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Ferrocene compounds. XXXIV. 1′-(*tert*-Butoxycarbonylamino)-ferrocene-1-carboxylic acid

Gordana Pavlović,[a] Lidija Barišić,[b] Vladimir Rapić[b]* and Veronika Kovač[b]

[a]Faculty of Textile Technology, University of Zagreb, Pierottijeva 6, HR-10000 Zagreb, Croatia, and [b]Laboratory of Organic Chemistry, Faculty of Food Technology and Biotechnology, University of Zagreb, Pierottijeva 6, HR-10000 Zagreb, Croatia
Correspondence e-mail: vrapic@pbf.hr

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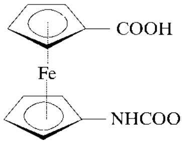
Heteroannularly substituted ferrocene derivatives can act as model systems for various hydrogen-bonded assemblies of biomolecules formed, for instance, by means of O—H···O and N—H···O hydrogen bonding. The crystal structure analysis of 1′-(*tert*-butoxycarbonylamino)ferrocene-1-carboxylic acid, [Fe($C_{10}H_{14}NO_2$)($C_6H_5O_2$)] or (C_5H_4COOH)Fe($C_5H_4NHCOOC(CH_3)_3$), reveals two independent molecules within the asymmetric unit, and these are joined into discrete dimers by two types of intermolecular hydrogen bonds, *viz*. O—H···O and N—H···O. The –COOH and –NHCOO*R* groups are archetypes for dimer formation *via* two eight-membered rings. The O—H···O hydrogen bonds [2.656 (3) and 2.663 (3) Å] form a cyclic carboxylic acid dimer motif. Another eight-membered ring is formed by N—H···O hydrogen bonds [2.827 (3) and 2.854 (3) Å] between the N—H group and an O atom of another carbamoyl moiety. The dimers are assembled in a herring-bone fashion in the *bc* plane.

Comment

Conjugates of metallocenes with natural amino acids and peptides are of great interest in the field of bioorganometallic chemistry. Over the past five decades, many *N*- and *C*-ferrocenylamino acids and their derived peptides have been synthesized and studied. Current investigations have concentrated on 1,1′-ferrocenylenebis(amino acids) and the corresponding peptides, especially as chemical models of β-sheet and α-helix arrays, having interesting electrochemical and chelating properties (Oberhoff *et al.*, 1996; Kraatz *et al.*, 1997; Saweczko *et al.*, 2001; Metzler-Nolte, 2001; Moriuchi *et al.*, 2001; Pal *et al.*, 2001).

Our investigations are directed towards the synthesis and characterization of a series of synthetic amino acids containing a skeletally bonded 1,1′-ferrocenylene unit. The first homologue of this class of heteroannularly substituted ferrocene compounds is 1′-aminoferrocene-1-carboxylic acid. The *C*- and/or *N*-protected derivatives of this compound, as well as its conjugates with natural amino acids (Barišić *et al.*, 2002; Rapić *et al.*, 2002; Barišić *et al.*, 2003), reveal various types of hydrogen bonds, such as N—H···O═C, O—H···O and C—H···O, and a range of hydrogen-bonding patterns (infinite chains, discrete dimers, *etc*.; Pavlović *et al.*, 2000; Pavlović, Barišić, Rapić & Leban, 2002; Pavlović, Barišić, Lapić & Rapić, 2002; Rapić *et al.*, 2002), which act as models for the study of hydrogen bonding in biological environments. Therefore, such carboxy derivatives can be used as organometallic building blocks for crystal engineering (Braga *et al.*, 2001), where $R_2^2(8)$ rings are the most frequent supramolecular synthons formed by carboxyl groups. In this context, the crystal structure of the title compound, (I), is presented.



(I)

Compound (I) crystallizes with Z' = 2 (Fig. 1). The two molecules have different conformations adjacent to the *tert*-butyl groups. The other parts of the molecules differ only slightly. Both molecules exhibit disorder of the carboxylic acid group, with H atoms occurring statistically with equal probability (see *Experimental*).

Within the ferrocenyl moieties, the mean Fe—C bond distances for substituted and unsubstituted C atoms do not exhibit significant differences, according to the 3σ crystallographic criterion, with a mean value for Fe—C(unsubstituted) of 2.044 (3) Å and for Fe—C(substituted) of 2.054 (3) Å. The cyclopentadienyl (Cp) rings are twisted away from the fully eclipsed conformation. The dihedral angles between the corresponding planes calculated through two C atoms and the centroids of rings C11–C15 (*Cg*1), C16–C19/C110 (*Cg*2), C21–C25 (*Cg*3) and C26–C29/C210 (*Cg*4) are in the ranges 11.7 (6)–12.6 (3)° and 12.7 (3)–13.2 (3)° for molecules 1 and 2, containing Fe1 and Fe2, respectively. The distances between the Fe atoms and the centroids are *Cg*1—Fe1 = 1.6633 (4), *Cg*2—Fe1 = 1.6490 (4), *Cg*3—Fe2 = 1.6618 (6) and *Cg*4—Fe2 = 1.6487 Å, and the angles are *Cg*1—Fe1—*Cg*2 = 179.15 (3) and *Cg*3—Fe2—*Cg*4 = 179.72 (4)°.

