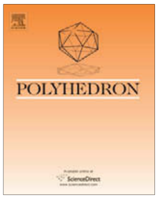
Polyhedron 29 (2010) 827–832

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



Synthesis of two new thioesters bearing ferrocene: Vibrational characterization and ab initio calculations. X-ray crystal structure of S-(2-methoxyphenyl)ferrocenecarbothioate

Isabel C. Henao Castañeda [a,d,1], Carlos O. Della Védova [a,b], Oscar E. Piro [c], Nils Metzler-Nolte [e], Jorge L. Jios [a,*]

[a] *Laboratorio de Servicios a la Industria y al Sistema Científico (UNLP-CIC-CONICET), Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 47 esq. 115, 1900 La Plata, Argentina*
[b] *CEQUINOR (UNLP-CONICET), Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 47 esq. 115, 1900 La Plata, Argentina*
[c] *Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata and Institute IFLP (CONICET, CCT-La Plata), C.C. 67, 1900 La Plata, Argentina*
[d] *Departamento de Farmacia, Facultad de Química Farmacéutica, Universidad de Antioquia, calle 67 No Medellín, Colombia*
[e] *Lehrstuhl für Anorganische Chemie I, Bioanorganische Chemie, Fakultät für Chemie und Biochemie, Ruhr-Universität Bochum, Universitätsstrasse150, D-44801 Bochum, Germany*

ARTICLE INFO

Article history:
Received 18 August 2009
Accepted 10 November 2009
Available online 13 November 2009

Keywords:
Metallocenes
Ferrocenecarbothioates
X-ray single crystal analysis
Vibrational analysis
Conformation analysis
Density functional calculations

ABSTRACT

Structural and conformational properties of S-benzyl ferrocenecarbothioate (**I**) and S-(2-methoxyphenyl) ferrocenecarbothioate (**II**) are analyzed using data obtained from X-ray diffraction, vibrational data and theoretical calculations. According to chemical quantum calculations, the synperiplanar and antiperiplanar forms are found as the first and second more stable conformations, respectively, for the title compounds. The geometric parameters and normal modes of vibration were calculated using a density functional theory method (B3LYP) and the $6\text{-}31+G^{**}$ basis set for all atoms except for iron. For this atom the calculations were carried out with the Lanl2dz basis set. The calculated parameters are in good agreement with the corresponding X-ray diffraction values. The combined experimental and theoretical approach allows a consistent assignment for most of the fundamental modes.

1. Introduction

In a previous paper we reported the vibrational and conformational analysis of aromatic thioester compounds [1]. In anticipation of a subsequent structure–activity relationship study and with the aim to obtain a deeper and general insight on the conformational and vibrational properties of thiol esters compounds of the type X–C(O)S–Y, we report in this work the spectroscopic and structural study of two new and close related compounds, S-benzyl ferrocenecarbothioate (**I**) and S-(2-methoxyphenyl) ferrocenecarbothioate (**II**) (see Fig. 1). Only a few examples of other closely related ferrocenyl containing thiol esters have been described in the literature. Of these, the synthesis of the isomeric S-ferrocenemethyl benzenecarbothioate [2] and S-(*p*-methylphenyl)ferrocenecarbothioate [3] compounds are worth mentioning. Our interest in the conformational and vibrational properties of thioesters is also due of their structural connection with biological system such as acetyl coenzyme A, malonyl coenzyme A, the complement system in different organisms [4,5] and several human endogenous molecules [6,7]. Beside, some substances containing the –C(O)–S– moiety such as acetiamine are used as vitamin-B1 source [8]. Antiviral activity against HIV-1 virus [9,10] and *in vitro* anti-cancer activity [11–14] were found in some thioester compounds. Also, the inclusion of the ferrocene moiety in the title compounds may be of interest since ferrocene itself exhibits interesting properties as anti-anemic or cytotoxic agent and it have been conjugated with well-known medicines like antibiotic, anti-inflammatory, antineoplastic and antimalarial drugs [15].

