

C2—N1—C5	114.11 (14)	N3—C4—C5	106.65 (13)
N1—C2—N3	106.79 (14)	N1—C5—C51	111.72 (13)
N1—C2—S	128.75 (13)	N1—C5—C61	109.64 (13)
N3—C2—S	124.46 (12)	C51—C5—C61	114.46 (13)
C2—N3—C4	112.51 (14)	N1—C5—C4	99.93 (12)
O—C4—N3	126.7 (2)	C4—C5—C51	107.29 (13)
O—C4—C5	126.66 (15)	C4—C5—C61	112.87 (14)
N1—C5—C51—C52	29.2 (2)	N1—C5—C61—C62	68.9 (2)
N1—C5—C51—C56	-156.2 (2)	N1—C5—C61—C66	-106.9 (2)
C4—C5—C51—C52	-79.4 (2)	C4—C5—C61—C62	179.3 (2)
C4—C5—C51—C56	95.2 (2)	C4—C5—C61—C66	3.5 (2)

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

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...S ⁱ	0.84 (2)	2.56 (2)	3.394 (2)	174 (2)
N3—H3...O ⁱⁱ	0.87 (2)	2.25 (2)	3.094 (2)	165 (2)

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

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *Xtal3.0* (Hall & Stewart, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976) and *PLUTON* (Spek, 1992). Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1365). Services for accessing these data are described at the back of the journal.

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Racemic 2-Hydroxy-2-phenylpropanamidinium Chloride and (S)-2-Hydroxy-2-phenylbutanamidinium (R)-2-Hydroxy-2-phenylethanoate

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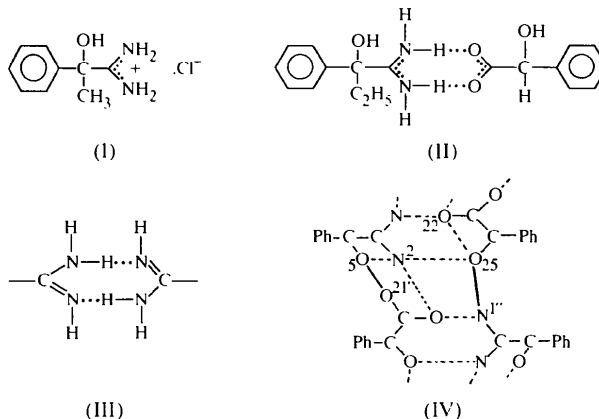
(Received 26 September 1997; accepted 9 February 1998)

Abstract

In 2-hydroxy-2-phenylpropanamidinium chloride, C₉H₁₃N₂O⁺.Cl⁻, the anion plays a central role in the hydrogen-bond network, chelating to one amidinium group and forming intermolecular links to neighbouring NH₂ and OH⁻ groups. The central feature in (S)-2-hydroxy-2-phenylbutanamidinium (R)-2-hydroxy-2-phenylethanoate, C₁₀H₁₅N₂O⁺.C₈H₇O₃⁻, is a ring linking the cation and anion through two hydrogen bonds. The structure is extended by intra- and intermolecular hydrogen bonds.

Comment

For almost 80 years, stereochemical studies of derivatives of mandelic (2-hydroxy-2-phenylethanoic) and atrolactic (2-hydroxy-2-phenylpropanoic) acids and the corresponding amidines have been carried out in what is now the University of Dundee (see e.g. McKenzie & Wren, 1919; Roger & Neilson, 1959). The supramolecular structures of the title compounds, (I) and (II), have now been investigated as part of a study of extended hydrogen-bond systems (Barnes & Barnes, 1996; Barnes *et al.*, 1998), using crystals from the original preparations (Roger & Neilson, 1959).