The carboxylic acid moieties are coplanar with the ferrocenyl moieties to which they belong, and the planarity is slightly more pronounced in one molecule than in the other; the dihedral angle between the planes defined by atoms C16–C110 and C116/O3/O4 is 2.4 (5)°, while that between the planes defined by atoms C26–C210 and C216/O7/O8 is 4.2 (5)°. The $C_{ring}—C_{carboxyl}$ bond distances (C16—C116 and C26—C216) of 1.469 (5) and 1.464 (4) Å, respectively, have significant π character, due to the coupling of the π electrons of the Cp ring and the carboxyl moiety. These bonds are comparable with the analogous value of 1.466 (2) Å in the

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structure of ferrocene-1,1′-dicarboxylic acid (FDAH; neutron study at 78 K; Takusagawa & Koetzle, 1979), but noticeably longer than the value of 1.407 (15) Å in the structure of ferrocenecarboxylic acid (FCAH; Cotton & Reid, 1985). A later more precise study of FCAH at low temperature gave a value of 1.462 (2) Å (Lin *et al.*, 1998), consistent with the calculated value of 1.460 Å for the $C_{\rm ring}—C_{\rm carboxyl}$ bond distance.

The –NHCOO– groups are inclined towards the Cp rings at angles of 16.7 (2) and 6.9 (2)°, which are more twisted than the carboxyl groups. This is in accordance with the bulkiness of the *tert*-butyl substituents. π-Delocalization through the –NHCOO– groups and Cp rings is indicated by the N1—C111 and N2—C211 bond distances of 1.344 (4) and 1.356 (4) Å, respectively, which are between single- and double-bond values. The other geometric parameters within the carboxyl and Boc, NHCOOC$(CH_3)_3$, moieties are normal (Allen *et al.*, 1987).

The two independent molecules in (I) form discrete dimers through hydrogen bonding (Fig. 2). In a similar manner, FCAH (Cotton & Reid, 1985) and FDAH (Takusagawa & Koetzle, 1979) are dimerized in the solid state into units containing O—H···O hydrogen bonds [2.714 (14) Å in FCAH and 2.5997–2.6597 Å for the two independent molecules in FDAH], as is found in most structures of carboxylic acid derivatives (Leiserowitz, 1976). The dimers in (I) are formed by two eight-membered rings. One ring resembles those in carboxylic acid dimers, with O—H···O intermolecular hydrogen bonds (Table 2) of 2.656 (3) Å for O4···O7 and 2.663 (3) Å for O8···O3. The other ring is formed by N—H···O intermolecular hydrogen bonds between the –NHCOO– group and an O atom from another carbamoyl moiety. These N—H···O hydrogen bonds are longer, as expected, being 2.827 (3) and 2.854 (3) Å for N1···O6 and N2···O2, respectively. The two eight-membered rings are twisted with respect to each other by 5.9 (6)°.

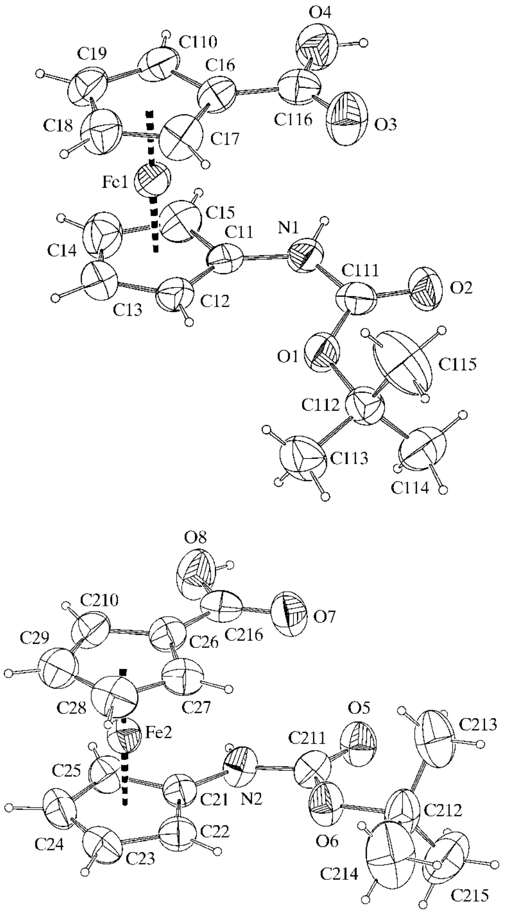

Figure 1
A view of the two independent molecules in the structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