Thiol esters (sulfenyl carbonyl compounds) generally present planar conformation around the τ (O–C–S–Y) dihedral angle, with the possibility of conformational equilibrium between synperiplanar (τ (O–C–S–Y) = 0°) and antiperiplanar (τ (O–C–S–Y) = 180°) conformations. The synperiplanar form was found the most stable conformation for both organic and inorganic molecules [16]. Moreover, in a previous work we have found that the +anticlinal conformation is present as second most stable conformation [1].

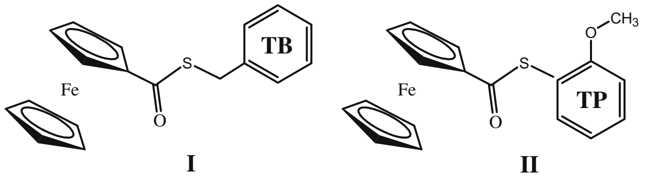
In this paper we report the crystal structure of the S-benzyl ferrocenecarbothioate (**I**). Furthermore, the infrared and Raman spectra of the title compounds were recorded. The conformational energies, the geometric parameters and IR and Raman intensities and vibrational frequencies were calculated by the B3LYP method using the $6\text{-}31G^{**}$ basis set for hydrogen, carbon, oxygen and sulfur nuclei, and Lanl2dz for iron. The calculated spectra afford a basis

---

[*] Corresponding author. Fax: +54 221 4714527.
E-mail address: jljios@quimica.unlp.edu.ar (J.L. Jios).

[1] Predoctoral fellow of the Consejo Nacional de Investigaciones Científicas y Técnicas, CONICET, Argentina.

0277-5387/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2009.11.006



I II

Fig. 1. Structure of the studied compounds and labeling of the phenyl rings.

for the assignments of the experimental infrared and Raman bands. The comparison between theoretical and experimental parameters assists in the determination of intra- or inter-molecular interactions of the free molecules or in the packed molecules, respectively.

2. Experimental

S-benzyl- and S-(2-methoxyphenyl)ferrocenecarbothioate were synthesized as follows: ferrocenoyl chloride [17] (1.15 g, 5 mmol) was dissolved in dry pyridine (1 ml) and stirred mechanically at 20 °C. Then 6 mmol of S-benzyl- or S-(2-methoxyphenyl) hydrosulfide were added and the reaction mixture was kept at 20–22 °C with stirring under Ar for 2 h. The product was treated with dichloromethane, the organic layer washed with HCl 1 M, filtered through magnesium sulfate anhydrous and dried in vacuum. The product was recrystallized from petroleum ether (fraction 40–60).

The ^{1}H (250.13 MHz) and ^{13}C (62.98 MHz) NMR spectra of compound I and II were measured at 298 K on a Bruker AC 250 spectrometer. The compounds were dissolved in $CDCl_3$. Chemical shifts, δ, are given in ppm relative to TMS ($\delta = 0$ ppm) and are referenced by using the residual undeuterated solvent signal. Coupling constants, J, are reported in Hz, multiplicities being marked as: singlet (s), broad singlet (br.s), doublet (d), double double doublet (ddd), triplet (t), double triplet (dt) or multiplet (m).

Single crystals of **I** suitable for X-ray structural analysis were obtained by slow evaporation from an acetonitrile solution. Diffraction data were collected on an Enraf–Nonius CAD4 equipment (graphite monochromate Cu Kα radiation, $\lambda = 1.54184$ Å) with EXPRESS [18] and reduced with XCAD4 [19]. The data were corrected numerically for absorption with PLATON [20]. The structure was solved by direct and Fourier methods with SHELXS [21] and its non-H atom refined by full-matrix least-squares with SHELXL [22]. The hydrogen atoms were positioned stereo-chemically and refined with the riding model. Crystal data and structure refinement parameters are summarized in Table 1.

Table 1
Crystal data and structure refinement results for $C_{18}H_{16}FeOS$ (**I**).