Allowing for chirality, the stereochemistries of (I) (Fig. 1) and of the cation and anion in (II) (Fig. 2) are similar. In each, the hydroxyl group is involved in both intramolecular interactions and intermolecular hydrogen bonds. The motif $N2-H21 \cdots O5-H51 \cdots C1'$ in (I) corresponds to $N2-H2B \cdots O5-H5A \cdots O21'$ for the cation in (II) and $O22 \cdots H25A-O25 \cdots H1B''-N1''$ for the anion (symmetry positions are given in Tables 2 and 4). The intramolecular interaction in the rings $N2-H21 \cdots O5-C4-C3$, $N2-H2B \cdots O5-C4-C3$ and $O22 \cdots H25A-O25-C24-C23$ requires a very small angle at the H atom: $109(1)^\circ$ in (I), $116(4)^\circ$ in the cation of (II) and $128(4)^\circ$ in the anion of (II). The torsion angles $N2-C3-C4-O5$ are $-25.8(2)^\circ$ in (I) and $9.0(4)^\circ$ in (II), and $7.1(2)^\circ$ for $O22-C23-C24-O25$ in (II). In the Etter notation these rings are $R_1^1(5)$. (Bernstein *et al.*, 1995).

The hydrogen-bonding network in (I) has much in common with that in chiral benzamidinium chloride monohydrate (Thailambal *et al.*, 1986), in which the

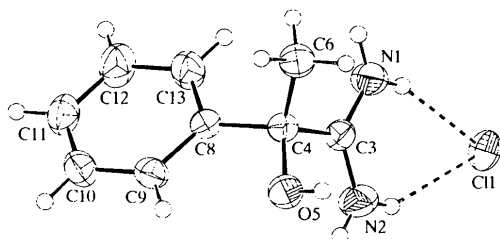


Fig. 1. Structure of (I), showing 50% probability displacement ellipsoids.

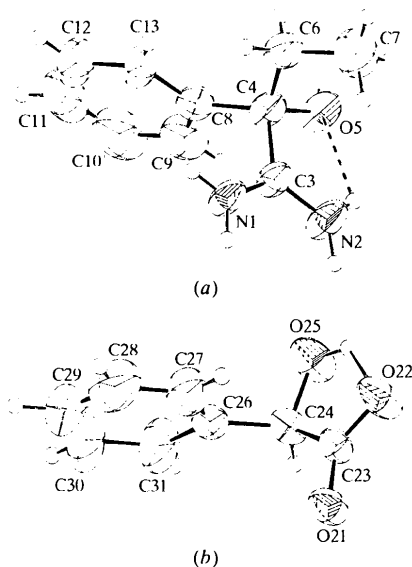


Fig. 2. Structures of (a) the (*S*)-2-hydroxy-2-phenylbutanamidinium cation and (b) the (*R*)-mandelate anion in (II), showing 50% probability displacement ellipsoids.

water molecule fulfils a similar role to the OH group in (I). Atoms C11, H11, N1, C3, N2 and H22 form a planar $R_2^2(6)$ ring, with $H11-C11-H22 = 54.57(8)^\circ$. The pseudo-tetrahedral environment of C11 is completed by hydrogen bonds to $H12'-N1'$ and $H51''-O5''$ of adjacent molecules, as shown in Fig. 3 (symmetry positions are given in Tables 2 and 4).

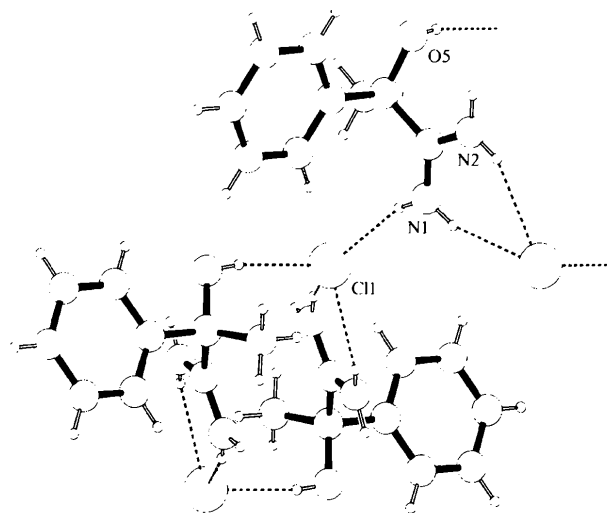


Fig. 3. Hydrogen-bonding network in (I), showing the tetrahedral coordination of C11.

