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Crystal and molecular structure of 4-(ferrocenylhydroxyphenylmethyl)-4-butanolide

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Abstract

The crystal structure of 4-(ferrocenylhydroxyphenylmethyl)-4-butanolide has been determined by an X-ray diffraction study. This compound, $C_{21}H_{20}FeO_3$, crystallizes in the triclinic space group $P\bar{1}$, with unit cell parameters a 7.454(1), b 8.557(1), c 13.752(1) Å, α 92.75(1), β 95.25(1), γ 102.14(1)°, V 851.9(1) Å^3. The most interesting feature of its molecular structure is the specific orientation of the hydroxy group; i.e. the hydrogen atom does not form an inter- or intramolecular hydrogen bond with oxygens of the lactone ring but is turned towards the iron atom of the ferrocene moiety.

Introduction

4-(Ferrocenylhydroxyphenylmethyl)-4-butanolide was isolated as one of several reaction products from the reaction of ferrocene with 5-phenyl-5-(4-butenolide) under conditions of Friedel–Crafts alkylation. Rearrangement of the 6-membered lactone ring to that of a 5-membered ring was possible because of the formation of the key intermediate, the β-ferrocenylcarbenium ion. This ion, however, rearranged to the more stable α-ferrocenylcarbenium ion, whereupon the substituted 5-membered lactone ring was formed. Despite the fact that various spectra of the above-mentioned compound were recorded, only an X-ray diffraction study confirmed its structure unambiguously [1].

Results and discussion

The numbering scheme of the compound under consideration is shown in Fig. 1. The interatomic distances, bond and torsion angles are listed in Table 1; the positional and thermal parameters are listed in Table 2.

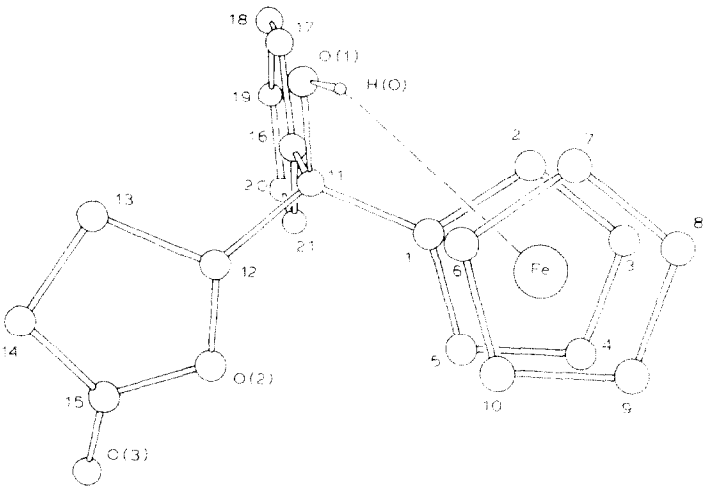

Fig. 1. Molecular structure of 4-(ferrocenylhydroxyphenylmethyl)-4-butanolide. H atoms bonded to carbons have been omitted.

The ferrocenyl fragment has an eclipsed conformation (within $\pm 1°$). The dihedral angle between the planes of the cyclopentadienyl rings is 5.0°, the largest distance is that between the C(1) and C(6) atoms.

The distance of the iron atom from the plane of the substituted cyclopentadienyl ring (A) is 1.641 Å while from the unsubstituted ring (B) it is 1.649 Å. Ring B exhibits strong rotational motion, with an average temperature factor for carbon atoms of $B_{eq} = 7(1)$ Å^2 while in ring A $B_{eq} = 3.6(6)$ Å^2. As a result, shortening of the Fe–C and C–C distances is observed in ring B (av. 2.024(6) and 1.38(1) Å) compared with ring A (2.037(8) and 1.419(7) Å).

The C(12), C(14), C(15) and O(2) atoms of the lactone ring are coplanar within ± 0.01 Å and the atoms O(3) and C(13) are displaced from the plane by 0.03 and 0.45 Å respectively. As a result the lactone ring adopts an envelope like conformation folded along the C(12) · · · C(14) line by 28.4°.

