

The zwitterion of 4-nitro-2-*(E)*-[2-(piperidin-1-yl)ethyl]iminomethyl]-phenol

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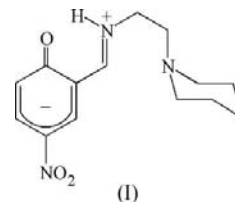
The title Schiff base compound, 4-nitro-1-oxo-2-*(E)*-[2-(piperidin-1-yl)ethyl]iminomethyl]cyclohexadienide, C₁₄H₁₉N₃O₃, exists as a zwitterion, with the H atom of the phenol group being transferred to the imine N atom. The C=O, C_{Ar}–C_{Ar} and C–N bond lengths are in agreement with the oxocyclohexadienide–iminium zwitterionic form. The iminium H atom is engaged in a strong intramolecular hydrogen bond with the O atom of the keto group (N⁺–H···O) to form an *S*(6) motif. Soft C–H···O interactions in the *ac* plane lead to the development of hydrogen-bonded tapes, which are π -stacked through the oxocyclohexadienide ring and iminium group. The significance of this study is in providing crystallographic evidence, supported by NMR and IR data, of the predominance of the oxocyclohexadienide–iminium zwitterion form over the noncharged canonical form in the title Schiff base.

Comment

Aromatic imines and their derivatives are an important group of molecules in organic chemistry, in particular those that have aryl groups bound to N or C atoms. They have been used successfully to study resonance-assisted hydrogen bonds (RAHBs; Krygowski & Stepien, 2005; Sobczyk *et al.*, 2005). Imines substituted in the aromatic ring have offered the opportunity to study the substituent effects in RAHBs. In this context, the molecular structure of the title compound, (I) (Fig. 1), is reported here.

The single-crystal structure of the title Schiff base compound is built up by discrete molecules in the monoclinic space group *P2₁/c*, with one molecule in the asymmetric unit. A summary of bond lengths and angles is presented in Table 1. The N8–C7 and O1–C1 bond lengths are in agreement with

the double-bond character for the imine (ν at 1601 cm⁻¹) and keto-carbonyl groups (ν at 1657 cm⁻¹), respectively (Allen, 2002). Moreover, the bond lengths in the C1–C6 ring show



clear alternation in the delocalized C2–C6 portion. The nitro group is tilted out of the mean plane of the adjacent ring by –11.1 (3)°, whereas the C4–N4 distance is in the characteristic range suggesting limited conjugation with the ring. Thus, the whole geometry is in agreement with the predominance of the oxocyclohexadienide–iminium zwitterion bonding scheme (see scheme) (Krygowski & Stepien, 2005), in close agreement with the reported configurations of *p*-nitrophenolates of alkali metal cations (Butt *et al.*, 1987).

The iminium H atom (located in a difference map) is coplanar with the oxocyclohexadienide ring and on the same side of the molecule as the O atom of the keto group, allowing the formation of an intramolecular N–H···O hydrogen bond

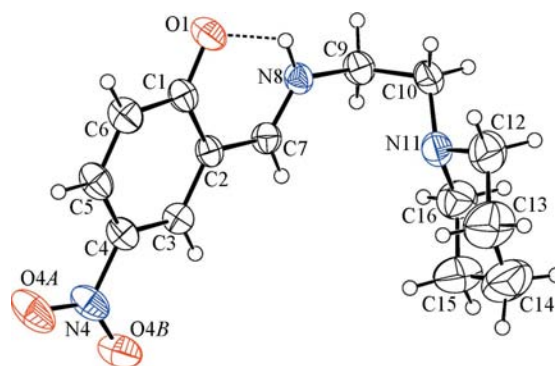


Figure 1

The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

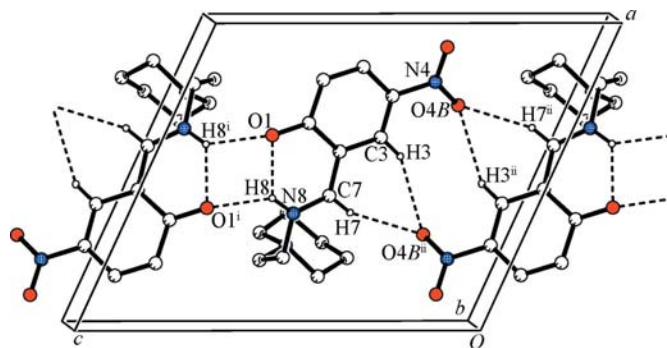


Figure 2

Hydrogen-bonded tapes formed by N–H···O and C–H···O interactions along the *c* axis. H atoms not involved in the motifs shown have been omitted for clarity. [Symmetry codes: (i) $-x + 1, y, -z + \frac{3}{2}$; (ii) $-x + 1, y, -z + \frac{1}{2}$.]

