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The constitution of a ferrocenyl diketone: solution and solid state NMR spectroscopy. Crystal structure of 1-ferrocenyl-3-hydroxybut-2-en-1-one

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Abstract

The title compound has been shown by ^1H and ^{13}C NMR spectroscopy to exist in solution as an enol/keto mixture, with an isomer ratio at ambient temperature in chloroform of approx. 17:1. CP–MAS ^{13}C NMR spectroscopy shows that only the enol form occurs in the crystalline state. This conclusion was confirmed by a single crystal X-ray structure determination. The O–C–C–C–O fragment of the molecule is planar, with an asymmetric intramolecular hydrogen bond; there are no intermolecular hydrogen bonds.

Introduction

Both in solution and in the vapour phase [1], 1,3-diketones $R^1COCH_2COR^2$ generally exist as equilibrium mixtures of keto and enol tautomers, where the enol tautomer contains a six-membered hydrogen-bonded ring. In the solid state, however, the enol form is generally the sole form observed.

There are two extreme forms for the intramolecular hydrogen bonding, symmetric (**1**) and asymmetric (**2**), in which the ring hydrogen is bound much more tightly to one oxygen atom than to the other.

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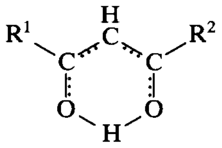
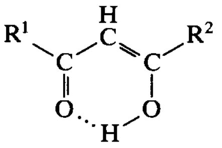
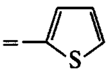
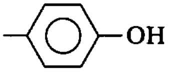
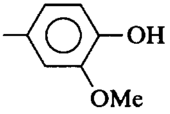
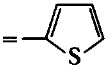


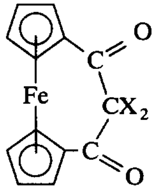
(1) **a** $R^1 = R^2 = (CH{=}CH){-}Ph$
b $R^1 = Ph, R^2 = Me$
c $R^1 = R^2 = Ph$



(2) **a** $R^1 = R^2 = Ph$
b $R^1 = R^2 =$ 
c $R^1 = R^2 = (CH{=}CH)$ 
d $R^1 = R^2 = (CH{=}CH)$ 
e $R^1 = Ph, R^2 = p\text{-}CH_3C_6H_4$
f $R^1 = CF_3, R^2 =$ 

Symmetric hydrogen bonds have been observed in examples having identical substituents R^1, R^2 (**1a**) [2] or different substituents (**1b**) [3], while markedly asymmetric hydrogen bonds have been observed both for identical substituents, **2a**–**2d** [4–7], and for different substituents, **2e** [8] and **2f** [9]. The fine balance between symmetric and asymmetric hydrogen bonding is indicated by the occurrence of the symmetric and asymmetric forms in two polymorphs of the same compound, **1c** [10] and **2a** [4].

In contrast to the formation of hydrogen-bonded enols in **1a**–**1c** and in **2a**–**2f**, the ferrocenophanedione (**3a**) exists in the solid state entirely as the dione [11], with C–C and C–O bond lengths very similar to those in the related dione (**3b**), where enolization is structurally impossible [12]. Since the lack of enolization in **3a** may result from either its geometric inability to form intramolecular hydrogen bonds, although intermolecular hydrogen bonding is not prevented, or from the presence of the ferrocene nucleus, we have investigated the structure of 1-ferrocenylbutane-1,3-dione (**4**) as part of a wider project on hydrogen bonding in organometallics.



(3) **a** $X_2 = H_2$
b $X_2 = CHPh$

Experimental

Solution NMR spectra were recorded at 294 K using a Bruker AM 300 spectrometer, operating at 300.133 MHz for ^1H and 75.469 MHz for ^{13}C. Solid-state CP–MAS NMR spectra were recorded using a Bruker MSL 500 operating at

125.758 MHz for ^{13}C; spectra were recorded at 296 K and at three different spinning speeds in order to assign the isotropic peaks.

