Görbitz & Torgersen, 1999). Furthermore, U_{ii} (i = 1, 2 or 3) and U_{12} values are the same for A and C, and for B and D, while U_{13} and U_{23} values for C and D were constrained to be $-U_{13}$ and $-U_{23}$ for the corresponding atoms in A and B, respectively. Finally, milder *SAME* 0.005 0.008 restraints were used for the geometries of the four 2-propanol molecules. A loose *SAME* 0.01 0.01 restraint was also used for bond lengths and bond angles in the two 2-propanol molecules of AF2p.

For all compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structures: *SHELXTL*; program(s) used to refine structures: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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4,8-Dibenzyl-2′,4′,6′-trinitrospiro[1,3-dioxa-azulenium-2,1′-cyclohexadienide]

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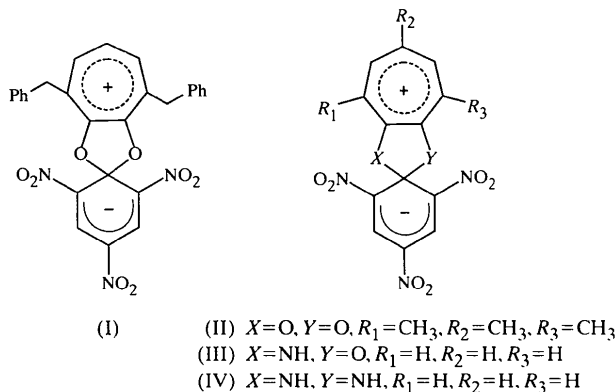
Abstract

In molecules of the title compound, $C_{27}H_{19}N_3O_8$, the nitro groups have almost equivalent geometries. Similar observations were made for some related anionic σ complexes. However, equalization of bond lengths within the conjugated system of the cyclohexadienide ring is stronger than that in other Meisenheimer complexes.

Comment

The synthetic chemistry of electron-deficient aromatics and heteroaromatics is circumscribed by the two major mechanisms of nucleophilic aromatic substitution, *i.e.* SNAr and Vicarious Nucleophilic Substitution (VNS; Artamkina *et al.*, 1982; Buncel *et al.*, 1995). These displacement reactions form the backbone of numerous important syntheses of pharmaceuticals and potential drugs and several other classes of bioactive agents. The key intermediate in both the SNAr and VNS mechanisms is a negatively charged σ complex commonly termed a Meisenheimer complex.

Dipolar spirocyclic Meisenheimer complexes with tropylium cations are a special class of such complexes and, in general, can be considered as a new class of heterocyclic compounds. In addition, these compounds are of great interest because their formation involves acylotropic rearrangements (Knyazev & Drozd, 1995; Kurbatov *et al.*, 1997).

However, the structures of only a few such σ complex derivatives of 2,4,6-trinitrobenzene have been determined using X-ray methods (Furmanova *et al.*, 1980; Olekhnovich *et al.*, 1982). Compounds of this series contain different combinations of heteroatoms [O,O (II), N,O (III) and N,N (IV)] at the spiro C atom. We now report the result of an X-ray investigation of a dipolar Meisenheimer complex, (I), analogous to (II) but carrying bulky benzyl substituents on the seven-membered ring.

(I)

(II) X=O, Y=O, R_1=CH$_3$, R_2=CH$_3$, R_3=CH$_3$
(III) X=NH, Y=O, R_1=H, R_2=H, R_3=H
(IV) X=NH, Y=NH, R_1=H, R_2=H, R_3=H

The cyclohexadienide ring in (I) is almost planar, with C3—C4 [1.385 (4) Å] and C4—C5 [1.385 (4) Å] bond lengths somewhat longer than the C2—C3 [1.367 (5) Å] and C5—C6 [1.352 (5) Å] distances. However, this difference is less pronounced than that in (II)–(IV) (Furmanova *et al.*, 1980; Olekhnovich *et al.*, 1982) or in Meisenheimer complexes of 2,4,6-trinitrobenzene with a potassium cation (Borbulevych *et al.*, 1998).

In (I), there are no significant differences between the C—N bond lengths for the three nitro groups (Table 1), a similar situation to that found in molecules (II) and (III). However, in (III), the C—N bond to the nitro group in the *para*-position is very short [1.407 (5) Å] (Olekhnovich *et al.*, 1982) compared with the C—N bonds to the other nitro groups, which have lengths similar to those in (I).

The nitro groups bound to C2 and C4 are nearly coplanar with the cyclohexadienide ring [the O1—N1—C2—C1 and O3—N2—C4—C3 torsion angles are −2.7 (4) and −3.3 (5)°, respectively] in spite of the presence of short intramolecular contacts listed in Table 2. However, the third nitro group is rotated out of the plane of the ring. The torsion angle O6—N3—C6—C1 is 10.1 (4)°.

The dioxolane ring in (I) adopts a flattened envelope conformation. Deviation of the O8 atom from the plane of the other atoms of this ring is 0.054 (4) Å. The dihedral angle between the least-squares mean planes of the six- and five-membered rings is 89.32 (8)°.

Bond distances in the seven-membered ring of (I) are nearly equal (Table 1), in agreement with previous data for (II) and (IV), but in (III), alternation in these

bond lengths was observed (Furmanova *et al.*, 1980; Olekhnovich *et al.*, 1982).