The familiar hydrogen-bond motif, $R_2^2(8)$, found in carboxylic acid dimers is also known in amidines, (III) (Sohar, 1967). The same motif occurs in some 2-hydroxyamidinium carboxylate salts such as (II) (Fig. 4) and (*S*)-*o*-bromomandelamidinium (*R*)-mandelate (Iball *et al.*, 1982). These workers also examined the less stable diastereomer (*R*)-*o*-bromo-

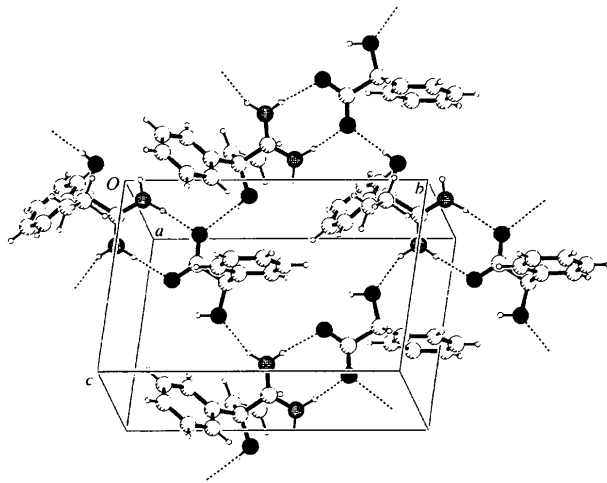


Fig. 4. Hydrogen-bonding network in (II); O atoms are shown solid and N atoms are shown hatched.

mandelamidinium (*R*)-mandelate, (IV), in which the R₂²(8) motif is replaced by an R₂²(9) ring involving the hydroxyl group of the mandelate. The facile resolution of the series of racemic amidines into their pure (*R*)- or (*S*)-mandelate salts (Roger & Neilson, 1959) must be associated with these alternative hydrogen-bonding schemes.

Experimental

Crystals were available from the original preparation by Roger & Neilson (1959).

Compound (I)

Crystal data

C₉H₁₃N₂O⁺.Cl⁻

M_r = 200.66

Monoclinic

*P*2₁/*n*

a = 8.8847 (6) Å

b = 10.483 (1) Å

c = 11.6776 (13) Å

β = 108.375 (8)°

V = 1032.18 (17) Å³

Z = 4

D_x = 1.291 Mg m⁻³

D_m not measured

Data collection

Enraf–Nonius CAD-4
diffractometer

ω–2θ scans

Absorption correction: none

2193 measured reflections

1814 independent reflections

1573 reflections with

I > 2σ(*I*)

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.054

wR(*F*²) = 0.155

S = 1.823

1814 reflections

92 parameters

H atoms treated by a

mixture of independent
and constrained refinement

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25
reflections

θ = 14–15°

μ = 0.334 mm⁻¹

T = 293 (2) K

Block

0.34 × 0.27 × 0.18 mm

Colourless

*R*_{int} = 0.011

θ_{max} = 24.97°

h = -1 → 10

k = 0 → 12

l = -13 → 13

3 standard reflections

frequency: 60 min

intensity decay: 3%

w = 1/[σ²(*F_o*²) + (0.0493*P*)²
+ 0.2343*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.078

Δρ_{max} = 0.677 e Å⁻³

Δρ_{min} = -0.475 e Å⁻³

Extinction correction: none

Scattering factors from

*International Tables for
Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °) for (I)