Empirical formula	$C_{18}H_{16}FeOS$
Formula weight	336.22
Temperature (K)	296(2)
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	5.986(1)
b (Å)	9.947(1)
c (Å)	13.268(1)
α (°)	83.813(7)
β (°)	89.02(1)
γ (°)	75.11(1)
Volume (Å^3)	759.0(2)
Z, calculated density (Mg/m^3)	2, 1.471
Absorption coefficient (mm^{-1})	9.197
F(0 0 0)	348
Crystal size (mm)	0.28 × 0.20 × 0.08
θ Range data collection (°)	3.35–67.91
Index ranges	$0 \le h \le 6$, $-11 \le k \le 11$, $-15 \le l \le 15$
Reflections collected/unique	2959/2672 [$R_{(int)} = 0.0512$]
Observed reflections [$I > \sigma(I)$]	2294
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2672/0/191
Goodness-of-fit (GOF) on F^2	1.069
Final R-index [$I > 2\sigma(I)$]^e	$R_1 = 0.0572$, $wR_2 = 0.1446$
R indices (all data)	$R_1 = 0.0707$, $wR_2 = 0.1612$
Largest peak and hole (e A^{-3})	0.759 and −0.598

The infrared spectra were recorded in KBr pellets in the range of 4000 and 400 cm^{-1} on a Thermo-Nicolet IR200 FT-IR spectrometer (2 cm^{-1} resolution). The Raman spectra were measured using a FT Bruker IFS85 spectrometer (spectral resolution 4 cm^{-1}) between 3500 and 150 cm^{-1}. The 1064-nm radiation line of an Nd/YAG laser has been used for excitation. The samples were handled in Pyrex capillaries at room temperature.

Quantum chemical calculations were carried out with GAUSSIAN 03 [23] program package, implemented on a personal computer. The geometric structures for the more stable conformers were subsequently calculated using the B3LYP method with 6-31G** and Lanl2dz basis set. The same method was used to determine the frequencies of the normal modes of vibration. Assignment of vibrational modes was obtained by visual inspection of displacement vectors. The calculations have been performed for molecules in vacuum and therefore environmental effects were not considered.

3. Results and discussion

3.1. Synthesis and NMR characterization

3.1.1. S-benzyl ferrocenecarbothioate (*I*)

Orange–red solid; yield 85%; m.p. 76–77 °C; ^{1}H NMR ($CDCl_3$, 250 MHz, 25 °C): $\delta = 7.25$–7.23 (m, 5H, C_6H_5), 4.85 (t, $J = 2$ Hz, 2H, H_{21}, H_{24}), 4.47 (t, $J = 2$ Hz, 2H, H_{22}, H_{23}), 4.24 (s, 2H, CH_2), 4.15 (s, 5H, C_5H_5) ppm; ^{13}C RMN ($CDCl_3$, 62.98 MHz, 25 °C): $\delta = 193.0$ (C=O), 128.9 (C_3, C_5), 128.5 (C_2, C_6), 127.1 (C_4), 123.9 (C_1), 79.0 (C_{25}), 71.8 (C_{21}, C_{24}), 70.5 (C_5H_5), 68.9 (C_{22}, C_{23}), 32.7 (CH_2) ppm.

3.1.2. S-(2-methoxyphenyl) ferrocenecarbothioate (*II*)

Orange–red solid, yield 87%; m.p. 125.0–126.0 °C; ^{1}H NMR ($CDCl_3$, 250 MHz, 25 °C): $\delta = 7.47$ (dd, $J = 7.5$ and 1.5 Hz, 1H, H_6), 7.43 (ddd, $J = 8$, 8 and 2 Hz, 1H, H_4), 7.02 (dt, $J = 8$ and 1 Hz, 1H, H_5), 7.00 (br.d, $J = 8$ Hz, 1H, H_3), 4.94 (t, $J = 2$ Hz, 2H, H_{21}, H_{24}), 4.50 (t, $J = 2$ Hz, 2H, H_{22}, H_{23}), 4.32 (s, 5H, C_5H_5), 3.88 (s, 3H, CH_3) ppm; ^{13}C RMN ($CDCl_3$, 62.98 MHz, 25 °C): $\delta = 190.7$ (C=O), 159.7 (C_2), 137.4 (C_6), 131.5 (C_4), 121.0 (C_5), 115.8 (C_1), 111.4 (C_3), 78.9 (C_{25}), 71.8 (C_{21}, C_{24}), 70.7 (C_5H_5), 69.1 (C_{22}, C_{23}), 55.8 (CH_3) ppm.

