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Crystal structure of 1,3-benzene-bis(1-ferrocenyl-3-hydroxyprop-2-en-1-one), $(C_5H_5)Fe(C_{22}H_{16}O_4)Fe(C_5H_5)$

Y.-C. Shi*, H.-J. Cheng, R. Zhou and Y. Lu

Yangzhou University, School of Chemistry, 130 Xi-Men-Wai Street, Yangzhou 225002, P. R. China

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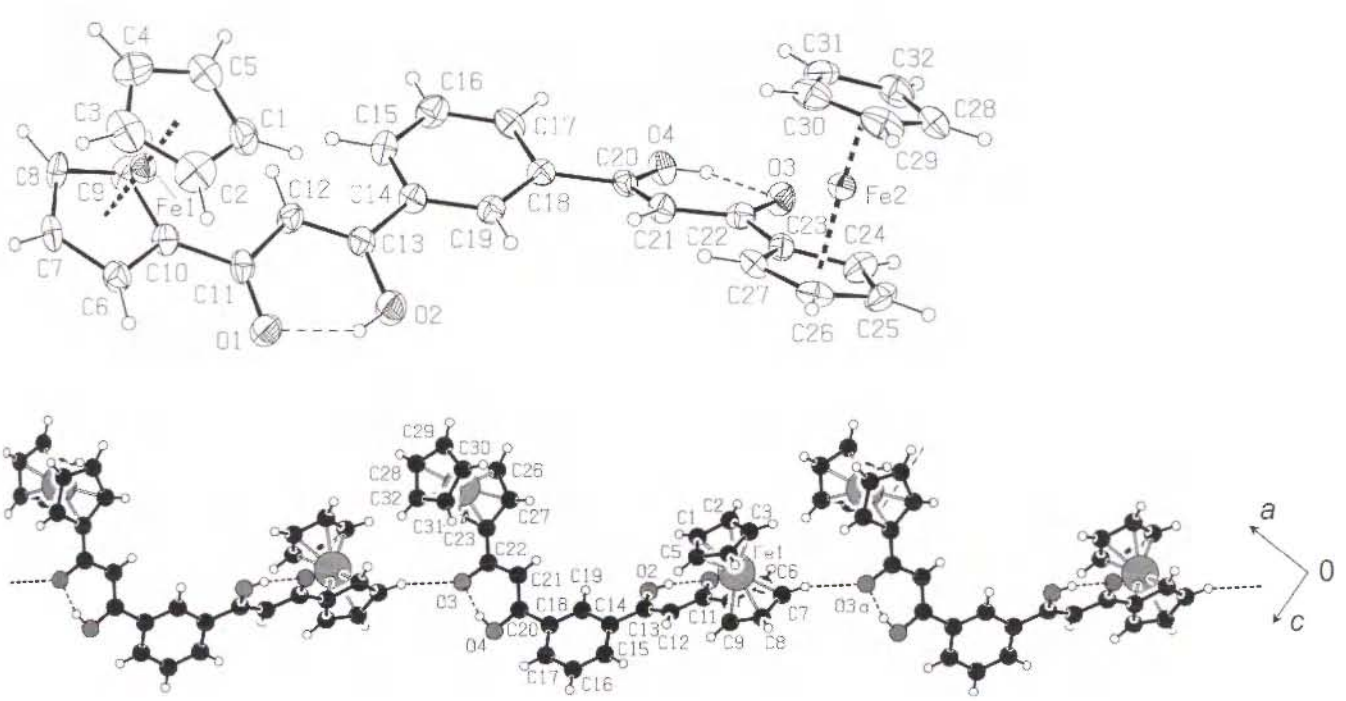

Abstract

$C_{32}H_{26}Fe_2O_4$, monoclinic, $C12/c1$ (no. 15), a = 19.831(4) Å, b = 9.994(2) Å, c = 25.913(5) Å, β = 94.38(3)°, V = 5120.7 Å^3, Z = 8, $R_{gt}(F)$ = 0.053, $wR_{ref}(F^2)$ = 0.148, T = 295 K.

Source of material

Acetylferrocene was obtained from the reaction of ferrocene and acetic anhydride as described previously [1]. A solution of sodium ethoxide (5.036 g, 74 mmol), acetylferrocene (16.877 g, 74 mmol) and dimethyl isophthalate (7.157 g, 37 mmol) in 60 ml THF was refluxed under nitrogen for 3 h. The yellow solid was filtered, washed with THF, then dissolved in hot water and finally acidified with aqueous acetic acid to afford the title compound (8.032 g, yield 37 %) as dark red solid. Recrystallization from dichloromethane and hexane gave crystals suitable for X-ray analysis (m.p. 184.5-185.7 °C).