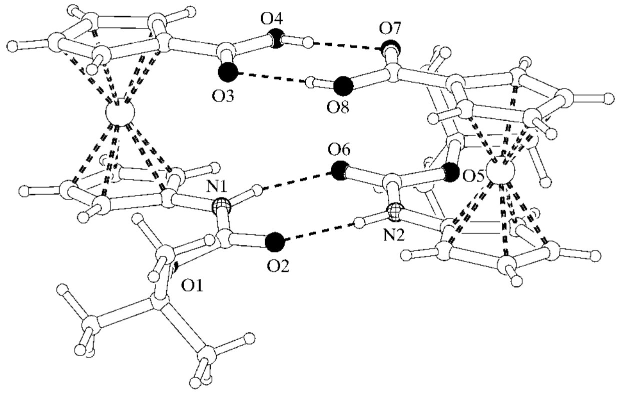

Figure 2
The dimerization of the two crystallographically independent molecules of (I) in the unit cell. Two eight-membered rings are formed by intermolecular hydrogen bonds between the two molecules. The hydrogen bonds are indicated by dashed lines.

Experimental

The synthesis of compound (I) was published recently by Barišić *et al.* (2002). Diffraction quality crystals of (I) were obtained from a solution in dichloromethane–*n*-pentane (1:2).

Crystal data

$[Fe(C_{10}H_{14}NO_2)(C_6H_5O_2)]$
$M_r = 345.17$
Monoclinic, $P2_1/n$
$a = 10.1876\,(7)$ Å
$b = 18.8055\,(15)$ Å
$c = 16.7034\,(13)$ Å
$\beta = 94.590\,(7)°$
$V = 3189.8\,(4)$ Å^3
$Z = 8$

$D_x = 1.438$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 72 reflections
$\theta = 10.0$–$18.3°$
$\mu = 0.96$ mm^{-1}
$T = 293\,(2)$ K
Prism, orange
0.53 × 0.26 × 0.13 mm

Data collection

Philips PW1100 diffractometer, updated by Stoe
ω scans
Absorption correction: ψ scan (*X-RED*; Stoe & Cie, 1995)
$T_{\rm min} = 0.630$, $T_{\rm max} = 0.885$
11 087 measured reflections
9280 independent reflections
3237 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.027$
$\theta_{\rm max} = 30°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 26$
$l = 0 \rightarrow 23$
4 standard reflections
frequency: 120 min
intensity decay: 3.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.113$
$S = 0.94$
9280 reflections
405 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0359P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.28$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mean Fe—C(unsubst.)	2.044 (3)	O5—C212	1.480 (4)
Mean Fe—C(subst.)	2.054 (3)	O6—C211	1.216 (4)
O1—C111	1.344 (4)	O7—C216	1.266 (4)
O1—C112	1.460 (4)	O8—C216	1.278 (4)
O2—C111	1.223 (4)	N1—C111	1.346 (4)
O3—C116	1.260 (4)	N1—C11	1.409 (4)
O4—C116	1.276 (4)	N2—C211	1.357 (4)
O5—C211	1.332 (4)	N2—C21	1.409 (4)
C211—O5—C212	120.4 (3)	C211—N2—C21	129.9 (3)
C111—N1—C11	130.1 (3)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O6	0.86	1.98	2.827 (3)	166
N2—H2···O2	0.86	1.99	2.854 (3)	177
O4—H4···O7	0.82	1.85	2.656 (3)	167
O8—H8···O3	0.82	1.86	2.663 (3)	167

The statistical disorder (Leiserowitz, 1976) of the H atoms belonging to the carboxylic acid groups was established due to the possible rotation about the C16—C116 and C26—C216 single bonds. The relatively large displacement parameters of carboxylic acid atoms O3, O4, O7 and O8 [$U_{\rm eq} = 0.0617$ (7)–0.0730 (9) Å^2] are also an indication of the presence of disorder, along with the C116—O3 and C116—O4, and C216—O7 and C216—O8 bonds, which are all longer than typical C=O bonds in C$_{\rm ar}$—C(=O)—OH and shorter than typical C$_{\rm ar}$—O bonds (Allen *et al.*, 1987). H atoms were treated as riding, with O—H distances of 0.82 Å, N—H distances of 0.86 Å and C—H distances in the range 0.93–0.96 Å.

Data collection: *STADI*4 (Stoe & Cie, 1995); cell refinement: *STADI*4; data reduction: *X-RED* (Stoe & Cie, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1998); 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: GD1239). Services for accessing these data are described at the back of the journal.

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