3.2. Crystal structure analysis

The S-benzyl ferrocenecarbothioate (I) belongs to a series of compounds with the general formula X–C(O)S–Y. It presents synperiplanar conformation around the dihedral angle of the sulfenyl carbonyl moiety –C(O)–S–. A value of 0° would be expected for the dihedral angle τ (O–C–S–Y) according to the reported study on the conformational transferability of sulfenyl carbonyl compounds [24]. In this work, a marked deviation of 14.5° from the planarity was found for the corresponding dihedral angle τ (O–C8–S–C7) (see Table 2 and Fig. 2). This value is also larger than experimental data found for the dihedral angle τ (O–C–S–C) in similar molecules. Values of 4.89–5.40°, 4.5°, and 2.0° [25], 1.43° [26] and 0.6–3.7° [27] were reported for the *syn* form of thioester compounds. This deviation is attributed to the packing effect, since computational study showed a planarity around the sulfenyl carbonyl function for the free molecule (see below). Such packing arrangement, allows a short intra-molecular distance of 2.35 Å between the carbonyl oxygen atom and the hydrogen H7b bonded to carbon C7 (see Fig. 2). This hydrogen atom and the atoms of the sulfenyl

Table 2
Selected[a] homologous experimental (X-ray diffraction) and calculated (B3LYP/6-31G** and Lanl2dz) intra-molecular bond distances (Å) and angles (°) of S-benzyl ferrocenecarbothioate (**I**) and S-(2-methoxyphenyl) ferrocenecarbothioate (**II**).

	I		**II**		**I**		**II**
	Experimental	Calculated	Calculated		Experimental	Calculated	Calculated
Bond distances (Å)							
C(1)–C(6)	1.372(9)	1.40	1.40	C(8)–C(25)	1.462(6)	1.47	1.48
C(1)–C(2)	1.375(8)	1.40	1.41	C(21)–C(22)	1.408(7)	1.42	1.42
C(1)–C(7)	1.493(7)	1.51		C(21)–C(25)	1.418(6)	1.44	1.44
C(1)–S			1.78	C(22)–C(23)	1.411(7)	1.43	1.43
C(7)–S	1.825(5)	1.85		C(23)–C(24)	1.417(7)	1.42	1.42
C(8)–O	1.204(6)	1.22	1.21	C(24)–C(25)	1.427(7)	1.44	1.44
C(8)–S	1.768(5)	1.81	1.83				
Bond angles							
C(6)–C(1)–C(2)	117.8(6)	118.81	119.60	C(8)–S–C(7)	98.5(3)	99.38	
C(6)–C(1)–C(7)	120.6(6)	120.72		C(8)–S–C(1)			101.04
C(2)–C(1)–C(7)	121.6(5)	120.47		C(6)–C(1)–S			119.29
O–C(8)–C(25)	126.4(5)	121.14	123.62	C(2)–C(1)–S			121.04
C(22)–C(21)–C(25)	108.1(4)	107.89	107.93	C(1)–C(7)–S	112.1(4)	113.97	
C(21)–C(22)–C(23)	108.5(4)	108.29	108.25	O–C(8)–S	119.4(4)	122.29	122.64
C(22)–C(23)–C(24)	107.9(4)	108.35	108.32	C(25)–C(8)–S	114.1(4)	114.56	113.73
C(23)–C(24)–C(25)	107.8(4)	107.72	107.77	C(21)–C(25)–C(8)	122.8(4)	123.11	122.99
C(21)–C(25)–C(24)	107.6(4)	107.75	107.73	C(24)–C(25)–C(8)	129.2(4)	129.04	129.23
C(8)–C(25)–Fe	120.5(3)	122.57	123.57				
Torsion angles							
C(1)–C(7)–S–C(8)	80.6	90.85		S–C(8)–C(25)–C(24)	1.5	4.67	4.67
C(1)–S–C(8)–C(25)			179.33	O–C(8)–C(25)–C(21)	−7.1	−0.44	0.85
C(2)–C(1)–C(7)–S	−105.3	−90.15		O–C(8)–C(25)–C(24)	−178.4	−176.22	−176.34
C(2)–C(1)–S–C(8)			−68.93	C(8)–C(25)–C(24)–Fe	113.1	116.17	117.50
C(6)–C(1)–S––C(8)			113.91	C(8)–C(25)–Fe–C(24)	−124.1	−124.18	−124.45
C(3)–C(2)–C(1)–C(7)	178.8	179.72		C(8)–C(25)–C(21)–Fe	−113.9	−116.58	−117.71
C(3)–C(2)–C(1)–S			−177.84	C(7)–S–C(8)–O	14.5	5.63	
C(5)–C(6)–C(1)–C(7)	−177.2	−179.71		C(1)–S––C(8)–O			0.33
C(5)–C(6)–C(1)–S			177.21	C(7)–S–C(8)–C(25)	−165.4	−172.25	
C(6)–C(1)–C(7)–S	73.4	89.80		S–C(8)–C(25)–C(21)	172.9	−179.55	−178.15