(Table 2) in an $S(6)$ motif (Bernstein *et al.*, 1995), with dimensions in agreement with the usual values (Krygowski *et al.*, 1997; Steiner 1998, 2002). The $N8 \cdots O1$ distance has almost the same value as the RAHB of 2.607 (3) Å found in 3-[[diphenoxythiophosphoryl]hydrazine]methylidene-3,4-dihydro-2*H*-1-benzopyran-2,4-dione (Rybarczyk-Pirek *et al.*, 2002). The iminium H atom is also engaged in $N-H \cdots O$ hydrogen bonding with the O atom from the keto group of a neighbouring molecule, forming dimers with an almost square $R_2^2(4)$ motif (Fig. 2).

The first dimension of the extended structure is built up by soft $C-H \cdots O$ interactions with the participation of one of the O atoms from the nitro group, in a monocoordinative fashion (Allen *et al.*, 1997), as the acceptor of two hydrogen bonds (Table 2) to form an $R_2^2(6)$ motif. The whole hydrogen-bonding scheme, makes up tapes propagating along the direction of the c axis. All $C-H \cdots ON$ and $C \cdots ON$ distances are shorter than the mean values of 2.7 (2) and 3.5 (2) Å, respectively, found in a study of nitrobenzenes (André *et al.*, 1997), although the $C-H \cdots ON$ angles are within the accepted range [$C-H \cdots O = 133(20)^\circ$]. Even when $C-H \cdots O$ interactions involving an NO_2 group as acceptor are half as strong as $C-H \cdots O$ interactions (Allen *et al.*, 1997) involving a CO group as the acceptor, they play a significant role in packing owing to their co-operative action.

The second dimension is ruled by the zwitterionic nature of (I). The anionic oxocyclohexadiene ring and the cationic iminium group from neighbouring tapes are overlapped. The iminium N and C atoms are 3.257 (3) and 3.462 (3) Å, respectively, from the centroid of the cyclohexadienide ring at $(-x+1, -y, -z)$. These short distances strongly suggest not only ion pairing but also a π -stacking interaction between the iminium group, as acceptor, and the oxocyclohexadiene ring, as the donor of electron density (Fig. 3). These π -stacking interactions crosslink pairs of the hydrogen-bonded tapes

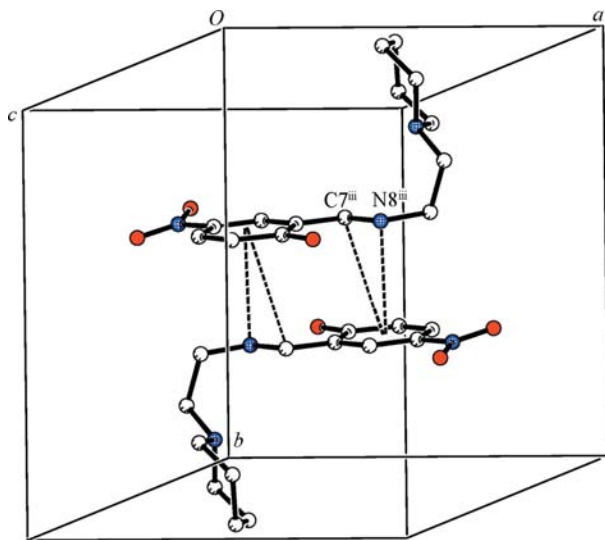


Figure 3

The centrosymmetric oxocyclohexadienide-iminium π -stacked pairs of compound (I). [Symmetry code: (iii) $-x+1, -y+1, -z+1$.]

described above to develop discrete centrosymmetric ribbons which propagate along the c axis.

