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Triethylammonium 8-acetyl-3-methyl-9-phenyl-7-oxo-2-azaspiro[4.5]dec-2-ene-4-nitronate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.043
wR factor = 0.125
Data-to-parameter ratio = 10.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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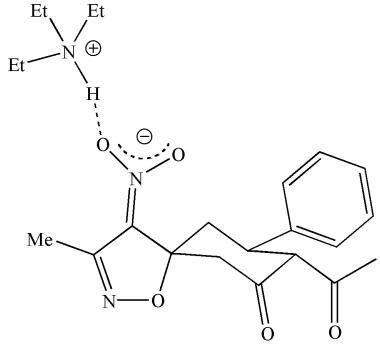
The acinitro group in the title compound, $C_6H_{16}N^+\cdot C_{17}H_{17}N_2O_5^-$, is almost coplanar with the isoxazoline ring, which assumes a flattened envelope conformation. The cyclohexanone ring adopts a half-chair conformation and carries a perpendicular [83.54 (10)°] phenyl ring and a bent [64.30 (17)°] acetyl group. The triethylammonium residue forms a hydrogen bond with the nitronate moiety. Intermolecular interaction is exerted through a hydrogen bond between the acidic H atom of the cyclohexanone ring and the N atom of the isoxazoline ring.

Comment

Spiroisoxazolines display a range of biological activity, including herbicidal, plant hormonal and anticancer properties (Howe & Shelton, 1990; De Amici *et al.*, 1990; Smietana *et al.*, 1999). The title compound, (I), was obtained from a highly stereoselective reaction in which three chiral centres are introduced in one step (Adamo *et al.*, 2002). The interest in the relative configuration of the chiral centres and the structural details of this novel 3-acinitroisoxazoline prompted us to undertake a detailed analysis of the structure of compound (I).



(I)

The nitronate moiety is almost coplanar [4.62 (9)°] with the isoxazoline ring. The conjugation has only a small effect on the C=N bond length in the nitronate [N2—C14 = 1.321 (3) Å] and on the C=N and N—O bonds in the isoxazoline ring [N1—C13 = 1.289 (3) and N1—O2 = 1.425 (2) Å]. In comparison, the length of a C=N bond in a non-conjugated 2-nitropropanate has been reported as 1.311 (7) Å (Reetz *et al.*, 1995) and the lengths of a C=N and an N—O bond in a non-conjugated nitroisoxazoline as 1.272 (4) and 1.419 (3) Å, respectively (Donati *et al.*, 1994). These data exclude significative push–pull effects.

The isoxazoline ring assumes a very flattened envelope conformation, with puckering parameters (Cremer & Pople, 1975) $\varphi = -173\ (2)^\circ$ and $Q = 0.062\ (2)$ Å, and asymmetry

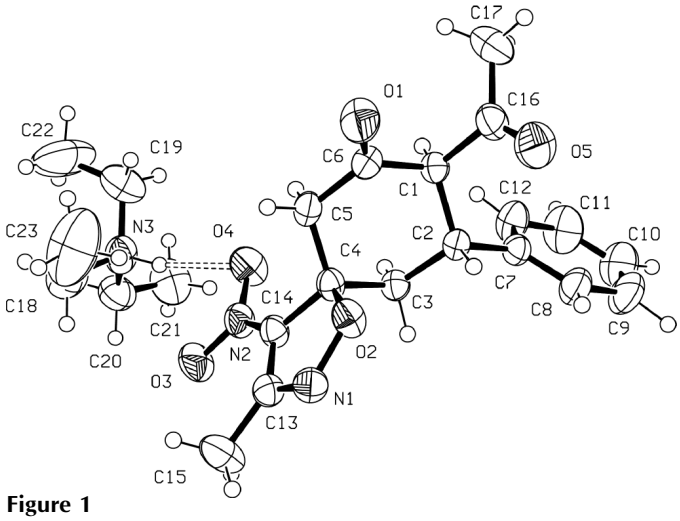


Figure 1
View of (I), with the atomic numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

parameter (Nardelli, 1983) Δ_s (C4) 0.006 (1). The cyclohexanone ring is perpendicular [85.84 (7)°] to the isoxazoline ring and assumes a chair conformation, with puckering parameters θ = 172.6 (2)° and Q_T = −0.533 (2) Å. The phenyl group is approximatively perpendicular [83.54 (10)°] to the least-squares plane through the cyclohexanone, while the acetyl group forms an angle of 64.30 (17)° with this plane.

