

Note

# Ferrocene derivatives (I). Synthesis and X-ray structure determination of *N*-*o*-methylphenylferrocenesulfonamide

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## Abstract

*N*-*o*-Methylphenylferrocenesulfonamide was synthesized from the reaction of ferrocenesulfonyl chloride with *o*-toluidine. The structure was determined by single-crystal diffraction. Crystal data: monoclinic,  $P2_1/c$ , with unit cell dimensions of  $a = 10.436(2)$ ,  $b = 12.377(3)$ ,  $c = 12.6431(3)$  Å, and  $\beta = 107.42(1)^\circ$ ,  $V = 1558.1(6)$  Å<sup>3</sup>,  $Z = 4$ . The most stable structure of the complex in theory was obtained by the Hartree–Fock SCF of GAUSSIAN 98W, and the two results have been compared. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Ferrocene; Ferrocenesulfonyl chloride; Ferrocenesulfonamide; X-ray structure

## 1. Introduction

The search for biologically active ferrocene derivatives has attracted considerable attention [1,2]. On the other hand, sulfonamides have the qualities of antibiotic and anti-inflammation. The highly efficient sulfonyl-urea-type herbicides have been developed [3,4]. By the analyses of structures and biological activities, it has been found that sulfonamide group forms the key part. It is thus clearly known that the ferrocenesulfonamides have high biological activity. The synthesis of ferrocenesulfonamide ( $\text{FcSO}_2\text{NH}_2$ ) was first reported by Pauson et al. in 1958 [5]. In the subsequent years, syntheses of *N*-monosubstituted and *N,N*-disubstituted ferrocenesulfonamides have been reported [6]. In 1998, Besenyei et al. reported the derivatives of *N*-ferrocenesulfonyl carbamic acid and the X-ray structure determination of the related compounds [7].

We have prepared and characterized a number of ferrocene derivatives with strong biological activity [8,9]. In order to continue our research project, some

ferrocenesulfonamides have been synthesized. In this paper, we report the synthesis and X-ray structure determination of *N*-*o*-methylphenylferrocenesulfonamide (Fig. 1) and compare the optimized spatial structure by GAUSSIAN 98W with the results obtained.

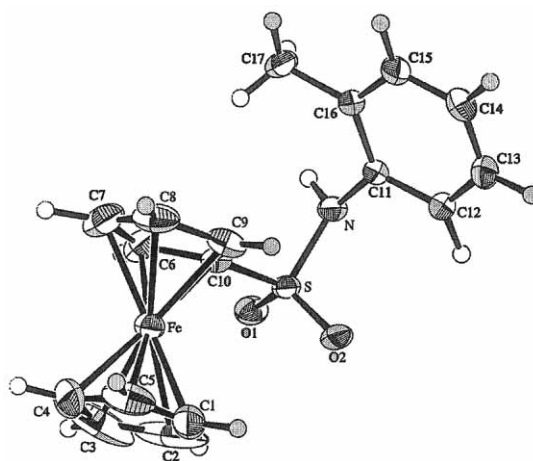


Fig. 1. Molecular diagram for *N*-*o*-methylphenyl-ferrocenesulfonamide by X-ray determination.

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Table 1  
Selected bond lengths (Å) and bond angles (°) for the complex by X-ray determination

Bond lengths					
Fe–C(7)	2.066(4)	Fe–C(8)	2.055(3)	Fe–C(9)	2.028(3)
Fe–C(10)	2.004(3)	S–O(1)	1.434(2)	S–O(2)	1.429(2)
S–N	1.641(2)	S–C(10)	1.744(3)	N–C(11)	1.744(3)
C(6)–C(7)	1.412(5)	C(6)–C(10)	1.427(4)	C(7)–C(8)	1.414(6)
C(8)–C(9)	1.421(6)	C(9)–C(10)	1.423(4)		
Bond angles					
C(1)–Fe–C(2)	37.9(3)	C(2)–Fe–C(3)	38.6(3)	C(3)–Fe–C(4)	40.4(3)
C(4)–Fe–C(5)	39.9(2)	C(1)–Fe–C(5)	38.8(2)	C(6)–Fe–C(7)	40.1(1)
C(7)–Fe–C(8)	40.1(2)	C(8)–Fe–C(9)	40.7(2)	C(9)–Fe–C(10)	41.3(1)
C(6)–Fe–C(10)	41.2(1)	O(1)–S–O(2)	119.6(1)	O(1)–S–N	106.0(1)
O(1)–S–C(10)	108.1(1)	O(2)–S–N	107.6(1)	O(2)–S–C(10)	108.9(1)
N–S–C(10)	105.8(1)	S–N–C(11)	1119.0(2)	C(6)–C(7)–C(8)	108.8(3)
C(7)–C(8)–C(9)	108.3(3)	C(8)–C(9)–C(10)	107.1(3)	C(9)–C(10)–C(6)	108.6(3)
C(10)–C(6)–C(7)	107.2(3)				

