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CRYSTAL AND MOLECULAR STRUCTURE OF 2-BENZYLIDENE[3]FERROCENOPHANE-1,3-DIONE *

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Summary

2-Benzylidene[3]ferrocenophane-1,3-dione, $C_{20}H_{14}FeO_2$, crystallizes in the triclinic space group $P\bar{1}$. The unit cell contains two molecules and has the dimensions: a 8.711(2), b 7.625(2), c 11.908(3) Å, α 104.95(5), β 103.86(5), γ 90.17(5)°. The structure was solved using Patterson and Fourier syntheses and refined by the full-matrix least-squares method to a final R value of 0.036 for 2190 reflections. The two cyclopentadienyl rings are tilted 13.57° with respect to each other and staggered by 34.10° . The α -carbon atoms are deviated outside the planes of the cyclopentadienyl rings by 0.407 and 0.256 Å, respectively, both closer to the iron atom. The dihedral angles between the cyclopentadienyl rings and corresponding carbonyl groups are 27.49° and 41.94° .

Introduction

A bridge between the cyclopentadienyl rings of ferrocene usually causes deformation of the ideal structure of ferrocene where the parallel cyclopentadienyl (cp) rings are staggered by exactly 36° [1]. The strain in $[m]$ ferrocenophane derivatives can be released by:

(1) forcing the cp ring out of coplanarity (ring tilting),

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- (2) pushing the α -carbon atoms (adjacent to the cp rings) out of the cp ring planes (usually towards the iron atom),
 (3) staggering the cp rings by less than 36° .

X-ray analysis of [5]ferrocenophane-1-one has not yet been carried out. Cameron et al. [2] have found that the ring tilt in [4]ferrocenophane-1-one is only 4.4° and the cp rings are almost ideally staggered. Though both α -carbon atoms are out of the plane of the cp rings (and closer to the iron atom), the deviation of the carbonyl α -carbon atom is 0.33 \AA (with a dihedral angle of 18.3°) while the deviation of the methylene α -carbon atom is only 0.02 \AA . Jones et al. [3] found that for [3]ferrocenophane-1-one the ring tilt was 8.8° and that the cp ring staggering was 11.8° . The carbonyl carbon atom was 0.301 \AA out of the plane of the cp ring, closer to the iron atom, while the methylene α -carbon atom is 0.123 \AA out of the plane, away

TABLE I

POSITIONAL PARAMETERS OF THE ATOMS ($\times 10^5$) (Standard deviations in parentheses)

Atom	x	y	z
Fe	11890(5)	21810(6)	35564(4)
O(1)	12394(28)	- 28148(29)	28980(24)
O(2)	55637(26)	11867(32)	34187(25)
C(11)	6500(34)	- 1384(39)	22854(27)
C(12)	10105(37)	12862(43)	17898(28)
C(13)	- 991(43)	26100(46)	19614(32)
C(14)	- 11510(39)	20260(47)	25536(32)
C(15)	- 7110(36)	3345(42)	27464(30)
C(21)	34396(35)	19536(41)	43032(28)
C(22)	32407(39)	38231(42)	43021(32)
C(23)	21181(41)	44748(45)	49547(32)
C(24)	16394(41)	30684(49)	53988(30)
C(25)	24502(38)	15053(45)	49991(28)
C(1)	17199(36)	- 14972(40)	26465(29)
C(2)	42824(35)	7070(42)	35200(29)
C(3)	34802(35)	- 11259(40)	27909(29)
C(4)	43789(36)	- 23871(45)	23193(29)
C(31)	39142(36)	- 41941(43)	14923(29)
C(32)	25418(39)	- 45829(46)	5660(31)
C(33)	22191(42)	- 62692(49)	2337(32)
C(34)	32497(44)	- 76328(47)	- 1336(33)
C(35)	46040(45)	72706(49)	7852(36)
C(36)	49498(40)	- 55705(49)	15725(33)
H(12)	18934	13354	13967
H(13)	- 1324	37722	17192
H(15)	- 12562	4082	31298
H(22)	38035	45327	38971
H(23)	17266	57233	50838
H(24)	8684	31551	59082
H(25)	23516	2995	51760
H(32)	17759	- 36249	4748
H(33)	12291	- 65191	- 8978
H(34)	30129	- 88592	7276
H(35)	53476	82531	8694
H(36)	59614	53232	22173

from the iron atom. A similar situation was found in the case of 3-methyl-3-phenyl[3]ferrocenophane-1-one by Lecomte et al. [4]. The dihedral angle between the cp ring and the carbonyl group was found to be 42.1°.