The most interesting feature of the structure is the orientation of hydroxy group: its hydrogen atom H(O) does not form inter- or intra-molecular hydrogen bonds with oxygen atoms of the lactone ring but is turned towards the iron atom of ferrocenyl moiety. The observed length of the O(1)–H(O) bond (0.79(3) Å) is shorter than the real value, as is usual for structures deduced from X-ray crystallography. If this bond is elongated to the normal value of 0.96 Å [2] the H(O) · · · Fe distance of 2.94 Å and the O(1)–H(O)–Fe angle of 121° are obtained (for the observed position H(O) 3.03(3) Å and 123(2)°, respectively), while the O(1) · · · Fe distance is 3.572(2) Å. Thus, the H(O) · · · Fe distance is somewhat shorter than the sum of Van der Waals radii (Fe – 2.1, H – 1.2 Å) [3] and also shorter than the sum of radii of non-interacting atoms obtained from the quantum chemistry data (Fe – 2.29, H – 1.24 Å) [4]. However, it is not fully evident whether this approaching is due to the attractive H(O) · · · Fe interaction or to some other factors. Though, bending of the ferrocenyl sandwich can help H(O) to come into closer proximity to the Fe atom, its deformation can be due to the steric influence of the bulky phenyl

Table 1

Bond distances (Å), bond and torsion angles (°)

Fe–C(1)	2.049(3)	C(4)–C(5)	1.416(4)	C(14)–C(15)	1.492(4)
Fe–C(2)	2.043(3)	C(5)–C(1)	1.423(4)	C(15)–O(2)	1.356(3)
Fe–C(3)	2.026(3)	C(6)–C(7)	1.392(6)	C(15)–O(3)	1.198(4)
Fe–C(4)	2.030(3)	C(7)–C(8)	1.374(6)	O(2)–C(12)	1.457(3)
Fe–C(5)	2.039(3)	C(8)–C(9)	1.370(5)	C(16)–C(17)	1.388(4)
Fe–C(6)	2.030(5)	C(9)–C(10)	1.395(6)	C(17)–C(18)	1.373(5)
Fe–C(7)	2.026(4)	C(10)–C(6)	1.364(6)	C(18)–C(19)	1.373(5)
Fe–C(8)	2.026(3)	C(1)–C(11)	1.513(4)	C(19)–C(20)	1.374(4)
Fe–C(9)	2.016(4)	C(11)–C(12)	1.535(4)	C(20)–C(21)	1.385(4)
Fe–C(10)	2.020(3)	C(11)–C(16)	1.535(4)	C(21)–C(16)	1.389(4)
C(1)–C(2)	1.428(4)	C(11)–O(1)	1.443(3)	O(1)–H(O)	0.79(3)
C(2)–C(3)	1.409(4)	C(12)–C(13)	1.528(4)	H(O) · · · Fe	3.03(3)
C(3)–C(4)	1.421(4)	C(13)–C(14)	1.509(4)	C–H	0.90(4)–1.06(4)

C(2)C(1)C(5)	106.9(2)	C(1)C(11)O(1)	109.5(2)	C(14)C(15)O(3)	129.7(3)
C(2)C(1)C(11)	124.2(3)	C(1)C(11)C(12)	113.1(2)	O(2)C(15)O(3)	120.4(3)
C(5)C(1)C(11)	128.8(2)	C(1)C(11)C(16)	108.6(2)	C(12)O(2)C(15)	110.5(2)
C(1)C(2)C(3)	108.6(2)	O(1)C(11)C(12)	104.4(2)	C(11)C(16)C(17)	120.9(2)
C(2)C(3)C(4)	108.2(3)	O(1)C(11)C(16)	107.2(2)	C(11)C(16)C(21)	120.6(2)
C(3)C(4)C(5)	107.7(3)	C(12)C(11)C(16)	113.8(2)	C(17)C(16)C(21)	118.4(2)
C(4)C(5)C(1)	108.7(2)	C(11)C(12)O(2)	110.6(2)	C(16)C(17)C(18)	120.1(3)
C(7)C(6)C(10)	107.8(4)	C(11)C(12)C(13)	115.4(2)	C(17)C(18)C(19)	120.9(3)
C(6)C(7)C(8)	107.9(4)	C(13)C(12)O(2)	104.6(2)	C(18)C(19)C(20)	119.4(3)
C(7)C(8)C(9)	108.4(4)	C(12)C(13)C(14)	102.9(2)	C(19)C(20)C(21)	120.2(3)
C(8)C(9)C(10)	107.7(4)	C(13)C(14)C(15)	103.6(2)	C(20)C(21)C(16)	120.9(3)
C(9)C(10)C(6)	108.2(4)	C(14)C(15)O(2)	109.9(2)	C(11)O(1)H(O)	108(2)

Torsion angles

C(2)C(1)C(11)O(1)	−42.9(3)
C(2)C(1)C(11)C(12)	−158.9(4)
C(2)C(1)C(11)C(16)	73.8(3)
O(1)C(11)C(16)C(17)	3.3(2)
C(1)C(11)O(1)H(O)	−41(3)

substituent at the C(1) atom as well. In fact, the bulky (but wholly inert to Fe) carboranyl substituent gives rise to the tilting of the Cp rings by 4.2° in $Me_4C_4B_8H_7(C_5H_4)Fe(C_5H_5)$ [5] and 3.3° in 3-ferrocenyl-*o*-carborane [6].