## 2. Results and discussion

In Table 1, the Fe–C distances range from 2.004(3) to 2.066(4) Å with the mean values of 2.040 Å for the substituted Cp ring, and 2.018 Å for the unsubstituted ring, respectively, in good agreement with the average Fe–C bond length in ferrocene (2.031 Å). The Fe–C distances for the substituted Cp ring follow a particular order: Fe–C (7) > Fe–C (8) > Fe–C (6) > Fe–C (9) > Fe–C (10). Such results show that an interaction between the sulfonyl group and iron atom may exist, causing a light distortion in the structure. This conclusion is also supported by the following facts: the first angle of 1.77° is between the substituted and unsubstituted Cp plan; the second of 41.92° is between the unsubstituted cp plan and phenyl plan; and the third angle of 40.89° is between the substituted Cp plan and phenyl plan. The distance between the two Cp ring is 3.301 Å (3.32 Å in ferrocene).

The C–C distances in the substituted Cp ring range from 1.412(5)–1.426(4) Å, the mean values is 1.419 Å (1.402 Å in ferrocene). The average C–C distances in the unsubstituted Cp ring is a little shorter, i.e. 1.351 Å. The aminosulphonyl substitution on the Cp ring influences the elongation of bonds in C(9)–C(10) and C(10)–C(6), with the distances of these two bonds being 1.423(4) and 1.427(4) Å, respectively, the longest ever in the Cp moiety.

The average S–O (1.434 Å) and the S–C (1.744 Å) bond distances are in good agreement with the respective values observed for  $\text{FcSO}_2\text{NH}_2$  (1.434 and 1.734 Å) [7]. However, the S–N bond (1.641 Å) is certainly longer than the corresponding value in ferrocenesulfonamide (1.608 Å).

The adjacent C–Fe–C angles of the ferrocene moiety are nearly equal, e.g. C(1)–Fe–C(2) (37.9°), and C(1)–Fe–C(5) (38.8°), C(9)–Fe–C(10) (41.3°) and C(6)–Fe–C(10) (41.2°). The C–C–C angles of the substi-

tuted Cp ring range from 107.1 to 108.8°. Each value is in good agreement with the interior angle of the regular pentagon. The average O–S–C (108.5°) and the O–S–O (119.6°) angles are in agreement with the respective values in ferrocenesulfonamide (107.9 and 119.4°). The average O–S–N (106.8°) is a little less than the corresponding value in  $\text{FcSO}_2\text{NH}_2$  (107.9°) [7].

Like ferrocenesulfonamide, the sulfur atom was placed in a distorted tetrahedron, with the bonds around sulfur atom (1.429–1.743 Å) and the angles (106.0–119.6°).

We used the GAUSSIAN 98W [10] to calculate the most stable structure of the complex in the theory with the method of Hartree–Fock SCF and the basis set of LanL2MB [11,12] to obtain the values of bond lengths, and bond angles (Table 2). The results of the calculation and determination are compared in the Table 3. From the table, we find there is a little difference in the Fe–C, S–O, S–N bonds between the two results. The electrons on the outer space contribute to this sequence. If we consider all electrons to be self-consistent and the workload too hard to carry, then we can reduce the contribution of the electrons on the inner shields for bond formation and regard these inner electrons as a ‘nucleus’. In addition, we consider only the contribution of those valence electrons that give such a difference. The differences between O–S–N, C–N–S, O–S–O angles formed are based on the same reasons. However, the calculated values of C–C, C–N bond length and the C–C–C bond angles of Cp ring, are in good agreement with the corresponding values obtained.

## 3. Experimental

$^1\text{H-NMR}$  spectra were recorded on a Varian INOVA-400 MHz spectrometer with TMS as an internal standard. IR spectra were obtained by using neat capil-

Table 2  
Selected bond lengths (Å) and bond angles (°) for the complex by GAUSSIAN 98W

