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9-Cyano-10-methylacridinium hydrogen dinitrate

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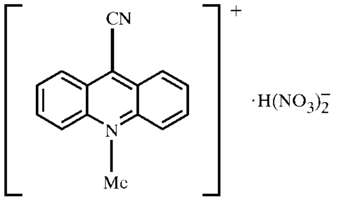
The title compound, $C_{15}H_{11}N_2^+\cdot HN_2O_6^-$, crystallizes in the monoclinic space group *C*2/*c* with four molecules in the unit cell. The planar 9-cyano-10-methylacridinium cations lie on crystallographic twofold axes and are arranged in layers, almost perpendicular to the *ac* plane, in such a way that neighbouring molecules are positioned in a 'head-to-tail' manner. These cations and the hydrogen dinitrate anions are linked through C—H···O interactions involving four of the six O atoms of the anion and the H atoms attached to the C atoms of the acridine moiety in ring positions 2 and 4. The H atom of the hydrogen dinitrate anion appears to be located on the centre of inversion relating two of the four O atoms engaged in the above-mentioned C—H···O interactions. In this way, columns of either anions or cations running along the *c* axis are held in place by the network of C—H···O interactions, forming a relatively compact crystal lattice.

Comment

9-Cyano-10-methylacridinium salts (McCapra & Richardson, 1964), such as 9-carboxy-10-methylacridinium phenyl ester salts (Rak *et al.*, 1999) or other 9-substituted-10-alkylacridinium salts (Dodeigne *et al.*, 2000), can act as chemiluminescent or spectral indicators or as the chemiluminogenic fragments of chemiluminescent labels (Zomer *et al.*, 1991). The possible applications of these compounds are principally dependent on the stability of their crystalline phases. The reasons for undertaking our present investigations were, therefore, first, to investigate which 9-cyano-10-methylacridinium salts can be obtained in the crystalline state, secondly, to determine their structures and thirdly, to demonstrate to what extent structural features can influence their stability. We succeeded in crystallizing the title hydrogen dinitrate salt, (I), which is readily soluble in water and several organic solvents, and can thus be used in analytical and spectroscopic investigations.



(I)

The stoichiometric unit of (I) is shown in Fig. 1. The cation of (I) is planar in the crystalline phase. Atoms C9 and N10, as well as the respective cyano group and methyl C atom attached to them, are arranged linearly along a crystallographic twofold axis (Table 1). The H atoms of the methyl group occupy two orientations, each with occupancy 0.5. This is typical of compounds in which the H atoms of the methyl group do not interact with the O atoms of the anions, unlike the 10-methylacridinium halides, where C—H interactions with anions fix the methyl group in one position (Storoniak *et al.*, 2000). The central $N1-O1\cdots H1B\cdots O1^{iii}-N1^{iii}$ moiety of the hydrogen dinitrate anion appears to be planar, as in other inorganic (Duke & Llewellyn, 1950; Faithful & Wallwork, 1967; Roziere *et al.*, 1976) and organic (Al-Zamil *et al.*, 1982; Roziere *et al.*, 1979) compounds containing this anion [symmetry code: (iii) $-x, -y, -z$]. The other two O atoms of each nitrate anion are twisted out of this plane by 14.7 (2)°.

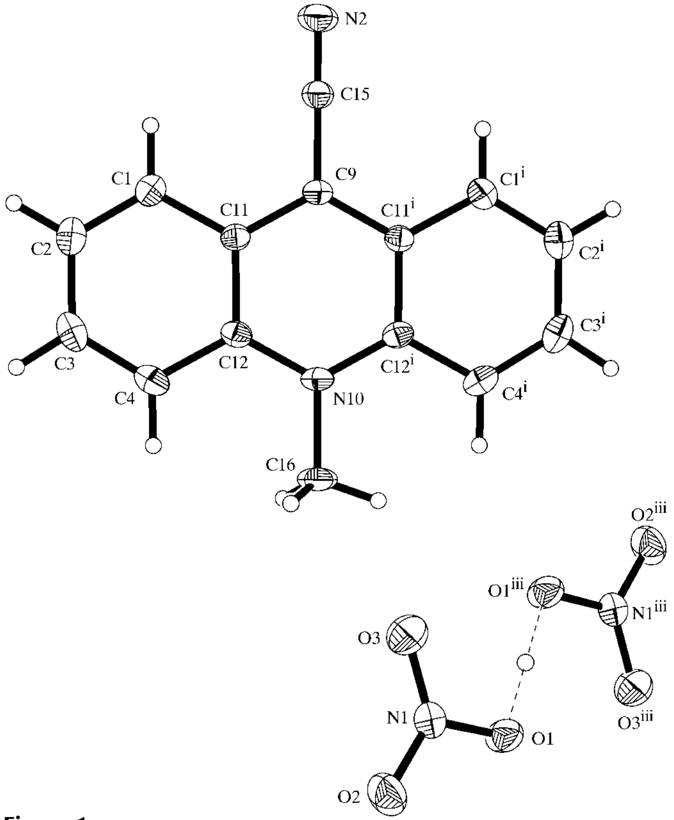


Figure 1
The molecular structure of (I) showing the atom-labelling scheme and 50% probability displacement ellipsoids [symmetry codes: (i) $-x, y, \frac{1}{2}-z$; (iii) $-x, -y, -z$].