Compound **4** was prepared by the published method [13]. Recrystallization from methylene chloride/hexane gave red needles, m.p. 98–98.5°C (lit: 97–97.5°C [14]). Infrared, CCl_4 solution: ν(CO) 1613 cm^{-1} (broad). NMR ($CDCl_3$): δ(H) (enol form) 2.08 (s, 3H, CH_3), 4.18 (s, 5H, C_5H_5), 4.49 (m, 2H, C_5H_4), 4.76 (m, 2H, C_5H_4), 5.71 (s, 1H, CH); (keto form) 2.32 (s, 3H, CH_3), 3.83 (s, 2H, CH_2), 4.22 (s, 5H, C_5H_5), 4.56 (m, 2H, C_5H_4) and 4.78 (m, 2H, C_5H_4), enol/keto ratio 17:1; δ(C) (enol form) 24.4 (q, CH_3), 70.5 (d, C_5H_5), 68.8 (d, C_5H_4), 72.2 (d, C_5H_4), and 77.9 (s, C_5H_4), 97.3 (d, CH), 186.5 (s) and 192.8 (s) (2 × CO); (keto form) 56.2 (t, CH_2), 70.3 (d, C_5H_5), 70.2 (d, C_5H_4) and 73.0 (d, C_5H_4). Solid state CP–MAS: δ(C) 24.7 (CH_3), 71.1 (br, $C_5H_5 + C_5H_4$), 79.8 and 82.3 (C_5H_4), 98.8 (CH), 185.7 and 195.4 (2 × CO).

X-Ray crystallography

Crystals were grown from dichloromethane/hexane mixtures.

Crystal data

$C_{14}H_{14}FeO_2$, M_r 270.11. Orthorhombic, $a = 5.812(1)$, $b = 12.455(1)$, $c = 16.478(1)$ Å, $V = 1192.8$ Å^3, space group $P2_12_12_1$ (No. 19), $Z = 4$, $D_x = 1.504$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.71069$ Å, μ (Mo-K_α) = 12.47 cm^{-1}, $F(000) = 560$.

Data collection

Data were collected at 293 K using an Enraf–Nonius FAST area diffractometer, using procedures described elsewhere [15]. Reflections (4990) were measured in the range $1.5° \leq \theta \leq 27.0°$ of which 2152 were unique, and 1864 had $F_o \geq \sigma(F_o)$. Lorentz and polarization corrections were applied, and the data were corrected for absorption using the DIFABS method [16].

Structure solution and refinement

Direct methods were followed by difference Fourier methods. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in the refinement as riding atoms, with grouped isotropic temperature factors. Two parallel series of refinements were undertaken in which the central carbon of the dione fragment was assigned either one or two hydrogen atoms. The final R factors were $R = 0.034$, $R_G = 0.036$ and $R = 0.052$, $R_G = 0.057$ for the two refinements; hence the former refinement was chosen.

The final refined coordinates are given in Table 1 and selected bond lengths and angles are given in Table 2. A perspective view of the molecule, showing the atom numbering scheme is shown in Fig. 1. Supplementary data available from the authors include: anisotropic temperature parameters; hydrogen atom coordinates; a complete listing of bond lengths and angles; observed and calculated structure factors.

Results and discussion

The compound **4** was prepared by the published procedure [13]. The use of lithium diisopropylamide, rather than sodium amide [14], to deprotonate acetylfer-