The atom N3 of the triethylammonium residue is linked *via* a hydrogen bond with atom O4 of the acinitro group; it is not coplanar with this group, with a C14—N2—O4···N3 torsion angle of 148.1 (2)°. There is also an intermolecular hydrogen bond between H1 of the cyclohexanone ring and N1 of the isoxazoline ring. Other short contact interactions are reported in Table 2.

Experimental

A solution of 3-methyl-4-nitro-5-styrylisoxazole (1.15 g, 5.6 mmol) and acetylacetone (1.5 g, 15 mmol) in triethylamine (20 ml) and tetrahydrofuran (20 ml) was stirred at 353 K. After 3 h the reaction mixture was allowed to cool to room temperature. The resulting solid was filtered and washed with cold acetone (m.p. 428 K from ethanol).

Crystal data

$C_{17}H_{17}N_2O_5\cdot C_6H_{16}N$
M_r = 431.52
Monoclinic, *Cc*
a = 21.815 (3) Å
b = 10.464 (2) Å
c = 11.222 (2) Å
β = 108.55 (1)°
V = 2428.6 (7) Å^3
Z = 4
D_x = 1.180 Mg m^{-3}
Mo Kα radiation
Cell parameters from 44 reflections
θ = 3–25°
μ = 0.08 mm^{-1}
T = 293 (3) K
Prism, colourless
0.4 × 0.4 × 0.2 mm

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
7207 measured reflections
3539 independent reflections
2723 reflections with $I > 2\sigma(I)$
R_{int} = 0.017
θ_{max} = 30.0°
$h = -30 \rightarrow 30$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 15$
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.125
S = 1.00
3539 reflections
345 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0828P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.014
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O2—N1	1.425 (3)	C3—C4	1.527 (3)
O2—C4	1.466 (3)	C4—C5	1.525 (3)
O3—N2	1.283 (3)	C4—C14	1.500 (3)
O4—N2	1.294 (3)	C13—C15	1.487 (5)
N1—C13	1.289 (3)	C13—C14	1.432 (3)
N2—C14	1.321 (3)		
N1—O2—C4	110.10 (17)	N1—C13—C14	111.8 (2)
O2—N1—C13	109.28 (18)	C14—C13—C15	128.8 (2)
O3—N2—O4	117.5 (2)	N1—C13—C15	119.4 (2)
O3—N2—C14	122.5 (2)	C4—C14—C13	107.33 (19)
O4—N2—C14	120.0 (2)	N2—C14—C4	125.37 (19)
O2—C4—C3	107.52 (16)	N2—C14—C13	127.3 (2)
O2—C4—C5	107.75 (17)	N3—C18—C23	113.4 (5)
O2—C4—C14	101.11 (16)	N3—C19—C22	114.1 (4)
O1—C6—C1	121.8 (2)	N3—C20—C21	113.4 (3)
O1—C6—C5	122.0 (2)		
O4—N2—C14—C4	−3.8 (3)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H32···O4^{i}	0.89 (4)	1.96 (4)	2.836 (3)	168 (4)
C1—H1···N1^{ii}	0.96 (3)	2.44 (3)	3.352 (3)	159 (3)
C5—H5*A*···O4	0.96 (3)	2.47 (3)	3.032 (3)	117 (2)
C20—H20*B*···O1^{iii}	0.97	2.60	3.402 (4)	140

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

3488 Friedel pairs were merged before refinement. The absolute configuration was not determined. The H atoms of the isoxazoline moiety were located from difference Fourier maps and freely refined with isotropic displacement parameters. The H atoms of the triethylammonium cation were placed geometrically and treated as riding using *SHELXL*97 (Sheldrick, 1997) defaults, with a common displacement parameter free to refine for the methyl groups.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*3 (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 1999).

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