The benzyl group at C8 has a +ac orientation with respect to the C7—C8 and C8—C14 bonds [the C7—C8—C14—C15 and C8—C14—C15—C20 torsion angles are 101.2 (3) and 103.4 (4)°, respectively], while the substituent on C12 is +sc with respect to the C13—C12 and C12—C21 bonds [the C13—C12—C21—C22 and C12—C21—C22—C23 torsion angles are 73.3 (4) and 69.1 (4)°, respectively].
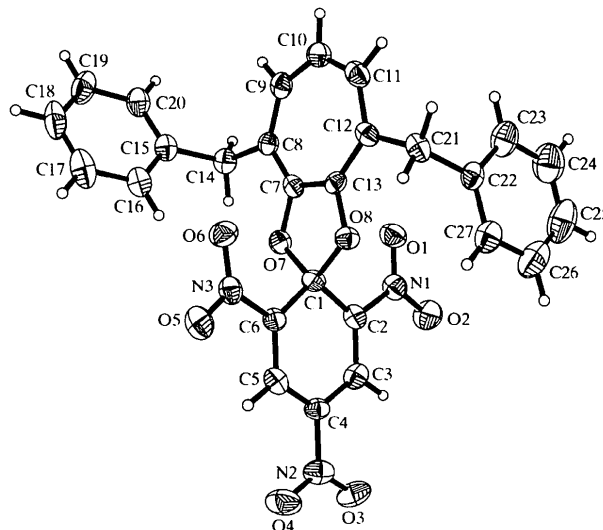
Fig. 1. View of the title compound. The non-H atoms are shown with displacement ellipsoids drawn at the 50% probability level and H atoms are drawn as circles of arbitrarily small radii for clarity.

Experimental

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

Crystal data

C$_{27}$H$_{19}$N$_3$O$_8$	Mo $K\alpha$ radiation
M_r = 513.45	λ = 0.71073 Å
Monoclinic	Cell parameters from 24
$P2_1/n$	reflections
a = 9.311 (5) Å	θ = 10–11°
b = 12.877 (7) Å	μ = 0.108 mm^{-1}
c = 19.806 (10) Å	T = 193 (2) K
β = 94.74 (4)°	Square prism
V = 2367 (2) Å^3	0.50 × 0.20 × 0.20 mm
Z = 4	Red
D_x = 1.441 Mg m^{-3}	
D_m not measured	

Data collection

Syntex $P2_1$/PC diffractom-	θ_{max} = 25.05°
eter	h = 0 → 11
$\theta/2\theta$ scans	k = 0 → 15
Absorption correction: none	l = −23 → 23

4458 measured reflections
4182 independent reflections
2066 reflections with
$I > 2\sigma(I)$
$R_{int} = 0.101$

2 standard reflections
every 98 reflections
intensity decay: 5%

-

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.072$
$wR(F^2) = 0.121$
$S = 1.225$
4117 reflections
343 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0683P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}
Extinction correction: none
Scattering factors from
International Tables for
Crystallography (Vol. C)

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

N1—C2	1.446 (4)	C5—C6	1.352 (5)
N2—C4	1.432 (4)	C7—C8	1.395 (4)
N3—C6	1.438 (4)	C7—C13	1.415 (4)
C1—C6	1.489 (4)	C8—C9	1.384 (4)
C1—C2	1.493 (4)	C9—C10	1.378 (5)
C2—C3	1.367 (5)	C10—C11	1.393 (5)
C3—C4	1.385 (4)	C11—C12	1.391 (5)
C4—C5	1.385 (4)	C12—C13	1.376 (4)
C3—C2—C1	124.0 (3)	C8—C7—C13	131.1 (3)
C2—C3—C4	120.3 (3)	C10—C9—C8	130.4 (3)
C3—C4—C5	120.6 (3)	C9—C10—C11	131.4 (4)
C6—C5—C4	120.6 (3)	C12—C11—C10	129.1 (3)
C5—C6—C1	124.6 (3)	C12—C13—C7	132.7 (3)
C13—O8—C1—O7	−3.7 (3)	C1—O8—C13—C7	3.8 (3)
C7—O7—C1—O8	2.2 (3)	O7—C7—C13—O8	−2.4 (3)
C1—O7—C7—C13	−0.1 (3)		

Table 2. *Intramolecular contact distances (Å) and van der Waals radii*

		Radius†
O1···C7	2.816 (4)	3.00
O1···C13	2.777 (4)	3.00
O2···H3	2.369 (5)	2.45
O3···H3	2.428 (5)	2.45
O4···H5	2.395 (4)	2.45
O5···H5	2.359 (4)	2.45
O6···C7	2.896 (4)	3.00
O6···C13	2.959 (4)	3.00

† van der Waals radii are taken from Zefirov & Zorky (1989).

The slightly high value of R_1 is attributed to the limited quality of available crystals.

Data collection: *P3* (Siemens, 1989). Cell refinement: *P3*. Data reduction: *PROFIT* (Strel'tsov & Zavodnik, 1989). 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*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1362). Services for accessing these data are described at the back of the journal.

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2-Benzoyl-2-methyl-1,3-dithiane

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Abstract

The crystal structure of the title compound, $C_{12}H_{14}OS_2$, shows a 1,3-dithiane ring adopting a chair conformation with the 2-benzoyl group orientated axially. The carbonyl-O atom lies above the heterocycle, but is asymmetrically disposed with respect to both S atoms. Thus, the conformation can mainly be discussed on the basis of electrostatic dipole–dipole attraction (anomeric effect) of the C—S and C=O dipoles, together with *exo*-orientation of the phenyl group as a consequence of its steric demand. The observed bond distances do not support an $n \rightarrow \sigma^*$ delocalization as a further reason for the axial orientation of the carbonyl group.

Comment

2-Acyl-1,3-dithianes represent important key intermediates and may, after sulfoxidation, be used as stereocon-