Table 1

Fractional atomic coordinates $(\times 10^4)$ for C(14)H(14)O(2)Fe

	x	y	z
Fe(1)	−1570.7(10)	−1919.6(4)	−3191.1(3)
C(1)	−3059(10)	−452(4)	−3258(4)
C(2)	−867(10)	−398(4)	−3578(3)
C(3)	−737(10)	−1113(4)	−4228(3)
C(4)	−2846(11)	−1613(4)	−4319(3)
C(5)	−4320(10)	−1203(5)	−3703(4)
C(6)	813(6)	−3084(4)	−2960(2)
C(7)	832(8)	−2308(4)	−2324(3)
C(8)	−1394(8)	−2273(3)	−1975(2)
C(9)	−2807(7)	−3022(4)	−2384(2)
C(10)	−1436(7)	−3526(3)	−3000(2)
C(11)	−2289(7)	−4353(3)	−3558(3)
O(1)	−4435(6)	−4599(3)	−3516(2)
C(12)	−839(8)	−4876(3)	−4115(3)
C(13)	−1648(10)	−5697(3)	−4592(2)
O(2)	−3805(6)	−5989(3)	−4554(2)
C(14)	−162(11)	−6312(4)	−5162(3)

rocene provides a much more reproducible synthesis of **4**, which can be obtained with high purity in acceptable yields.

In chloroform-*d* solution, the ^{1}H NMR spectrum shows the presence of both enol (major) and keto (minor) forms: all the expected resonances for such an equilibrium mixture were observed with the exception of the hydrogen-bonded hydrogen, which could not be located. Integration established the [enol/keto]

Table 2

Selected molecular dimensions

Bond lengths (Å)			
C(1)–C(2)	1.381(9)	C(10)–C(11)	1.468(7)
C(2)–C(3)	1.396(8)	C(11)–C(12)	1.406(7)
C(3)–C(4)	1.384(8)	C(12)–C(13)	1.373(7)
C(4)–C(5)	1.423(9)	C(13)–C(14)	1.490(8)
C(5)–C(1)	1.398(9)	C(11)–O(1)	1.287(6)
C(6)–C(7)	1.426(7)	C(13)–O(2)	1.307(7)
C(7)–C(8)	1.417(7)	O(1)···O(2)	2.462
C(8)–C(9)	1.415(7)		
C(9)–C(10)	1.435(6)		
C(10)–C(6)	1.420(7)		
Bond angles (°)			
C(10)–C(11)–C(12)	122.2(5)		
C(10)–C(11)–O(1)	117.5(5)		
O(1)–C(11)–C(12)	120.4(5)		
C(11)–C(12)–C(13)	120.9(5)		
C(12)–C(13)–C(14)	123.1(6)		
C(12)–C(13)–O(2)	120.6(5)		
O(2)–C(13)–C(14)	116.3(5)		

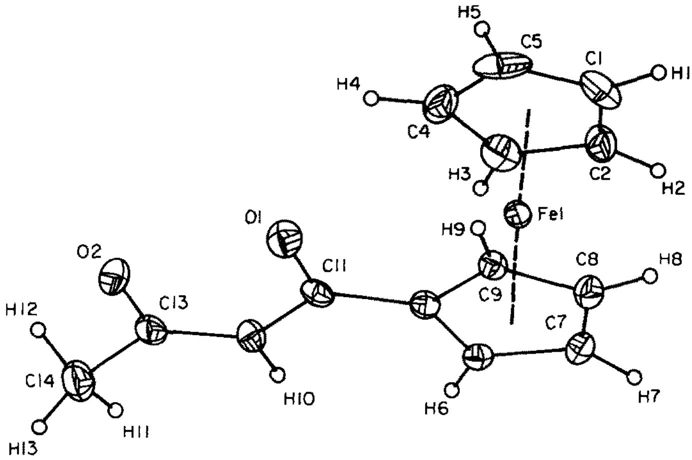


Fig. 1. Perspective view of the molecule of 1-ferrocenyl-3-hydroxy-but-2-en-1-one, showing the atom-numbering scheme.

concentration ratio as approx. 17 : 1 at 294 K. In the ^{13}C spectrum, also in $CDCl_3$ solution, all the expected resonances for the enol tautomer were readily assigned, using DEPT sequences: for the keto form, the three quaternary resonances, expected to be of extremely low intensity, could not be resolved, nor was a separate CH_3 resonance resolved from the CH_3 resonance of the enol tautomer.