N1—C3	1.299 (4)	C4—O5	1.414 (3)
N2—C3	1.306 (4)	C4—C6	1.526 (4)
C3—C4	1.530 (4)	C4—C8	1.542 (3)
N1—C3—N2	120.8 (3)	O5—C4—C8	107.01 (19)
N1—C3—C4	121.7 (2)	C6—C4—C8	110.1 (2)
N2—C3—C4	117.5 (3)	C3—C4—C8	108.86 (19)
O5—C4—C6	111.2 (2)	C9—C8—C13	120.0
O5—C4—C3	107.7 (2)	C9—C8—C4	119.53 (14)
C6—C4—C3	111.8 (2)	C13—C8—C4	120.43 (14)

N2—C3—C4—O5	-25.8 (2)	C3—C4—C8—C9	-124.50 (18)
C3—C4—O5—H51	-74 (3)	O5—C4—C8—C9	-8.3 (2)
N2—C3—C4—C8	90.1 (2)		

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

<i>D</i> — <i>H</i> ... <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> — <i>H</i> ... <i>A</i>
N1—H11...C11	0.91 (4)	2.29 (4)	3.166 (3)	161 (3)
N2—H22...C11	0.82 (4)	2.56 (4)	3.291 (3)	149 (4)
N1—H12...C11'	0.86 (4)	2.37 (4)	3.204 (3)	165 (3)
O5—H51...C11''	0.81 (4)	2.32 (4)	3.127 (2)	170 (4)

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

Compound (II)

Crystal data

C₁₀H₁₅N₂O⁺.C₈H₇O₃⁻

M_r = 330.38

Monoclinic

*P*2₁

a = 7.3793 (9) Å

b = 12.917 (4) Å

c = 10.2713 (13) Å

β = 109.407 (11)°

V = 923.4 (3) Å³

Z = 2

D_x = 1.188 Mg m⁻³

D_m not measured

Data collection

Enraf–Nonius CAD-4
diffractometer

ω–2θ scans

Absorption correction: none

2014 measured reflections

1865 independent reflections

1487 reflections with

I > 2σ(*I*)

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25
reflections

θ = 14.1–15.3°

μ = 0.084 mm⁻¹

T = 293 (2) K

Prism

0.50 × 0.41 × 0.09 mm

Colourless

*R*_{int} = 0.012

θ_{max} = 24.97°

h = 0 → 8

k = -1 → 15

l = -12 → 11

3 standard reflections

frequency: 60 min

intensity decay: 3%

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.037

wR(*F*²) = 0.107

S = 1.111

1865 reflections

208 parameters

H atoms treated by a

mixture of independent
and constrained refinement

w = 1/[σ²(*F_o*²) + (0.0590*P*)²
+ 0.0456*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.009

Δρ_{max} = 0.121 e Å⁻³

Δρ_{min} = -0.141 e Å⁻³

Extinction correction: none

Scattering factors from

*International Tables for
Crystallography* (Vol. C)

Absolute structure: Flack

(1983)

Flack parameter = 2.4 (17)

Table 3. Selected geometric parameters (Å, °) for (II)

N1—C3	1.310 (3)	C6—C7	1.502 (6)
N2—C3	1.293 (4)	O21—C23	1.2468
C3—C4	1.524 (4)	O22—C23	1.2512
C4—O5	1.415 (3)	C23—C24	1.5212
C4—C8	1.533 (3)	C24—O25	1.4266
C4—C6	1.536 (5)	C24—C26	1.4993 (19)
N2—C3—N1	121.5 (3)	C9—C8—C4	117.28 (13)
N2—C3—C4	118.2 (2)	C13—C8—C4	122.72 (13)
N1—C3—C4	120.3 (3)	O21—C23—O22	125.6
O5—C4—C3	104.3 (2)	O21—C23—C24	118.5
O5—C4—C8	111.3 (2)	O22—C23—C24	115.9
C3—C4—C8	109.2 (2)	O25—C24—C26	110.16 (10)