[a] A complete list of the data in Table 2 is included as Supplementary data.

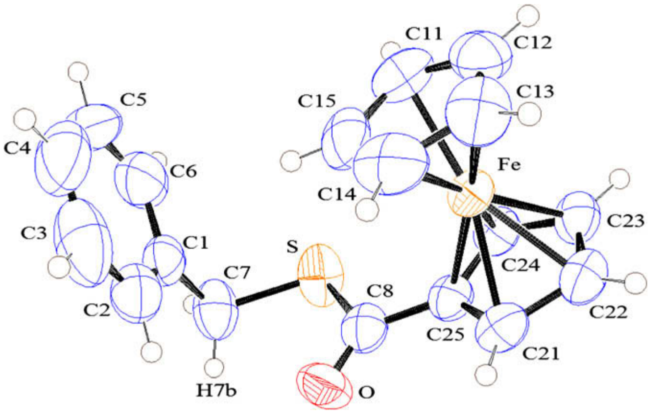


Fig. 2. Molecular diagram of S-benzyl ferrocenecarbothioate (**I**), showing the labeling of the non-H atoms, except for H7b, and their displacement ellipsoids at the 50% probability level.

carbonyl moiety, –S–C=O, are all involved in a plane that enable a hydrogen bond interaction in solid state. The strength of this interaction could be classified between weak and moderate taking into account the short interatomic H···O distance mentioned above. Moreover, the calculated bond angles O–C8–S and C8–S–C7 for the free molecule (122.3 and 99.4, respectively) are larger than the experimental ones (119.4 and 98.5, respectively. See Table 2). The decrease of these angles in solid state is consistent with a more effective H bond interaction. Further evidence can be found by comparing the bond angles for close related compounds in which this hydrogen bond was not possible or not detected. The O–C8–S and C8–S–C7 bond angles in these compounds are larger, ranging from 121.7 to 122.6 and 99.8 to 100.6, respectively. The required geometric arrangement for this attractive intra-molecular effect force C7 to deviate from planarity. Similar interaction is not possible in the previously reported aromatic thioesters of the type X–C(O)–S–Ar in which the dihedral angle of the O=C–S–C moiety approach to zero.

The bond distances around the sulfenyl carbonyl moiety in the general structure X–C(O)–S–Y deserves further analysis. The distances C8–S and C8–O are 1.77 Å and 1.20 Å, respectively, and are in agreement with the corresponding bond distances reported in the literature: C–S (1.77–1.79 Å) and C=O (1.18–1.21 Å). However, the bond distances X–C (C8–C25) and S–Y (S–C7) are 1.46 Å and 1.83 Å, respectively. Values reported in the literature are slightly longer for the first bond (X–C: 1.49–1.50 Å); and markedly shorter for the last bond (S–Y: 1.76–1.78 Å). In the previously reported structures, the carbon of the S–Y bond belongs to a sp^2-hybridized atom, whereas in the title compound, the sp^3-hybridized C7 enables as expected, a lengthening of the S–Y bond.