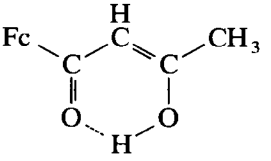
For the enol tautomer the ^{13}C shift of the side-chain CH resonance δ 97.3 is very similar to the corresponding shift in pentane-2,4-dione in $CDCl_3$ solution, δ 99.0, and the two C–O shifts, δ 186.5 and 192.8 are likewise very close to the C–O shift, δ 188.5, in pentane-2,4-dione. It is not possible to determine from the chemical shift data alone the sense in which the enolization of **4** occurs or indeed whether the enolized system is asymmetric with essentially localized double-bonds or symmetric with delocalized π-bonds.

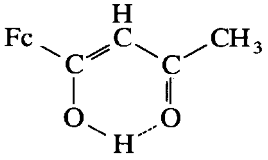
In the solid-state spectrum, there is a resonance at δ 98.8, corresponding to the side-chain CH of the enol tautomer, but no resonance is present assignable to the CH_2 group of the keto tautomer. Overall there is very close correspondence between the solid-state ^{13}C shifts, and those of the enol tautomer in $CDCl_3$ solution and hence the CP–MAS spectrum indicates that in the solid state only the enol form persists. This conclusion was confirmed by single-crystal X-ray analysis.

Crystal and molecular structure of 4

The structure comprises isolated molecules with the carbon side chain in the extended conformation. All of the heavy atoms in the side chain C(11)–C(14), O(1) and O(2) are coplanar, with the two oxygen atoms on the same side of the chains, and separated by 2.462 Å. This is the same overall conformation as adopted in all other enolized 1,3-diketones [2–10], but different from those of the non-enolized tautomer of pentane-2,4-dione [1] and of the non-enolized diketones **3a** [11] and $(PhCO)_2CHEt$ [17].

The distances C(11)–C(12) and C(12)–C(13) are 1.406(7) and 1.373(7) Å, respectively, and these values lie within the ranges, 1.403–1.432 and 1.343–1.392 Å, respectively, found for the distinct C–C bonds in asymmetric enolized 1,3-diones. Similarly the C(11)–O(1) and C(13)–O(2) distances, 1.287(6) Å and 1.307(7) Å, lie close to the ranges observed in such enols for the two types of C–O distance, 1.269–1.283 Å and 1.306–1.337 Å. On the other hand, in non-enolized 1,3-diketones, the C–C and C=O bond distances lie in the ranges 1.507–1.537 Å and 1.212–1.221 Å respectively [11,12,17], wholly different from the values found here. These values and the co-planarity of the six side-chain atoms point first to the enol structure and second to the tautomer **4a** rather than **4b** as being the form existing in the crystal.


(4a)


(4b)

$Fc = [(C_5H_5)Fe(C_5H_4)]$

All attempts to locate the hydrogen in the O–H · · · O system were unsuccessful, as occurred also with **2b** [5]. However the absence of any close intermolecular contacts, in particular the absence of close intermolecular O · · · O contacts, is indicative of intramolecular, rather than intermolecular, hydrogen bonding.

In compound **2f**, the site of enolization is the carbonyl group adjacent to the strongly electron-withdrawing CF_3 group [9], whereas in the present compound **4**, the enolization involves the carbonyl group remote from the strongly electron-donating ferrocenyl group. The site of enolization in unsymmetrically substituted dione **2** may depend on the electron withdrawing or donating properties of the substituents R^1, R^2; at present, there are too few examples for a reliable assessment to be attempted.

Within the ferrocenyl fragment, the mean Fe–C distances for the two independent rings are identical within the experimental uncertainty: however the mean C–C distances within the two cyclopentadienyl rings are significantly different. In the unsubstituted ring the average C–C distance is 1.396 Å, and in the substituted ring it is 1.423 Å. Such a difference occurs in some acyl-substituted ferrocenes [18,19], but not in others [20,21].

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