O5—C4—C6	109.8 (2)	O25—C24—C23	108.5
C3—C4—C6	108.2 (2)	C26—C24—C23	112.76 (9)
C8—C4—C6	113.5 (2)	C27—C26—C24	121.05 (16)
C7—C6—C4	115.0 (3)	C31—C26—C24	118.91 (16)
C9—C8—C13	120.0		
O5—C4—C8—C9	34.2 (2)	C3—C4—C8—C9	-80.43 (19)
O22—C23—C24—C26	-115.15 (11)	N2—C3—C4—C6	-107.9 (3)
O22—C23—C24—O25	7.1 (2)	C3—C4—C6—C7	61.2 (3)
C23—C24—C26—C27	38.69 (16)	N2—C3—C4—O5	9.0 (4)
N2—C3—C4—C8	128.1 (3)		

Table 4. Hydrogen-bonding geometry (Å, °) for (II)

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1A...O22	0.87 (4)	2.01 (4)	2.810 (3)	153 (3)
N1—H1B...O25 ^a	0.88 (4)	2.04 (4)	2.869 (3)	159 (3)
N2—H2A...O21	0.94 (5)	1.85 (5)	2.784 (3)	175 (4)
N2—H2B...O5	0.89 (4)	1.98 (4)	2.504 (3)	116 (4)
O5—H5A...O21 ^b	0.71 (4)	1.97 (5)	2.675 (3)	176 (5)
O25—H25A...O22	0.89	1.89	2.535 (2)	128.3

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

For both compounds, data collection: *CAD-4/PC* (Enraf-Nonius, 1993); cell refinement: *CAD-4/PC*; data reduction: *XCAD4* (Harms & Wocadlo, 1996); program(s) used to solve structures: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997b); molecular graphics: *PLATON92* (Spek, 1992a) and *PLUTON92* (Spek, 1992b); software used to prepare material for publication: *SHELXL97*.

Thanks are extended to Dr D. G. Neilson for the crystals, and for his interest in the work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1392). Services for accessing these data are described at the back of the journal.

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sp-9-[*o*-(β-Chloro-α,α-dimethylethyl)-phenyl]fluorene: an Unanticipated Exclusive Product from the Reaction of *sp*-9-(*o*-*tert*-Butylphenyl)-9-fluorenol with Thionyl Chloride

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Abstract

The reaction of *sp*-9-(*o*-*tert*-butylphenyl)-9-fluorenol, (1), with thionyl chloride in CHCl₃ at room temperature quantitatively provided the title compound [(2), C₂₃H₂₁Cl], instead of the expected 9-(*o*-*tert*-butylphenyl)-9-chlorofluorene. Chlorination of an alkyl group under the conditions in which (1) was converted into (2) is apparently unprecedented. While the unexpected structure of (2) was suggested by ¹H and ¹³C NMR, unequivocal characterization required X-ray crystallographic analysis. Surprisingly, introduction of the Cl atom in (2) imposes only a few minor changes in the bonding parameters compared with its non-chlorinated counterpart, *sp*-9-(*o*-*tert*-butylphenyl)fluorene.

Comment

Thionyl chloride is the commonly used reagent in the classical conversion of an alcohol into its alkyl chloride, presumably through the S_Ni mechanism (Schreiner *et al.*, 1993). Accordingly, in our plan to convert *sp*-9-(*o*-*tert*-butylphenyl)-9-fluorenol [(1); Robinson *et al.*, 1998; Nakamura *et al.*, 1977] into the corresponding 9-(*o*-*tert*-butylphenyl)-9-chlorofluorene, (3), to determine whether it would be the *ap* or *sp* rotamer, or both (Meyers *et al.*, 1997), we treated (1) with SOCl₂ in the usual manner (see Scheme below). The colorless crystalline product had the molecular formula of the desired product and a sharp melting point, and was isolated in quantitative yield, but its ¹H and ¹³C NMR spectra were incorrect for compound (3). The presence of a singlet for a CH₂ group together with a singlet representing two identical CH₃ groups suggested that the *tert*-butyl group had been monochlorinated. Such a transformation under these conditions was unprecedented. An X-ray diffraction study was thus undertaken to verify the structure.