3.3. Computational study

The experimental and calculated geometric parameters for compounds I and II are shown together in Table 2 to facilitate the comparison. The potential energy curves around the sulfenylcarbonyl moiety were calculated for the dihedral angles τ O–C8–S–C7 and τ O1–C8–S–C1 for compounds **I** and **II**, respectively and are depicted in Fig. 3. These curves show two minima being the synperiplanar rotamer the conformer of lowest energy, in concordance with most of the thioester compounds. In contrast with our previous results the second minimum is located in the antiperiplanar instead of +anticlinal conformation. The antiperiplanar

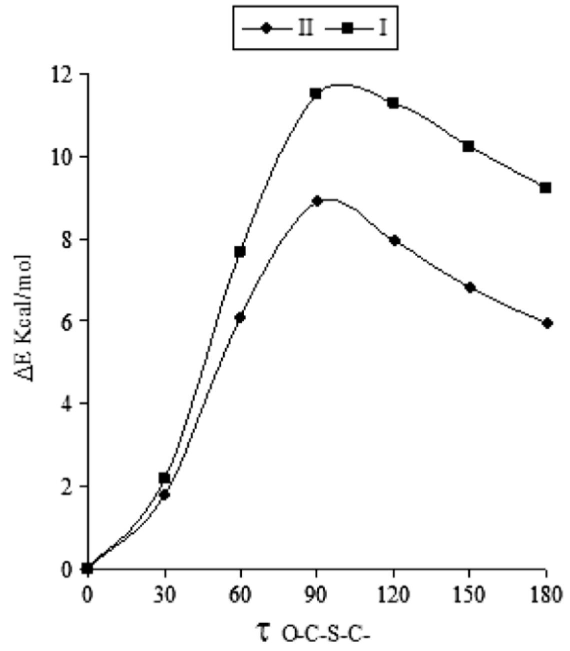


Fig. 3. Potential energy curve as a function of the torsion angle (τ) of the O–C8–S–C7 (compound I) and O–C8–S–C1 (compound **II**), calculated with the HF/6-31G level of approximation.

conformer is higher in energy with differences of 9 Kcal/mol and 6 Kcal/mol for compounds **I** and **II**, respectively.

3.4. Vibrational analysis

Compounds **I** and **II** present 105 and 108 normal modes of vibration, respectively. In Table 3 are shown the calculated and observed (IR and Raman) vibration mode wavenumbers and intensities. A tentative assignment of the experimental spectra is also proposed. For convenience in the assignments description of Table 3, the phenyl rings of the compounds I and II are symbolized as TB and TP, respectively (see Fig. 1). The patterns of the ring modes TP(k) and TB(k) for $k = 1–34$ are included as Supplementary data.

The calculated and observed wavenumbers are in good agreement and is illustrated in Fig. 4 by comparing the simulated and the experimental IR spectra and the experimental Raman obtained for compound I.

Fundamental bands corresponding to C=O stretching mode are at 1626 cm^{-1} and 1670 cm^{-1} for compounds **I** and **II**, respectively. The region of the stretching frequency in compound **II** is similar to those reported for the S-(2-methoxyphenyl) 4-substituted-benzenecarbothioates (1678–1671 cm^{-1}). The change in the hybridization of the carbon atom linked to the sulfur atom in the S–Y portion expressed by the lengthening of this bond seems to be responsible for the red shift in compound **I** with respect to both

Table 3

Selected data of calculated (B3LYP/6-31+G**) and experimental (IR and Raman) wavenumbers (cm^{-1}), relative intensities and tentative assignments for **I** and **II**[a,b].