Discussion

Enaminones have been studied not only as ligands in coordination chemistry [2], but also as chiral auxiliaries in organic synthesis [3]. In continuation of investigation of the chemistry of organometallic enaminones, the title compound, as an intermediate, has been synthesized via the Claisen condensation of acetylferrocene and dimethyl isophthalate [4,5]. ^{1}H NMR spectroscopy shows that the compound exists in the *enol*, and not in the *keto* form in solution. Interestingly, IR spectroscopy displays only the *enol* form in the solid state, this fact has been fully confirmed by the crystal structure (figure, top). As also noted for the related structure of (*Z*)-1-ferrocenyl-3-hydroxy-3-(2-pyridyl)-prop-2-en-1-one [6], the O=C–C=C–O fragments are planar. The bond lengths indicate electron delocalization [7]. Two O=C–C=C–O planes are twisted with respect to the benzene ring (C6 – C10) and the substituted cyclopentadienyl ring (C23 – C27) by 26.0(3)°, 7.2(3)° and 22.9(3)°, 9.3 (3)°, respectively. The two cyclopentadienyl rings in the ferrocenyl group are almost parallel (dihedral angles are 2.1(4)° for the first ferrocenyl group and 2.9(4)° for the second one) and adopt a different conformation, viz. eclipsed for the first ferrocenyl group and staggered for the second. Furthermore, two ferrocenyl groups are *cis* with respect to the benzene ring. The C13—C14 and C18—C20 bonds of 1.481(7) Å and 1.484(7) Å, respectively, which are typical of a single C_{sp2}—C_{sp2} bond, suggest that the benzene ring is not involved in the conjugation of the O=C–C=C–O groups. In addition to the intramolecular hydrogen bonds (O–H···O=C), intermolecular hydrogen bond (C–H···O=C) is also present in the crystal structure of the title compound (figure, bottom).

* Correspondence author (e-mail: yzssyc@yzcn.net)

Table 1. Data collection and handling.

Crystal:	red block, size 0.10 × 0.10 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	11.71 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, $\omega/2\theta$
$2\theta_{max}$:	49.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8991, 4499
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2225
$N(param)_{refined}$:	345
Programs:	SHELXS-97 [8], SHELXL-97 [9]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(2O)	8*f*	0.5249	0.5761	0.1989	0.092
H(4O)	8*f*	0.8175	0.5201	0.4017	0.069
H(4)	8*f*	0.4131	1.2932	0.1320	0.101
H(5)	8*f*	0.4942	1.1720	0.1971	0.093
H(1)	8*f*	0.4350	0.9633	0.2285	0.085
H(2)	8*f*	0.3168	0.9561	0.1815	0.093
H(3)	8*f*	0.3031	1.1595	0.1215	0.093
H(9)	8*f*	0.5524	1.0078	0.0998	0.064
H(6)	8*f*	0.3742	0.7852	0.0842	0.059
H(7)	8*f*	0.3589	0.9931	0.0270	0.063
H(8)	8*f*	0.4674	1.1293	0.0367	0.065
H(12)	8*f*	0.5892	0.8631	0.1664	0.053
H(15)	8*f*	0.7024	0.8301	0.1858	0.061
H(16)	8*f*	0.8079	0.8396	0.2293	0.065
H(17)	8*f*	0.8290	0.7257	0.3056	0.055
H(19)	8*f*	0.6379	0.5899	0.2954	0.049
H(21)	8*f*	0.6539	0.5581	0.3814	0.048
H(31)	8*f*	0.6984	0.7510	0.5193	0.068
H(32)	8*f*	0.7523	0.5988	0.5858	0.072
H(28)	8*f*	0.6628	0.5130	0.6402	0.083
H(29)	8*f*	0.5528	0.6142	0.6060	0.083
H(30)	8*f*	0.5751	0.7564	0.5291	0.075
H(26)	8*f*	0.5201	0.3801	0.5137	0.068
H(27)	8*f*	0.5710	0.5011	0.4415	0.053
H(24)	8*f*	0.7223	0.3139	0.5282	0.060
H(25)	8*f*	0.6132	0.2618	0.5665	0.065