In our previous work [5] we have studied the molecular structure of [3]ferrocenophane-1,3-dione and have found that the ring tilt was 9.8° and the cp rings staggered by only 6°. Both carbonyl groups were found to be non-equivalent. The carbonyl carbon atom of the first group was forced out of the plane of the cp ring by 8.3°, dihedral angle being 45.2°; for the second carbonyl group the values 9.7 and 38.6° were found. On the other hand, according to ¹H and ¹³C NMR measurements the molecular structure of [3]ferrocenophane-1,3-dione in solution should be symmetrical [6].

The main goal of this work was to solve the molecular structure of 2-benzylidene[3]ferrocenophane-1,3-dione and to find out the effect of insertion of the third C(sp²) carbon atom into the bridge. According to the NMR measurements the structure of this compound was found to be far from symmetrical [7].

Results and discussion

The final positional and thermal parameters of the atoms are listed in Tables 1 and 2. Selected bond distances and angles are shown in Table 3 and the least-squares planes in Table 4. An ORTEP drawing of the molecule is illustrated in Fig. 1.

From crystallographic data it follows that the molecule of C₂₀H₁₄FeO₂ is asymmetrical. This finding is in agreement with the NMR measurements in solution

TABLE 2

ANISOTROPIC THERMAL PARAMETERS OF THE ATOMS (The isotropic temperature factors of the hydrogen atoms were taken as 5.5 Å²)

Atom	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
Fe	2.12(2)	2.54(2)	3.01(2)	0.22(1)	0.17(1)	0.72(1)
O(1)	4.27(12)	3.01(10)	7.15(16)	0.46(9)	2.74(11)	2.03(10)
O(2)	2.36(10)	4.48(12)	7.50(16)	0.03(9)	1.50(10)	1.22(11)
C(11)	2.17(12)	2.86(13)	3.19(14)	-0.01(10)	0.43(10)	0.51(11)
C(12)	3.12(15)	3.94(15)	2.97(14)	0.09(12)	0.21(11)	1.33(12)
C(13)	4.25(18)	3.96(16)	3.99(17)	0.68(14)	-0.53(14)	1.63(14)
C(14)	2.71(15)	4.29(16)	4.23(17)	0.95(12)	-0.32(13)	0.58(13)
C(15)	2.34(13)	3.40(14)	4.03(16)	0.03(11)	0.63(12)	0.23(12)
C(21)	2.36(13)	3.25(14)	3.20(14)	0.10(11)	-0.17(11)	0.53(11)
C(22)	3.01(15)	2.90(14)	4.74(18)	-0.32(11)	0.02(13)	0.17(13)
C(23)	3.44(16)	3.45(15)	4.34(17)	0.43(12)	-0.22(13)	-0.33(13)
C(24)	3.46(16)	5.00(18)	3.12(15)	0.89(13)	0.48(12)	0.46(13)
C(25)	3.18(15)	4.17(16)	2.92(14)	0.74(12)	0.24(11)	0.94(12)
C(1)	2.75(14)	2.80(13)	3.82(15)	0.11(10)	1.19(12)	0.54(11)
C(2)	2.22(13)	3.61(14)	3.86(15)	0.47(11)	0.42(11)	1.34(12)
C(3)	2.32(13)	3.05(13)	3.67(15)	0.48(10)	0.70(11)	1.12(11)
C(4)	2.37(13)	4.30(16)	3.49(15)	0.61(12)	0.46(11)	0.92(12)
C(31)	2.65(14)	3.79(15)	3.28(14)	0.59(11)	0.97(11)	0.85(12)
C(32)	3.04(15)	4.33(16)	3.78(16)	0.82(12)	0.63(12)	1.05(13)
C(33)	3.56(16)	4.78(17)	3.67(16)	-0.33(14)	0.41(13)	0.57(14)
C(34)	4.51(18)	3.98(16)	4.17(18)	-0.01(14)	1.44(14)	0.48(14)
C(35)	4.24(18)	4.20(17)	5.16(20)	1.44(14)	1.16(15)	0.70(15)
C(36)	3.00(15)	4.77(17)	4.36(18)	1.17(13)	0.52(13)	0.58(14)

TABLE 3. INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°)

