

Charge-assisted N—H···I and C—H···I hydrogen bonding in (1*R*,2*S*)-1-(ferrocenylmethyl)-2-(methoxymethyl)pyrrolidinium iodide

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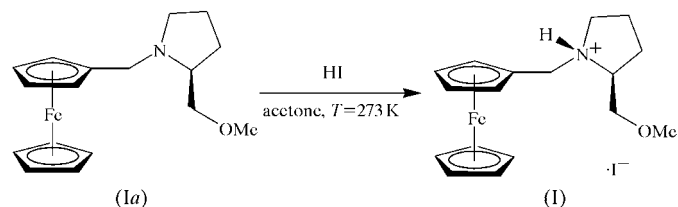
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In the title compound, [Fe(C₅H₅)(C₁₂H₁₉NO)]I, the ferrocene moiety has an eclipsed conformation, with mean Fe—C bond lengths of 2.031 (4) and 2.020 (6) Å for the substituted and unsubstituted cyclopentadienyl rings. The pyrrolidinium heterocycle adopts an envelope conformation and has its 1- and 2-substituents in a relative *trans* disposition. Strong (+/−)-charge-assisted N—H···I and C—H···I hydrogen bonds are present. The crystal structure is also stabilized by weak C—H···O interactions.

Comment

(*S*)-1-Ferrocenylmethyl-2-(methoxymethyl)pyrrolidine, (*Ia*), is a useful starting material for the synthesis of enantiomerically pure chiral ferrocenes, which are important for asymmetric catalysis (Ganter & Wagner, 1995). Since (*Ia*) is an oil, it could not be characterized by X-ray diffraction. However, we have found that the corresponding hydroiodide, (*I*), forms crystals suitable for crystallographic study. We report here the structure of (*I*), revealing the absolute configuration at the N atom and intermolecular hydrogen bonds influencing the crystal packing.



In (*I*), the cyclopentadienyl rings in the ferrocene moiety (substituted, Cp*A*, and unsubstituted, Cp*B*) are parallel [dihedral angle = 1.5 (2)°]. The Cp rings are essentially eclipsed, with C*n*A···C*g*A···C*g*B···C*n*B angles (*n* = 1–5; C*g*A

and C*g*B are the centroids of the corresponding Cp rings) averaging approximately 3°. The Fe···C*g*A and Fe···C*g*B distances are 1.6423 (4) and 1.6464 (4) Å, respectively, and the C*g*A···Fe···C*g*B angle is 179.2 (2)°. The small but systematic differences between the Fe—C*n*A bond lengths [2.025 (3)–2.040 (4) Å] and the shorter corresponding Fe—C*n*B distances [2.011 (5)–2.026 (5) Å], as well as the slight differences between the observed C—C distances in the two rings, could be the result of greater overall displacement, including libration, for ring Cp*B*. Methine atom C6 is tilted slightly from the plane of its carrier Cp ring, toward the Fe atom. The C1A—C6 bond forms an angle of 3.4 (2)° with the plane of ring Cp*A*, while the Fe···C6 distance is 3.090 (4) Å. The C6—N7 bond is in an antiperiplanar orientation with respect to the ferrocene moiety [Fe—C1A—C6—N7 = 176.3 (2)°].

The five-membered heterocyclic ring adopts an envelope conformation with atom C8 at the apex. The ring puckering parameters (Cremer & Pople, 1975) for the N7/C8—C11 ring are $q_2 = 0.307$ (4) Å and $\varphi_2 = -147.0$ (7)°. The corresponding asymmetry parameter (Nardelli, 1983) $\Delta S(C8)$ is 0.013 (2). The flat fragment of this ring, C9/C10/C11/N7, forms an angle of 41.2 (2)° with the plane of ring Cp*A*. The substituents at atoms N7 and C8 are equatorial and in a relative *trans* disposition. Torsion angles describing these features are presented in Table 1.

The molecule has two chiral centers, N7 and C8, and crystallizes in a chiral space group. The Flack (1983) parameter was refined, revealing the stereochemistry 1*R*(N7),2*S*(C8) (Fig. 1). Thus, protonation of the N atom in (*Ia*) proceeded in a diastereoselective manner, leading to the more stable *trans* arrangement of substituents at atoms N7 and C8.

Hydrogen bonding is important in the extended structure of (*I*). Table 2 lists all interactions with H···A distances shorter than the sum of the van der Waals radii (Bondi, 1964) minus 0.1 Å. There are three interactions in which the iodine anion acts as an acceptor, while positively charged atom N7 and two of the C atoms bonded to it (C6 and C8) act as donors.

The N7—H7···I[−] [symmetry code: (i) −1 + *x*, *y*, *z*] contact is an example of a charge-assisted hydrogen bond in which the

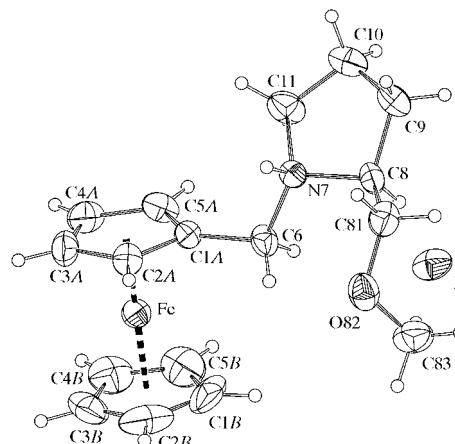


Figure 1
A view of the components of (*I*) (40% probability displacement ellipsoids).