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	8*f*	0.42198(4)	1.02203(9)	0.12425(3)	0.0417(5)	0.0488(6)	0.0412(5)	0.0016(4)	−0.0031(4)	0.0055(4)
Fe(2)	8*f*	0.63623(4)	0.51696(8)	0.53700(3)	0.0367(5)	0.0396(5)	0.0431(5)	0.0018(4)	0.0012(4)	−0.0035(4)
O(1)	8*f*	0.4683(2)	0.6533(5)	0.1504(2)	0.047(3)	0.056(3)	0.069(3)	−0.006(2)	−0.009(2)	0.013(2)
O(2)	8*f*	0.5609(2)	0.5795(5)	0.2166(2)	0.048(3)	0.068(3)	0.065(3)	−0.007(3)	−0.012(2)	0.016(3)
O(4)	8*f*	0.8132(2)	0.5505(4)	0.3722(2)	0.030(2)	0.064(3)	0.043(2)	0.009(2)	−0.001(2)	0.003(2)
O(3)	8*f*	0.7788(2)	0.4527(4)	0.4538(2)	0.034(2)	0.055(3)	0.060(3)	0.009(2)	−0.007(2)	0.010(2)
C(4)	8*f*	0.4037(5)	1.2097(8)	0.1499(3)	0.113(8)	0.052(5)	0.087(6)	0.009(5)	0.001(6)	−0.006(5)
C(5)	8*f*	0.4482(4)	1.1432(8)	0.1859(3)	0.091(6)	0.078(6)	0.060(5)	−0.010(5)	−0.011(5)	−0.007(4)
C(1)	8*f*	0.4160(4)	1.0285(8)	0.2032(2)	0.105(7)	0.074(5)	0.034(4)	0.006(5)	0.005(4)	−0.002(4)
C(2)	8*f*	0.3511(4)	1.0253(9)	0.1774(3)	0.064(5)	0.087(6)	0.084(6)	0.013(5)	0.024(4)	−0.003(5)
C(3)	8*f*	0.3435(4)	1.1363(9)	0.1439(3)	0.070(6)	0.092(7)	0.070(5)	0.036(5)	0.002(4)	−0.019(5)
C(9)	8*f*	0.5064(3)	0.9778(7)	0.0890(2)	0.039(3)	0.061(4)	0.061(4)	0.002(3)	0.003(3)	0.015(4)
C(10)	8*f*	0.4749(3)	0.8587(6)	0.1054(2)	0.035(4)	0.052(4)	0.041(4)	0.006(3)	0.001(3)	0.004(3)
C(6)	8*f*	0.4082(3)	0.8549(6)	0.0801(2)	0.044(4)	0.054(4)	0.049(4)	−0.002(3)	−0.007(3)	0.004(3)
C(7)	8*f*	0.4000(3)	0.9689(7)	0.0484(2)	0.055(4)	0.068(5)	0.032(3)	0.010(4)	−0.007(3)	0.005(3)
C(8)	8*f*	0.4597(3)	1.0439(7)	0.0538(2)	0.059(4)	0.065(5)	0.039(4)	0.002(4)	0.005(3)	0.022(3)
C(11)	8*f*	0.5017(3)	0.7580(6)	0.1429(2)	0.043(4)	0.053(4)	0.033(3)	0.011(3)	0.007(3)	0.004(3)
C(12)	8*f*	0.5662(3)	0.7838(6)	0.1717(2)	0.039(4)	0.044(4)	0.049(4)	0.004(3)	−0.004(3)	0.009(3)
C(13)	8*f*	0.5930(3)	0.6927(6)	0.2065(2)	0.044(4)	0.050(4)	0.035(3)	−0.006(3)	0.012(3)	0.001(3)
C(14)	8*f*	0.6601(3)	0.7059(6)	0.2353(2)	0.032(3)	0.044(4)	0.046(4)	0.009(3)	0.000(3)	−0.001(3)
C(15)	8*f*	0.7109(3)	0.7826(6)	0.2165(2)	0.055(4)	0.054(4)	0.044(4)	0.009(4)	0.007(3)	0.014(3)
C(16)	8*f*	0.7739(3)	0.7893(7)	0.2427(3)	0.043(4)	0.057(4)	0.064(5)	−0.006(3)	0.011(3)	0.009(4)
C(17)	8*f*	0.7862(3)	0.7216(6)	0.2883(2)	0.035(4)	0.060(4)	0.042(4)	−0.001(3)	0.007(3)	−0.013(3)
C(18)	8*f*	0.7355(3)	0.6461(6)	0.3096(2)	0.036(3)	0.039(4)	0.039(3)	0.006(3)	0.004(3)	−0.006(3)
C(19)	8*f*	0.6724(3)	0.6395(6)	0.2821(2)	0.043(4)	0.039(3)	0.042(3)	0.003(3)	0.007(3)	0.001(3)
C(20)	8*f*	0.7496(3)	0.5759(6)	0.3597(2)	0.046(4)	0.037(3)	0.033(3)	0.009(3)	−0.002(3)	−0.007(3)
C(21)	8*f*	0.6990(3)	0.5399(6)	0.3914(2)	0.026(3)	0.049(4)	0.046(3)	0.003(3)	−0.004(3)	0.003(3)
C(22)	8*f*	0.7168(3)	0.4763(6)	0.4383(2)	0.035(3)	0.036(3)	0.051(4)	0.004(3)	−0.002(3)	−0.003(3)
C(31)	8*f*	0.6762(4)	0.7048(6)	0.5441(3)	0.073(5)	0.045(4)	0.055(4)	−0.018(4)	0.015(4)	−0.009(3)
C(32)	8*f*	0.7065(3)	0.6199(7)	0.5817(3)	0.040(4)	0.069(5)	0.068(5)	0.004(4)	−0.011(4)	−0.016(4)
C(28)	8*f*	0.6563(4)	0.5714(8)	0.6123(3)	0.099(6)	0.067(5)	0.041(4)	−0.010(5)	−0.005(4)	−0.013(4)
C(29)	8*f*	0.5946(4)	0.6278(8)	0.5929(3)	0.052(5)	0.087(6)	0.071(5)	−0.011(4)	0.023(4)	−0.037(5)
C(30)	8*f*	0.6072(4)	0.7089(7)	0.5498(3)	0.058(5)	0.056(5)	0.074(5)	0.011(4)	0.004(4)	−0.023(4)
C(26)	8*f*	0.5657(3)	0.3813(6)	0.5076(3)	0.058(5)	0.049(4)	0.064(5)	−0.011(4)	0.010(4)	−0.020(4)
C(27)	8*f*	0.5946(3)	0.4499(6)	0.4668(2)	0.040(4)	0.052(4)	0.039(3)	−0.004(3)	−0.003(3)	−0.010(3)
C(23)	8*f*	0.6657(3)	0.4276(6)	0.4711(2)	0.046(4)	0.036(3)	0.035(3)	0.007(3)	0.004(3)	−0.002(3)
C(24)	8*f*	0.6797(3)	0.3440(6)	0.5157(2)	0.048(4)	0.042(4)	0.062(4)	0.008(3)	0.018(3)	−0.001(3)
C(25)	8*f*	0.6183(3)	0.3150(6)	0.5376(3)	0.080(5)	0.032(4)	0.054(4)	0.003(3)	0.021(4)	0.001(3)