Calculated	**I**		Calculated	**II**		Assignment[c]
	IR	Raman		IR	Raman	
1746 vs,s	1653 vs	1651 m	1779 vs,s	1669 vs	1674 m	ν (C=O)
1488 w,w	1444 m	1443 w	1488 w,m			ν C8–C25
			1317 vs,vw	1276 m	1276 vw	ν C2–O2
1274 vs,vw			1275 vs,m	1243 vs	1243 m	ν C8–C25
1247 vw,vw	sh	1219 w	1248 vw,vw	ovl	1214 vw	δ O–C8–C25
1229 vw,vw	1200 w	1204 w				ν C7–C1
1136 vw,vw	1105 w	1105 s	1137 vw,w	1106 vw	1106 s	ring breathing (CP + SCP)
			1061 vw,vw			ν(C1–S)
969 w,vw	948 m	952 w	965 w,vw	944 w	944 vw	δ i.p. (S–C8–C25)
828 w,vw	812 vs		832 w,vw	ovl	ovl	δ o.o.p. CH (CP+SCP) i.ph.
830 w,vw	822 sh	822 w	823 vs,w	818 vs		ν S–C8
822 vw,vw						ν (C7–C1)
786 vw,vw	767 m	773 w				δ i.p. (S–C7–C1)
			700 vw,vw		696 vw	ν (S–C1)
680 vw,w	686 m	686 w				ν S–C7)
			598 vw,vw	599 vw	599 vw	δ i.p. (C1–S–C8–C25)
583 vw,vw	573 m	574 w				δ i.p. (C7–S–C8–C25)
557 vw,vw			557 vw,vw			δ o.o.p. (S–C8–C25–C24)
			479 vw,vw	484 w	489 vw	δ S–C1–C6
459 w,vw	477 s		464 w,vw	454 vw	454 vw	δ CP–Fe–SCP
470 vw,vw		482 w	453 vw,vw			δ CP–Fe–SCP
448 vw,vw		438 w	448 vw,vw		ovl	ν as CP–Fe–SCP
423 vw,vw		397 w	415 vw,vw		397 vw	δ as (O1=C8–S)
365 vw,vw		335 s	355 vw,vw		325 vs	Ring tilt CP–SCP
354 vw,vw						δ o.o.p. (C1–C7–S)
340 vw,vw			340 vw,vw		ovl	ring tilt CP–SCP
311 vw,vw		304 vs				δ (C2–C1–C7–S)
278 vw,vw		277 w	281 vw,vw		275 vw	ν s (CP-Fe–SCP)
264 vw,vw		260 vw	266 vw,vw			δ C21–C25–C8–O)
207 vw,vw		209 w	202 v		200 vw	ring tilt CP–SCP
180 vw,vw		179 w	200 vw,vw		ovl	τ (O1–C8–S–C)
166 vw,vw		164 w	173 vw,vw		167 vw	ring tilt CP–SCP
131 vw,vw						δ (C25–C24–C8–S)

[a] A complete list of the data in this Table is included as Supplementary data.

[b] Intensities have been classified semi-quantitatively in terms of very strong (vs), strong (s), medium (m), weak (w) and very weak (vw). For the calculated band wave numbers, the first and the second intensity symbols are separated by points and refer to IR and Raman intensity, respectively. Shoulder and overlapping bands have been denoted by (sh) and (ovl), respectively.

[c] δ, deformation; ν, stretching; τ, torsion; ρ, rocking; s, symmetric; as, antisymmetric; wag, wagging; i.p., in plane; o.o.p., out of plane; CP, cyclopentadienyl ring; SCP, substituted cyclopentadienyl ring.

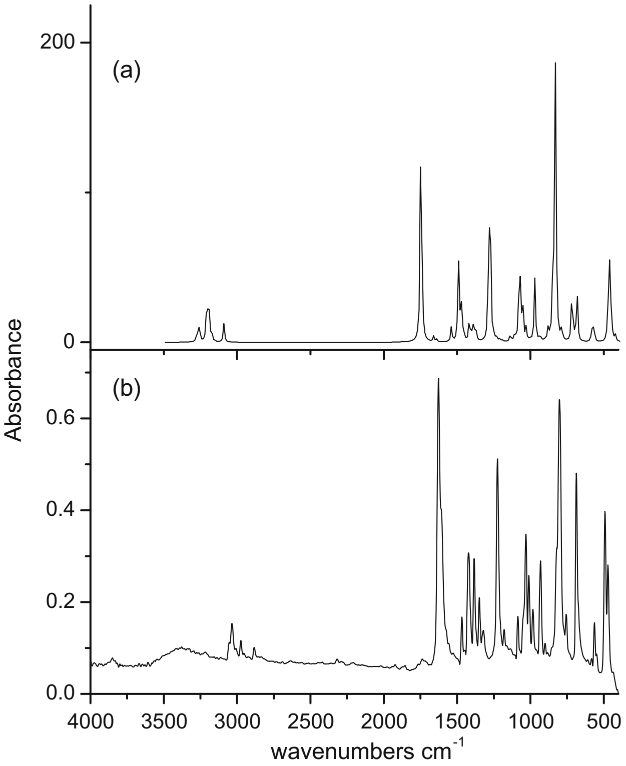


Fig. 4. Calculated (a) and experimental (b) IR spectra of S-benzyl ferrocenecarbothioate (**I**).