Experimental

Compound (I) was synthesized by amidation of ethyl 6-nitro-2-oxo-2*H*-chromene-3-carboxylate (0.5 g, 1.9 mmol), prepared according to Santos-Contreras *et al.* (2007), with 1-(2-aminoethyl)piperidine (0.26 ml, 1.9 mmol) and two drops of piperidine as catalyst in refluxing ethanol (10 ml) for 24 h. The resulting orange solution was treated with activated charcoal and evaporated to give 0.3 g of an orange solid in 57% yield. Crystals suitable for X-ray analysis were obtained by slow evaporation from a saturated ethyl acetate solution (m.p. 413 K). IR (cm^{-1}): ν ($C=O$) 1657, ($C=N$) 1601, ($C-NO$) 1535; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 6.90 (*d*, H6, $^3J = 9.0$ Hz), 8.16 (*dd*, H5, $^3J = 9.0$ and $^4J = 3.0$ Hz), 8.22 (*d*, H3, $^3J = 9.0$ Hz), 11.9 (*b*, NH), 8.31 (*s*, H7), 3.74 (*t*, 2H, $^3J = 6.2$ Hz, $^{-}\text{NHCH}_2^{-}$), 2.64 (*t*, 2H, $^3J = 6.2$ Hz, $^{-}\text{CH}_2\text{N}$), 2.46 [*m*, 4H, $\text{N}-(\text{CH}_2)_2$], 1.56 (*m*, 4H, $^{-}\text{CH}_2^{-}$), 1.46 (*m*, 2H, $^{-}\text{CH}_2^{-}$); $^{13}\text{C NMR}$: δ 173.1 (C1), 115.6 (C2), 129.7 (C3), 137.5 (C4), 129.0 (C5), 120.9 (C6), 165.3 (C7), 58.4 (C9), 53.2 (C10), 54.8 (C12), 26.2 (C13), 24.3 (C14).

Crystal data

$\text{C}_{14}\text{H}_{19}\text{N}_3\text{O}_3$	$V = 1484.2(4) \text{ \AA}^3$
$M_r = 277.17$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 10.5688(17) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$b = 12.1887(19) \text{ \AA}$	$T = 293(2) \text{ K}$
$c = 12.6816(15) \text{ \AA}$	$0.20 \times 0.17 \times 0.12 \text{ mm}$
$\beta = 114.696(10)^\circ$	

Data collection

Bruker APEXII area-detector diffractometer	2617 independent reflections
13954 measured reflections	2217 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.039$

Table 1

Selected geometric parameters (\AA , $^\circ$).

O1—C1	1.257 (3)	N11—C16	1.455 (3)
O4A—N4	1.227 (3)	C1—C2	1.447 (3)
O4B—N4	1.230 (3)	C1—C6	1.435 (3)
N4—C4	1.442 (3)	C2—C3	1.395 (3)
N8—C7	1.285 (3)	C3—C4	1.372 (3)
N8—C9	1.454 (3)	C4—C5	1.406 (3)
N11—C10	1.449 (3)	C5—C6	1.357 (3)
N11—C12	1.451 (3)	C9—C10	1.514 (3)
O4A—N4—O4B	122.9 (2)	O1—C1—C2	122.0 (2)
O4A—N4—C4	118.4 (2)	N4—C4—C5	119.6 (2)
O4B—N4—C4	118.7 (2)	N4—C4—C3	120.0 (2)
C7—N8—C9	123.6 (2)	N8—C7—C2	125.0 (2)
C10—N11—C12	111.9 (2)	N8—C9—C10	111.0 (2)
C10—N11—C16	112.7 (2)	N11—C10—C9	112.2 (2)
C12—N11—C16	109.9 (2)	N11—C12—C13	111.1 (3)
O1—C1—C6	122.3 (2)	N11—C16—C15	110.9 (3)

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N8—H8 \cdots O1	0.90 (2)	2.02 (3)	2.674 (3)	129 (3)
N8—H8 \cdots O1 ⁱ	0.90 (2)	2.13 (3)	2.857 (3)	137 (3)
C3—H3 \cdots O4B ⁱⁱ	0.93	2.57	3.400 (3)	149
C7—H7 \cdots O4B ⁱⁱ	0.93	2.44	3.302 (3)	155

Symmetry codes: (i) $-x+1, y, -z+\frac{3}{2}$; (ii) $-x+1, y, -z+\frac{1}{2}$.

Refinement

$$R[F^2 > 2\sigma(F^2)] = 0.066$$

$$wR(F^2) = 0.151$$

$$S = 1.20$$

2617 reflections

185 parameters

H atoms treated by a mixture of independent and constrained refinement

$$\Delta\rho_{\max} = 0.21 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$$

The amino H atom was located in a difference Fourier map and refined with an N—H distance of 0.90 (2) Å. All other H atoms were positioned geometrically and refined using a riding model [C—H = 0.93 and 0.97 Å for aromatic and CH₂ H atoms, respectively, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$].

Data collection: *APEX2* (Bruker, 2004); cell refinement: *S SAINT* (Bruker, 2004); data reduction: *S SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97* and *WinGX2003* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3261). Services for accessing these data are described at the back of the journal.

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