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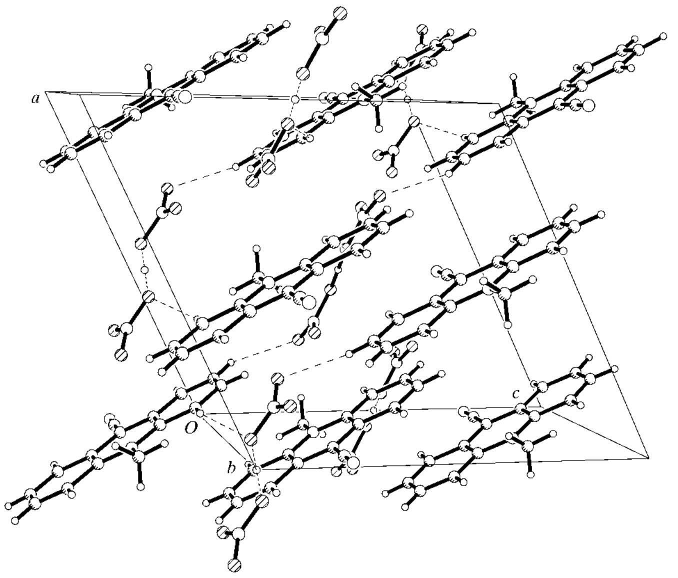

Figure 2
The packing diagram for (I) in the unit cell, viewed along the *b* axis. Hydrogen bonds are represented by dashed lines.

Compound (I) is a typical ionic substance in which electrostatic interactions between the ions are the main factor binding cations and anions in the lattice. As a result of these interactions, the lattice is relatively compact, and anions and cations are in contact with each other *via* O···H interactions (Table 2). The arrangement of the ions and the network of C—H···O interactions are shown in Fig. 2. It should be noted that the cations are arranged in layers, with the neighbouring molecules 'head-to-tail'. These layers are linked through C—H···O interactions involving four O atoms of the hydrogen dinitrate anion and the H atoms attached to the C atoms of the acridine moiety in ring positions 2 or 4. One H atom seems to be located on a centre of inversion and participates in a very short hydrogen bond. The distance between the two O atoms of the two nitrate moieties involved in this interaction is 2.440 (4) Å and the H atom is located exactly at the midpoint of these two O atoms.

The effect of the strong hydrogen bond in the hydrogen dinitrate anion causes the bonds between the N and O atoms involved to be longer than the four remaining N—O bonds, and the O—N—O valence angles to be inequivalent (Table 1). Another interesting feature is that the anions and cations form columns held in place by the network of C—H···O interactions. These multidirectional interactions undoubtedly stabilize the lattice and increase the attractiveness of the compound as an analytical indicator or a chemiluminogenic fragment of a label.

Experimental

9-Cyano-10-methylacridinium hydrogen dinitrate was prepared by the oxidation of 9-cyano-10-methylacridan (Kaufmann & Albertini, 1909, 1911) with dilute nitric acid (McCapra & Richardson, 1964). Yellow crystals of (I) suitable for X-ray investigation were grown from a solution in water.

Table 1
Selected geometric parameters (Å, °).

C9—C15	1.444 (3)	N1—O2	1.212 (2)
N10—C16	1.480 (3)	N1—O3	1.211 (2)
C15—N2	1.135 (3)	O1—H1*B*	1.220 (2)
N1—O1	1.295 (2)		
C11—C9—C15	119.08 (10)	O1—N1—O3	119.07 (17)
C12—N10—C16	118.87 (10)	O2—N1—O3	124.27 (19)
O1—N1—O2	116.65 (17)	N1—O1—H1*B*	110.55 (13)
C11^{i}—C9—C11—C12	−0.13 (11)	C12^{i}—N10—C12—C11	−0.13 (11)

Symmetry code: (i) $-x, y, \frac{1}{2}-z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2^{i}—H2*A*^{i}···O2	0.96	2.48	3.313 (3)	145
C4—H4*A*···O1^{ii}	0.96	2.49	3.337 (3)	147
O1—H1*B*···O1^{iii}	1.22	1.22	2.440 (4)	180 (3)

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

Crystal data

$C_{15}H_{11}N_2^{+}\cdot HN_2O_6^{-}$
$M_r = 344.29$
Monoclinic, *C*2/*c*
$a = 12.799$ (4) Å
$b = 10.015$ (3) Å
$c = 13.168$ (4) Å
$\beta = 115.96$ (4)°
$V = 1517.6$ (8) Å^3
$Z = 4$

$D_x = 1.507$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 50 reflections
$\theta = 6.0$–24.0°
$\mu = 0.12$ mm^{-1}
$T = 293$ (2) K
Prism, yellow
0.50 × 0.20 × 0.15 mm

Data collection

Kuma KM-4 diffractometer
$\theta/2\theta$ scans
2003 measured reflections
2003 independent reflections
1104 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 29°$

$h = -17 \rightarrow 15$
$k = 0 \rightarrow 13$
$l = -17 \rightarrow 15$
3 standard reflections every 200 reflections intensity decay: 3.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.169$
$S = 1.07$
2003 reflections
125 parameters
H-atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.096P)^2 + 0.220P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}

The H atom of the hydrogen dinitrate (H1*B*) was refined freely. The methyl H atoms attached to atom C16 were located from difference Fourier syntheses and refined as a rigid rotating group with C—H = 0.96 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C). As C16 is located on a diad, the H atoms were refined in three unique positions with an occupancy factor of 0.5. Other H atoms attached to C atoms were placed geometrically and refined using a riding model, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) and C—H = 0.96 Å.

Data collection: *KM*-4 *Software* (Kuma Diffraction, 1989); cell refinement: *KM*-4 *Software*; data reduction: *KM*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997);

molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1487). Services for accessing these data are described at the back of the journal.

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