Bond lengths					
Fe–C(7)	2.1846	Fe–C(8)	2.1839	Fe–C(9)	2.1847
Fe–C(10)	2.1396	S–O(1)	2.605	S–O(2)	2.7015
S–N	1.8952	S–C(10)	1.8666	N–C(11)	1.4668
C(6)–C(7)	1.4069	C(6)–C(10)	1.4181	C(7)–C(8)	1.4211
C(8)–C(9)	1.4071	C(9)–C(10)	1.4178		
Bond angles					
C(1)–Fe–C(2)	38.0482	C(2)–Fe–C(3)	38.0464	C(3)–Fe–C(4)	38.2425
C(4)–Fe–C(5)	38.0313	C(1)–Fe–C(5)	38.2457	C(6)–Fe–C(7)	37.5766
C(7)–Fe–C(8)	37.9685	C(8)–Fe–C(9)	37.5778	C(9)–Fe–C(10)	38.2596
C(6)–Fe–C(10)	38.278	O(1)–S–O(2)	111.6943	O(1)–S–N	118.1074
O(1)–S–C(10)	92.7099	O(2)–S–N	128.5386	O(2)–S–C(10)	91.6558
N–S–C(10)	98.0019	S–N–C(11)	111.5734	C(6)–C(7)–C(8)	108.3142
C(7)–C(8)–C(9)	108.3145	C(8)–C(9)–C(10)	107.2664	C(9)–C(10)–C(6)	108.769
C(10)–C(6)–C(7)	107.2647				

lary cells on a Bruker Equinox-55 instrument. Elemental analysis was performed using a PE-2400 analyzer.

### 3.1. Synthesis of $\text{FcSO}_2\text{NHC}_6\text{H}_4\text{-}o\text{-CH}_3$

The ferrocenesulfonamide is prepared according to the procedure outlined in the literature [7]. Under nitrogen atmosphere, 2.84 g of  $\text{FcSO}_2\text{Cl}$  (10 mmol) was added to 80 ml of dry  $\text{Et}_2\text{O}$ , and then 2.14 g of *o*-toluidine (20 mmol) was introduced dropwise. The reaction mixture was stirred for 3 h in an ice bath, and stirred for another 3 h with refluxing. The solvent was removed in vacuum. The residue was extracted with water and ether, and the organic layer was separated and dried by  $\text{MgSO}_4$ . The solvent was removed; recrystallization from  $\text{Et}_2\text{O}$  gave red crystals. Yield: 59.3%; m.p. (dec.): 158–159 °C.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.33 (m, 1H), 7.16 (m, 3H), 6.27 (s, 1H), 4.47 (s, 2H), 4.37 (s, SH), 4.31 (s, 2H), 2.09 (s, 3H). IR (KBr,  $\text{cm}^{-1}$ ): 3266.2 (s), 1608.3 (m), 1577.4 (s), 1488.8 (s), 1391.2 (m), 1329.7 (s), 1136.5 (s), 481.9 (s). Anal. Found: C, 57.79; H, 4.65; N, 4.05. Calc. for  $\text{C}_{17}\text{H}_{17}\text{FeNO}_2\text{S}$ , (MW 355.23): C, 57.70; H, 4.79; N, 3.95%.

### 3.2. X-ray structure determination of the product

The size of the single crystal chosen for the determination was  $0.20 \times 0.20 \times 0.30$  mm. The determination of the unit cell and data collections was performed on Rigaku AFC7R diffractometer (Mo– $\text{K}_\alpha$  radiation,  $\lambda = 0.71069$  Å, graphite monochromated). Selected bond lengths and bond angles are given in Table 1.

### 3.3. Theoretical optimized structure of the complex with GAUSSIAN 98W

We used the GAUSSIAN 98W to calculate the most stable structure in the theory with the method of

Hartree–Fock SCF and the basis set of LanL2MB, and obtained the values of bond lengths and bond angles. Selected bond lengths and bond angles are given in Table 2.

## 4. Conclusion

The single crystal structure of *N-o*-methylphenylferrocenesulfonamide was determined and the stable structure in the theory was calculated by GAUSSIAN 98W. The two results were compared and found to be essentially in good agreement. The related structural data of the complex and ferrocenesulfonamide were also very close.

Table 3  
Comparison of the calculation and determination of results

Mean value	Calc.	Found
Fe–C (sub. Cp ring) bond length (Å)	2.167	2.018
Fe–C (unsub. Cp ring) bond length (Å)	2.175	2.040
C–C (sub. Cp ring) bond length (Å)	1.414	1.419
C–C (unsub. Cp ring) bond length (Å)	1.414	1.351
C–C (phenyl ring) bond length (Å)	1.390	1.388
S–O bond length (Å)	2.653	1.432
S–N bond length (Å)	1.895	1.641
S–C bond length (Å)	1.866	1.744
N–C bond length (Å)	1.467	1.443
C(16)–C(17) bond length (Å)	1.528	1.505
C–C–C (sub. Cp ring) bond angle (°)	108.0	108.0
C–C–C (unsub. Cp ring) bond angle (°)	108.0	108.0
C–C–C (phenyl ring) bond angle (°)	120.0	120.0
O–S–O bond angle (°)	116.7	119.6
O–S–N bond angle (°)	123.3	106.8
Fe–C–S bond angle (°)	127.9	128.8
C–N–S bond angle (°)	111.6	119.0

## 5. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 161498. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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