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

F1—B	1.360 (2)	O2—C16	1.429 (2)
F2—B	1.368 (2)	N—C6	1.343 (2)
F3—B	1.373 (2)	N—C2	1.347 (2)
F4—B	1.387 (2)	N—C1	1.480 (3)
O1—C12	1.365 (2)	C4—C7	1.447 (3)
O1—C15	1.430 (3)	C7—C8	1.331 (3)
O2—C13	1.362 (2)	C8—C9	1.452 (3)
C12—O1—C15	116.3 (2)	F1—B—F4	110.1 (2)
C13—O2—C16	117.3 (2)	F2—B—F4	108.07 (15)
C6—N—C2	119.4 (2)	F3—B—F4	108.7 (2)
C6—N—C1	120.6 (2)	C3—C2—N	121.9 (2)
C2—N—C1	120.0 (2)	C8—C7—C4	125.1 (2)
F1—B—F2	110.2 (2)	C7—C8—C9	127.3 (2)
F1—B—F3	109.80 (15)	C14—C9—C8	122.5 (2)
F2—B—F3	109.9 (2)		
C5—C4—C7—C8	170.5 (2)	C15—O1—C12—C13	−174.4 (2)
C4—C7—C8—C9	−179.3 (2)	C16—O2—C13—C14	0.7 (3)
C7—C8—C9—C14	−3.8 (3)	C16—O2—C13—C12	180.0 (2)
C15—O1—C12—C11	6.4 (3)		

Table 2. *Contact distances (Å)*

$N\cdots F4^{i}$	3.214 (5)	$C9\cdots C13^{iii}$	3.479 (5)
$C6\cdots F4^{i}$	3.220 (5)	$C9\cdots C2^{iv}$	3.524 (5)
$C3\cdots F4^{ii}$	3.265 (6)	$C12\cdots C3^{iv}$	3.442 (6)
$C7\cdots O1^{iii}$	3.447 (5)	$C14\cdots C2^{iv}$	3.524 (6)
$C8\cdots O2^{iii}$	3.513 (5)		

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

Table 3. *Hydrogen-bonding geometry (Å, °)*

$D—H\cdots A$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
$C1—H1A\cdots F1^{i}$	2.47 (3)	3.318 (5)	148 (3)
$C6—H6\cdots F1^{i}$	2.74 (2)	3.281 (4)	116 (2)
$C3—H3\cdots F2^{ii}$	2.52 (2)	3.449 (7)	174 (2)
$C7—H7\cdots F3^{iii}$	2.57 (2)	3.462 (5)	156 (2)
$C2—H2\cdots F4^{ii}$	2.62 (2)	3.203 (7)	120 (1)
$C3—H3\cdots F4^{ii}$	2.65 (2)	3.265 (6)	124 (1)
$C1—H1B\cdots F3^{iv}$	2.77 (3)	3.392 (6)	126 (2)
$C1—H1C\cdots O1^{v}$	2.53 (4)	3.429 (6)	151 (3)
$C1—H1C\cdots O2^{v}$	2.66 (4)	3.002 (5)	101 (2)

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

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SHELXL*93 (Sheldrick, 1993). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *SHELXL*93. Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1254). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 140–142

4,9-Dihydroxy-4,9-dimethyl-4*H*,9*H*-1,2,5,6,6a,7,8-heptahydroimidazo[1,2,3-*ij*]-[1,8]naphthyridinium Benzoate

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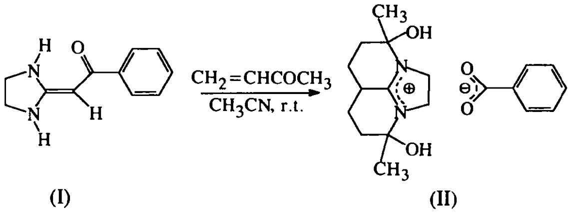
(*Received 3 March 1997; accepted 27 June 1997*)

Abstract

The crystal structure of the title compound, $C_{12}H_{21}N_2O_2^+.C_7H_5O_2^-$, consists of an imidazo[1,2,3-*ij*][1,8]naphthyridinium cation and a benzoate anion, which are held together by two strong O—H···O hydrogen bonds, with O···O non-bonded contact distances of 2.642 (2) and 2.681 (2) Å. In the tricyclic cation, the imidazoline ring is almost planar, while the two six-membered rings are twisted and adopt deformed half-chair conformations. The benzoate anion is not perfectly planar, with the negative charge delocalized over the carboxylate group.

Comment

Heterocyclic ketene aminals or cyclic 1,1-enediamines are versatile synthons for the synthesis of various heterocyclic or fused-heterocyclic compounds (Huang & Wang, 1994*a*,*b*). The reaction of benzoyl heterocyclic ketene aminal 2-benzoylmethyleneimidazolidine, (I), with methyl vinyl ketone unexpectedly afforded the title tricyclic molecule, (II). It is interesting that the ben-



(I)

(II)

zoyl group unexpectedly separated from compound (I) during the reaction. Details of the synthetic work will be published elsewhere. The crystal structure determination of the title compound was undertaken in order to confirm the expected structure.