Experimental

X-ray diffraction measurements were performed with a four-circle automated Hilger & Watts diffractometer (using Mo-K_α graphite-monochromated radiation) at room temperature. All calculations were made with an Eclipse S/200 computer using INEXTL programs [7]. Crystal data of $C_{21}H_{20}FeO_3$: triclinic, a 7.454(1), b 8.557(1), c 13.752(1) Å, α 92.75(1), β 95.25(1), γ 102.14(1)°, V 851.9(1) Å^3, space group $LP\bar{1}$, $Z = 2$, d_{calc} 1.47 g/cm^3, μ(Mo-K_α) 9.3 cm^{-1}. Intensities of 2735 independent reflections with $I \geqslant 2\sigma(I)$ and $2\theta \leqslant 60°$ were measured by the $\theta/2\theta$ scan method. The structure was solved by the heavy-atom method and refined by the least-squares method in anisotropic approximation for non-hydrogen atoms and isotropically for all hydrogen atoms (localized in the difference synthesis) to $R = 0.033$, $R_w = 0.033$ (weighing scheme $w = \sigma_F^{-2}$).

Table 2

Atomic coordinates of (Fe×10^5; C and O×10^4; H×10^3) and temperature factors ($Å^2$)

Atom	x	y	z	B_{eq} [a]	Atom [b]	x	y	z	B_{iso}
Fe	53144(5)	81780(5)	24392(3)	2.71(1)	H(O)	528(4)	464(4)	250(2)	4.5(7)
O(1)	4495(2)	4016(2)	2703(1)	3.76(6)	H(2)	532(4)	663(3)	414(2)	3.7(6)
O(2)	268(3)	4660(2)	1361(1)	3.57(5)	H(3)	532(4)	969(3)	419(2)	4.4(6)
O(3)	−2466(3)	3681(3)	533(2)	5.45(7)	H(4)	300(4)	1023(3)	282(2)	4.8(7)
C(1)	3303(3)	6416(3)	2884(2)	2.74(7)	H(5)	165(4)	744(3)	187(2)	3.2(6)
C(2)	4569(4)	7167(3)	3698(2)	3.60(8)	H(6)	657(6)	619(4)	119(3)	10(1)
C(3)	4579(4)	8817(4)	3759(2)	4.17(9)	H(7)	864(6)	740(5)	272(3)	10(1)
C(4)	3305(4)	9114(3)	2994(2)	4.09(9)	H(8)	851(5)	1032(4)	280(3)	9(1)
C(5)	2520(4)	7636(3)	2459(2)	3.39(8)	H(9)	611(5)	1082(4)	149(3)	8(1)
C(6)	6713(6)	7328(4)	1407(3)	8.5(2)	H(10)	498(6)	836(5)	49(3)	10(1)
C(7)	7922(5)	8016(5)	2219(3)	7.3(2)	H(12)	284(3)	490(3)	116(2)	2.9(5)
C(8)	7825(5)	9599(5)	2341(3)	5.9(1)	H(13)	131(4)	171(3)	177(2)	3.4(6)
C(9)	6564(5)	9901(4)	1625(3)	6.3(1)	H′(13)	272(4)	212(3)	101(2)	5.3(7)
C(10)	5879(5)	8482(6)	1043(2)	7.5(1)	H(14)	−79(4)	120(3)	40(2)	4.1(6)
C(11)	2833(3)	4632(3)	2615(2)	2.78(7)	H′(14)	31(4)	246(3)	−23(2)	5.8(8)
C(12)	2039(4)	4204(3)	1543(2)	3.17(7)	H(17)	342(3)	250(3)	393(2)	3.3(6)
C(13)	1645(4)	2424(3)	1213(2)	4.0(1)	H(18)	149(4)	131(3)	507(2)	5.8(8)
C(14)	17(5)	2240(3)	447(2)	4.3(1)	H(19)	−138(4)	194(3)	520(2)	4.2(6)
C(15)	−920(4)	3535(3)	753(2)	3.82(8)	H(20)	238(4)	374(3)	420(2)	5.0(7)
C(16)	1587(3)	3809(3)	3354(2)	2.74(6)	H(21)	−56(4)	492(3)	304(2)	4.4(7)
C(17)	2183(4)	2759(3)	3984(2)	3.31(7)					
C(18)	1066(5)	2078(3)	4677(3)	4.3(1)					
C(19)	−642(4)	2416(4)	4743(2)	4.4(1)					
C(20)	−1242(4)	3455(4)	4123(2)	4.4(1)					
C(21)	−135(4)	4155(3)	3438(2)	3.69(8)					

[a] $B_{eq} = 1/3\sum_{ij} B_{ij} a_i^* a_j^* (\mathbf{a}_i \mathbf{a}_j)$. [b] The hydrogen atoms have the same numbers as carbon atoms to which they are bonded.

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