Fe-C(11)	1.977(3)	Fe-C(21)	1.984(3)
Fe-C(12)	2.006(3)	Fe-C(22)	2.056(4)
Fe-C(13)	2.065(4)	Fe-C(23)	2.082(4)
Fe-C(14)	2.081(4)	Fe-C(24)	2.060(3)
Fe-C(15)	2.038(3)	Fe-C(25)	1.997(3)
C(11)-C(12)	1.430(5)	C(21)-C(22)	1.437(5)
C(12)-C(13)	1.410(5)	C(22)-C(23)	1.405(5)
C(13)-C(14)	1.416(5)	C(23)-C(24)	1.414(5)
C(14)-C(15)	1.406(5)	C(24)-C(25)	1.421(5)
C(15)-C(11)	1.431(4)	C(25)-C(21)	1.426(5)
C(11)-C(1)	1.473(4)	C(21)-C(2)	1.479(5)
C(1)-O(1)	1.220(4)	C(2)-O(2)	1.216(4)
C(1)-C(3)	1.519(5)	C(2)-C(3)	1.507(5)
C(3)-C(4)	1.338(5)	C(4)-C(31)	1.462(5)
C(31)-C(32)	1.390(5)	C(34)-C(35)	1.373(6)
C(32)-C(33)	1.370(5)	C(35)-C(36)	1.374(5)
C(33)-C(34)	1.386(5)	C(36)-C(31)	1.393(5)
C(15)-C(11)-C(12)	107.31(27)	C(25)-C(21)-C(22)	107.22(28)
C(11)-C(12)-C(13)	107.87(29)	C(21)-C(22)-C(23)	108.10(30)
C(12)-C(13)-C(14)	108.39(31)	C(22)-C(23)-C(24)	108.55(31)
C(13)-C(14)-C(15)	108.42(31)	C(23)-C(24)-C(25)	108.17(31)
C(14)-C(15)-C(11)	108.01(29)	C(24)-C(25)-C(21)	107.93(29)
C(1)-C(11)-C(15)	122.75(28)	C(2)-C(21)-C(25)	128.05(29)
C(12)-C(11)-C(1)	126.99(28)	C(22)-C(21)-C(2)	123.74(29)
O(1)-C(1)-C(11)	121.88(30)	C(21)-C(2)-O(2)	120.61(30)
C(3)-C(1)-O(1)	120.49(29)	O(2)-C(2)-C(3)	120.50(30)
C(11)-C(1)-C(3)	117.46(27)	C(3)-C(2)-C(21)	118.79(28)
C(4)-C(3)-C(1)	122.55(29)	C(31)-C(4)-C(3)	129.70(31)
C(2)-C(3)-C(4)	117.68(29)	C(32)-C(31)-C(4)	123.35(30)
C(1)-C(3)-C(2)	119.75(27)	C(4)-C(31)-C(36)	118.72(30)
C(36)-C(31)-C(32)	117.75(31)	C(33)-C(34)-C(35)	118.96(35)
C(31)-C(32)-C(33)	120.88(33)	C(34)-C(35)-C(36)	120.52(36)
C(32)-C(33)-C(34)	120.74(34)	C(35)-C(36)-C(31)	121.11(34)

[7]. Insertion of the third C(*sp*²) (C(3)) atom into the bridge causes:

- (1) cp ring tilt of 13.57° and stagger of 34.10°. The degree of staggering is defined as the angle between the planes of Fe-C(11)-C(1) and Fe-C(21)-C(2).
- (2) the carbonyl groups C(1)-O(1) and C(2)-O(2) to be *trans* to each other,
- (3) side chain O(1)-C(1)-C(3)-C(2)-O(2) non-coplanarity with the benzene ring even though they form a conjugated system.

The α -carbon atoms are deviated outside the planes of the cyclopentadienyl rings by 0.4072 and 0.2558 Å, respectively, both closer to the central iron atom. The dihedral angles between the cp rings and corresponding carbonyl groups are 27.49 and 41.94°.

Experimental

X-Ray data collection

A crystal of C₂₀H₁₄FeO₂ having dimensions 0.40 × 0.10 × 0.45 mm³ was selected for X-ray data collection. Diffraction measurements were made on a Syntex P2₁ four-circle automatic diffractometer with graphite-monochromatized Mo-K α radiation. Crystal data for C₂₀H₁₄FeO₂ (Mol. wt. = 342.18): *a* 8.711(2), *b* 7.625(2), *c*