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References

1. Graham, P. J.; Lindsey, R. V.; Parshall, G. W.; Peterson, M. L.; Whitman, G. M.: Some Acyl ferrocenes and their reactions. J. Am. Chem. Soc. **79** (1957) 3416-3420.
2. Kim, J.; Hwang, J. W.; Kim, Y.; Lee, M. H.; Han, Y.; Do, Y.: Synthesis, structure and ethylene polymerization behavior of zirconium complexes with chelating ketoiminate ligands. J. Organomet. Chem. **620** (2001) 1-7.
3. Christoffers, J.; Kreidler, B.; Unger, S.; Frey, W.: Regioselective enamine formation from oxonia-boranuida-betaines and their application in asymmetric Michael reactions. Eur. J. Org. Chem. (2003) 2845-2853.
4. Shi, Y.-C.; Yang, H.-M.; Shen, W.-B.; Yan, C.-G.; Hu, X.-Y.: Syntheses and crystal structures of ferrocene-containing enaminones and their copper complexes. Polyhedron **23** (2004) 15-21.
5. Shi, Y.-C.; Sui, C.-X.; Song, H.-B.; Jian, P.-M.: Syntheses and crystal structures of a tridentate enaminone and its copper complex. J. Coord. Chem. **58** (2005) 363-371.
6. Shi, Y.-C.; Cheng, H.-J.: (*Z*)-1-ferrocenyl-3-hydroxy-3-(2-pyridyl)-prop-2-en-1-one. Acta Crystallogr. **E61** (2005) m2139-m2141.
7. Gilli, P.; Bertolasi, V.; Ferretti, V.; Gilli, G.: Evidence for intramolecular N–H···O resonance-assisted hydrogen bonding in α-enaminones and related heterodienes. A combined crystal-structural, IR and NMR spectroscopic, and quantum-mechanical investigation. J. Am. Chem. Soc. **122** (2000) 10405-10417.
8. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
9. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.