The crystal structure of the title compound, (II), comprises imidazo[1,2,3-*i,j*][1,8]naphthyridinium cations and benzoate anions (Fig. 1). The cation and the anion are held together by two strong O—H···O hydrogen bonds, with O···O non-bonded contact distances of 2.642 (2) [O(1)···O(4)] and 2.681 (2) Å. In addition, some weak intermolecular C—H···O interactions are also observed in the structure and these hydrogen-bonding parameters are listed in Table 2.

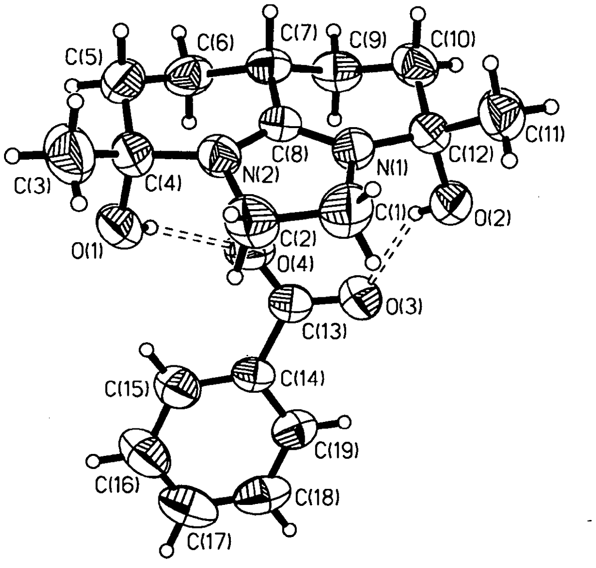


Fig. 1 An *ORTEP*II (Johnson, 1976) drawing showing the hydrogen-bonding interactions between the cation and anion. Displacement ellipsoids are drawn at the 50% probability level.

In the imidazo[1,2,3-*i,j*][1,8]naphthyridinium cation, the imidazoline ring is almost planar with a mean deviation of 0.040 (18) Å from the least-squares plane. The two six-membered rings are twisted relative to the imidazoline ring and adopt approximately half-chair conformations; atoms C(5) and C(6) are displaced on opposite sides of the best plane through atoms C(4), N(2), C(8) and C(7) [planar within 0.072 (1) Å] with displacements of 0.365 (4) and −0.332 (4) Å, respectively; similarly, atoms C(9) and C(10) are displaced from the best plane through atoms C(7), C(8), N(1) and C(12) [planar within 0.044 (1) Å] by −0.470 (4) and 0.253 (4) Å, respectively. The dihedral angle between the imidazoline plane and the plane defined by C(4), N(2), C(8) and C(7) is 8.7 (1)°, while the angle between the imidazoline plane and that defined by atoms C(7), C(8), N(1) and C(12) is 7.1 (1)°. The C(8)—N(1) and C(8)—N(2) bond lengths in the imidazoline ring are 1.314 (2) and 1.325 (2) Å, respectively. These values, which are comparable within 3σ, are intermediate between those for a C—N single bond (1.48 Å) and a C═N double bond (1.28 Å) (Allen *et al.*, 1987), indicating dispersion of positive charge over the N(1)—C(8)—N(2) fragment. The sums of the bond angles about N(1), C(8) and N(2) are 359.1 (2), 359.9 (2) and 355.6 (2)°, respectively, which are very close to the ideal value of 360°, suggesting an essentially sp^2 hybridization of these atoms with the lone-pair electrons available for π bonding. The distance between C(7) and C(8) [1.474 (2) Å] represents a normal C_{sp^2}—C_{sp^3} single bond. The C—N bonds C(1)—N(1), C(12)—N(1), C(2)—N(2) and C(4)—N(2) have bond lengths ranging from 1.466 (2) to 1.482 (2) Å, which are clearly single bonds in character, and thus delocalization is not across the other part of the imidazo[1,2,3-*i,j*][1,8]-naphthyridinium cation.

The benzoate anion is not exactly in a planar configuration, with a maximum deviation of 0.069 (1) Å at O(3) and a deviation of −0.051 (1) Å at O(4). The carboxylate group is slightly rotated with respect to the benzene ring by 4.5 (3)°, which is larger than that observed in the parent benzoic acid (1.5°; Bruno & Randaccio, 1980). The C—C bond lengths in the phenyl ring vary from 1.367 (4) to 1.385 (3) Å and the internal benzene angles from 118.1 (2) to 121.3 (2)°. They are comparable to the corresponding ones found in the parent benzoic acid [1.379 (6)–1.401 (6) Å and 119.7 (4)–120.5 (4)°, respectively; Bruno & Randaccio, 1980]. The phenyl ring is not coplanar with the imidazoline ring of the cation, the dihedral angle between them being 61.48 (7)°. The C(13)—O(3) bond length of 1.246 (2) Å is equal to that of C(13)—O(4) [1.250 (2) Å], within experimental error, showing that the negative charge is delocalized over the carboxylate group.