TABLE 4. LEAST-SQUARES PLANES

Plane	Atoms	Direction cosines	Other atoms	Deviation (Å)
1	C(11)		Fe	-1.6341(5)
	C(12)	-0.3935	O(1)	-0.1986(27)
	C(13)	-0.2451	C(1)	-0.4072(32)
	C(14)	-0.8861	C(3)	-1.1951(32)
	C(15)		C(4)	-0.8915(33)
2	C(21)		Fe	1.6357(5)
	C(22)	-0.5540	O(2)	-0.3168(27)
	C(23)	-0.0816	C(2)	0.2558(32)
	C(24)	-0.8285	C(3)	1.2942(32)
	C(25)		C(4)	1.2865(33)
3	C(31)		O(1)	-2.4240(26)
	C(32)	0.6516	O(2)	0.9473(26)
	C(33)	0.4719	C(1)	-1.4293(32)
	C(34)	-0.5939	C(2)	-0.0525(33)
	C(35)		C(3)	-0.4405(32)
	C(36)		C(4)	0.0860(33)
4	C(1)			
	C(2)	-0.1898		
	C(3)	0.4744		
	C(4)	-0.8596		
	O(1)			
	O(2)			
5	C(11)	0.0746		
	C(1)	-0.2814		
	O(1)	-0.9567		
6	C(21)	-0.2755		
	C(2)	0.5749		
	O(2)	-0.7704		
7	Fe	0.7893		
	C(11)	0.4131		
	C(1)	-0.4543		
8	Fe	0.3547		
	C(21)	0.8775		
	C(2)	-0.3227		

Some dihedral angles between planes (°)

1-2	13.57				
1-3	81.13	2-3	84.69		
1-4	43.94	2-4	38.87	3-4	52.36
1-5	27.49	2-6	41.94		
7-8	34.10				

11.908(3) Å, α 104.95(5), β 103.86(5), γ 90.17(5)°, V 740.1 Å³, d_c 1.54 g/cm³, $Z = 2$, μ 10.5 cm⁻¹, space group $P\bar{1}$.

Intensity data were collected within the range $0 < 2\theta < 50^\circ$. The θ - 2θ scan technique was used with a variable scan rate 2.0-29.3°/min. Two standard reflections were chosen as a check for crystal stability and correctness of intensity data.

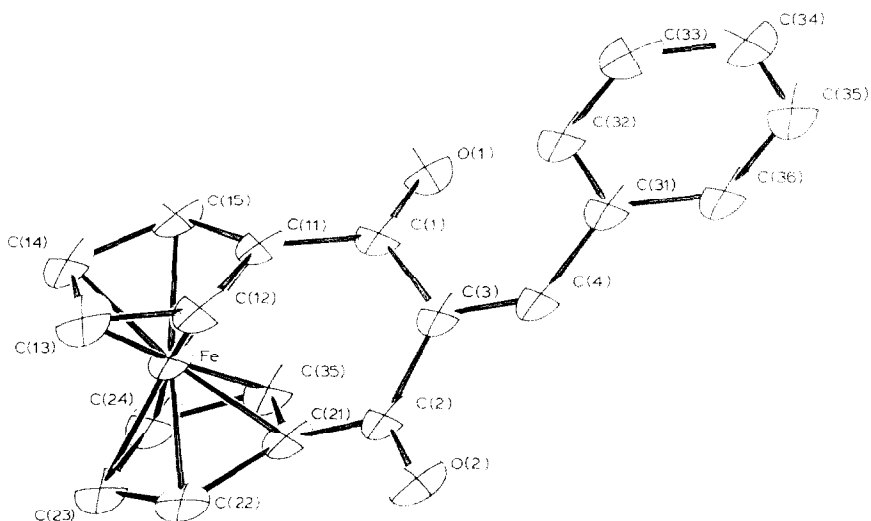


Fig. 1. ORTEP drawing of the molecule of $C_{20}H_{14}FeO_2$ showing the atom numbering scheme.

The maximum intensity change of these two reflections was 5%. A total of 2482 reflections were registered, 2190 of them with $I > 2\sigma(I)$ were employed in the structure analysis. The intensities were corrected for Lorentz and polarization effects, but no absorption corrections were made. The first absolute scale and the mean temperature factor were determined by Wilson's method.

Structure determination and refinement

The structure of $C_{20}H_{14}FeO_2$ was solved by the Patterson and Fourier syntheses and refined by the full-matrix least-squares method to the final values of $R_1 = 0.036$ and $R_2 = 0.041$ for 2190 observations. The positional parameters of the hydrogen atoms were found using difference Fourier synthesis, and the known geometry of the molecule. They were included in the final structure factor calculation, but not refined. The final difference Fourier map confirmed the proposed structural model; the residual electron density being 0.03 \AA^{-3} .

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