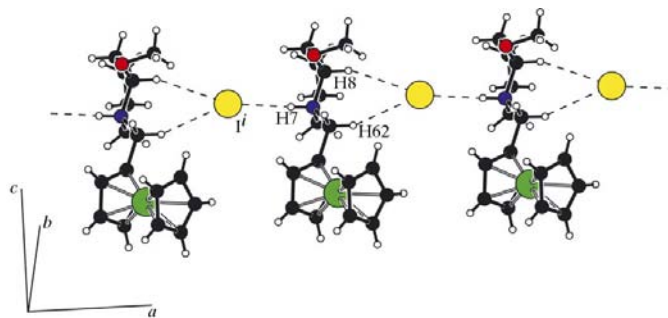


Figure 2
Charge-assisted hydrogen bonding in (I). The molecules form chains along the [100] direction.

donor and acceptor are oppositely charged ions [(+/-)CAHB]. This type of interaction, also called a salt bridge (Gilli & Gilli, 2000), is the strongest known hydrogen-bond type. There are 1453 cases of N—H...I hydrogen bonds in the Cambridge Structural Database (CSD; Version of November 2003; Allen, 2002), of which only about 14% (201 cases) may be classified as (+/-)CAHBs. The average (N)H...I distance is 2.958 Å for N—H...I hydrogen bonding without charge assistance, and 2.899 Å for (+)CAHBs, 2.855 Å for (-)CAHBs and 2.808 Å for (+/-)CAHBs. These differences in hydrogen-bond lengths are unsurprising, since the proton-acceptor distance correlates well with hydrogen-bond energy (Grabowski, 2003) and is often applied as a criterion for judging hydrogen-bond strength. On the basis of this distance, the N—H...I interaction in (I) may be considered to be relatively strong compared with all of the N—H...I (+/-)CAHB interactions found in the CSD. There are also two C—H...I interactions in (I), with atoms C6 and C8 acting as donors. It is known that Csp^3 atoms have limited proton-donating properties (Desiraju & Steiner, 1999), but in this case proximity to the positively charged N atom may enhance the capacity of atoms C6 and C8 to take part in hydrogen bonding. These weaker interactions complete a six-membered ring, with second-level graph-set descriptor $R_1^2(6)$ (Bernstein *et al.*, 1995), while the first-level graph-set descriptor $C(6)$ describes chains generated from a translation operation along [100], as shown in Fig. 2.

The crystal packing of (I) is also stabilized by weak C—H...O interactions. In one of these, C10—H102...O82ⁱⁱ [symmetry code: (ii) $-x, \frac{1}{2} + y, \frac{1}{2} - z$], the molecules are related by a 2_1 symmetry operation, which leads to the formation of $C(6)$ chains. A short H61...O82 distance suggests the existence of a further intermolecular interaction, C6—H61...O82, graph set $S(6)$. Overall, there is a three-dimensional network of hydrogen bonds of varying strength, which stabilizes the hydroiodide moiety in the crystal.

Experimental

The iodide salt was generated by reaction of (*S*)-1-ferrocenylmethyl-2-(methoxymethyl)pyrrolidine (Ganter & Wagner, 1995) with hydroiodic acid in acetone at 273 K for 1 h. X-ray-quality single crystals were obtained from a diethyl ether solution cooled to 278 K.

Crystal data

[Fe(C₅H₅)(C₁₂H₁₉NO)]I
 $M_r = 441.12$
 Orthorhombic, $P2_12_12_1$
 $a = 7.777(2) \text{ \AA}$
 $b = 11.575(3) \text{ \AA}$
 $c = 20.160(5) \text{ \AA}$
 $V = 1814.8(8) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.615 \text{ Mg m}^{-3}$

Data collection

Rigaku AFC-5S diffractometer
 ω scans
 14 192 measured reflections
 3559 independent reflections
 2211 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.051$
 $\theta_{\text{max}} = 26^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.044$
 $S = 0.82$
 3559 reflections
 191 parameters
 H-atom parameters constrained

Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 12.7\text{--}14.9^\circ$
 $\mu = 2.53 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Needle, orange
 $0.5 \times 0.1 \times 0.1 \text{ mm}$

$h = -9 \rightarrow 9$
 $k = -14 \rightarrow 14$
 $l = -24 \rightarrow 24$
 3 standard reflections
 every 150 reflections
 intensity decay: 2%

$w = 1/[\sigma^2(F_o^2) + (0.0149P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.52 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.50 \text{ e \AA}^{-3}$
 Absolute structure: Flack (1983),
 1508 Friedel pairs
 Flack parameter = $-0.03(2)$

Table 1

Selected geometric parameters (Å, °).

O82—C81	1.407 (4)	N7—C11	1.489 (4)
N7—C6	1.505 (4)	C6—C1A	1.488 (4)
N7—C8	1.522 (4)	C83—O82	1.420 (5)
C81—O82—C83	113.6 (3)	C11—N7—C6	114.0 (3)
C11—N7—C8	105.6 (3)	C1A—C6—N7	113.5 (3)
C6—N7—C8	114.6 (3)	C81—C8—N7	113.2 (3)
C6—N7—C8—C81	-80.6 (4)	C9—C10—C11—N7	1.7 (6)
C81—C8—C9—C10	-152.3 (4)	C6—N7—C11—C10	-147.2 (4)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N7—H7...I ⁱ	0.91	2.55	3.454 (5)	170
C6—H62...I	0.97	3.05	3.963 (6)	157
C8—H8...I	0.98	3.07	4.000 (7)	159
C6—H61...O82	0.97	2.48	3.138 (7)	125
C10—H102...O82 ⁱⁱ	0.97	2.56	3.441 (6)	151

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

All H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.93–0.98 Å, an N—H distance of 0.91 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1989); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

PLATON (Spek, 2003); software used to prepare material for publication: PARST (Nardelli, 1996).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1094). Services for accessing these data are described at the back of the journal.

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