Experimental

The title compound, (II), was synthesized by the reaction of 2-benzoylmethyleneimidazoline, (I), with methyl vinyl ketone in acetonitrile at room temperature in the presence of minor water. The crystal was obtained by recrystallization from an ethyl acetate–ethanol solvent mixture.

Crystal data

$C_{12}H_{21}N_2O_2^+.C_7H_5O_2^-$
$M_r = 346.42$
Monoclinic
$P2_1/n$
$a = 13.210\,(3)$ Å
$b = 9.801\,(3)$ Å
$c = 13.968\,(3)$ Å
$\beta = 91.728\,(12)°$
$V = 1807.7\,(7)$ Å^3
$Z = 4$
$D_x = 1.273$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 35 reflections
$\theta = 5$–$15°$
$\mu = 0.089$ mm^{-1}
$T = 293$ K
Prism
0.40 × 0.35 × 0.20 mm
Colourless

Data collection

Siemens *P*4 four-circle diffractometer
θ–2θ scans
Absorption correction: none
4095 measured reflections
3188 independent reflections
1906 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.027$
$\theta_{\rm max} = 25°$
$h = -1 \rightarrow 15$
$k = -1 \rightarrow 11$
$l = -16 \rightarrow 16$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.111$
$S = 0.919$
3188 reflections
232 parameters
Only H-atom *U*'s refined
$w = 1/[\sigma^2(F_o^2) + (0.0571P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.001$

$\Delta\rho_{\rm max} = 0.180$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.139$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0226 (18)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O(3)—C(13)	1.246 (2)	C(7)—C(8)	1.474 (2)
O(4)—C(13)	1.250 (2)	C(14)—C(15)	1.379 (3)
N(1)—C(8)	1.314 (2)	C(14)—C(19)	1.385 (3)
N(1)—C(1)	1.468 (2)	C(15)—C(16)	1.373 (3)
N(1)—C(12)	1.482 (2)	C(16)—C(17)	1.367 (4)
N(2)—C(8)	1.325 (2)	C(17)—C(18)	1.370 (3)
N(2)—C(2)	1.466 (2)	C(18)—C(19)	1.383 (3)
N(2)—C(4)	1.480 (2)		
C(8)—N(1)—C(1)	110.0 (2)	N(2)—C(8)—C(7)	123.7 (2)
C(8)—N(1)—C(12)	126.0 (2)	C(15)—C(14)—C(19)	118.1 (2)
C(1)—N(1)—C(12)	123.1 (2)	C(16)—C(15)—C(14)	121.3 (2)
C(8)—N(2)—C(2)	109.4 (2)	C(17)—C(16)—C(15)	119.9 (3)
C(8)—N(2)—C(4)	123.8 (2)	C(16)—C(17)—C(18)	120.2 (2)
C(2)—N(2)—C(4)	122.4 (2)	C(17)—C(18)—C(19)	119.8 (2)
N(1)—C(8)—N(2)	112.5 (2)	C(18)—C(19)—C(14)	120.7 (2)
N(1)—C(8)—C(7)	123.7 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O(1)—H(O1)···O(4)	0.82	1.906 (2)	2.642 (2)	149.0 (1)
O(2)—H(O2)···O(3)	0.82	1.980 (2)	2.681 (2)	143.1 (2)
C(1)—H(1*A*)···O(3$^{\rm i}$)	0.97	2.781 (3)	3.319 (3)	115.7 (3)
C(1)—H(1*B*)···O(2$^{\rm i}$)	0.97	2.579 (3)	3.325 (3)	133.8 (3)
C(7)—H(7)···O(3$^{\rm ii}$)	0.98	2.571 (2)	3.361 (2)	137.7 (3)
C(7)—H(7)···O(4$^{\rm ii}$)	0.98	2.642 (3)	3.574 (3)	159.0 (2)

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

All non-H atoms were refined anisotropically. H atoms were placed in geometrically calculated positions and allowed to refine, riding on the atoms to which they are attached, with a common isotropic displacement parameter.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976) and *XP* (Siemens, 1991). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1059). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). **C54**, 142–145

Ammonium and Isopropylammonium Salts of the Fumaric Acid Dianion

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(*Received 17 June 1997; accepted 16 October 1997*)

Abstract

The crystal structures of diammonium fumarate, $2NH_4^+.C_4H_2O_4^{2-}$, (I), and bis(isopropylammonium) fumarate, $2C_3H_7NH_3^+.C_4H_2O_4^{2-}$, (II), have been determined. The intermolecular N—H···O hydrogen bonds form a three-dimensional network in (I), whereas two-dimensional sheets are formed in (II) separated by layers of isopropyl groups. The N···O distances are 2.790 (1)–2.903 (1) Å in (I) and 2.747 (1)–2.807 (1) Å in (II). Differences between the solid-state photoreactivities of the fumaric acid ions in (I) and (II) are rationalized based on the crystal structures.

Comment

Organic solid-state reactions have the potential to control the stereoselectivity of chemical reactions. Many practical applications have been developed (Ramamurthy & Venkatesan, 1987; Toda, 1995; Gamlin *et al.*, 1996), since the topochemical photodimerization of *trans*-cinnamic acid was studied by Schmidt (1964).