compound **II** and others reported S-aryl benzenecarbothioates. In the last class of compounds, the 2-methoxyphenyl group bonded to the sulfur atom generates new resonance forms as is depicted in Fig. 5, such as (iv) that preclude the resonance form (iii), reinforce the weight of the form (i) and consequently produce a blue shift frequency. Furthermore, the form (iv) can explain the shortening of the S–Y bond in S-arylbenzenecarbothioates respect to the compound I. A complementary explanation regarding to the lengthening of S–Y bond in compound I was already stated in the crystal structure analysis.

Vibrational bands around the sulfenyl carbonyl group constitute the most interesting bands to be analyzed here. The bands found at 698 cm^{-1} (IR and Raman) in compound **I** and 692 cm^{-1} (IR) and 688 cm^{-1} (Raman) in compound **II** were assigned to the out-of-plane deformation of the carbonyl group. This mode results shifted to higher frequencies in comparison with the corresponding vibration of S-(2-methoxyphenyl) 4-substituted-benzenecarbothioates (from 636 to 642 cm^{-1}). The ferrocenyl moiety exerts a red shift effect of about 50 cm^{-1}. The most intense IR band for compound (**II**) at 1243 cm^{-1} was assigned to the C8–C25 stretching mode. For compound (**I**) this normal mode was assigned to the bands at 1246 cm^{-1} (IR) and 1247 cm^{-1} (Raman). The S–C8 stretching band shows a strong absorption at 822 and 818 cm^{-1} in the IR spectrum of compound **I** and **II**, respectively. The C7–S (compound **I**) and C1–S (compound **II**) stretching vibrations were assigned to the bands at 686 cm^{-1} (IR and Raman) for compound I and 692 cm^{-1} (IR) and 696 cm^{-1} (Raman) for compound II. The S–C8–C25 antisymmetric stretching was assigned to the bands at 948 cm^{-1} (IR) and 953 cm^{-1} (Raman) for compound **I** and at 944 cm^{-1} (IR and Raman) for compound **II**.

The bands found at 599 cm^{-1} in the IR and Raman spectra of compound **I** were assigned to the C7–S–C8–C25 in plane deformation mode, while the corresponding band in compound **II** (C1–S–C8–C25) appears at lower frequencies: 573 cm^{-1} (IR) and 574 cm^{-1} (Raman). The Raman bands at 397 cm^{-1} in both compounds were assigned to the O1–C8–S antisymmetric deformation mode.

Most of the vibrational modes corresponding to the ferrocene system are active in the Raman spectra. The ring breathing normal mode was assigned to the bands at 1105 cm^{-1} (IR) and 1106 cm^{-1} (Raman) for compound I and 1106 cm^{-1} (IR and Raman) for compound II. Strong and very strong Raman bands at 335 cm^{-1} and 325 cm^{-1} for compounds **I** and **II**, respectively, were assigned to the ring tilt of the ferrocene system. Weak Raman bands at 209 and 164 cm^{-1} for compound **I** and 200 and 167 cm^{-1} for compound **II** were also assigned to the same mode. The analysis of the cyclopentadienyl–Fe–cyclopentadienyl stretching modes deserves further analysis. The bands at 277 and 275 cm^{-1} in compounds **I** and **II**, respectively were assigned to the symmetric stretching mode and the band at 438 cm^{-1} found in the Raman spectra of compound **I** was assigned to the antisymmetric mode. The corresponding band for compound II is overlapping.

4. Conclusions

Following with our studies on conformational and structural properties around the –C(O)–S– moiety in thioester compounds we have arrived to a good agreement with the evidence from experimental and theoretical data. The predominant *syn* conformation is now extended to two new compounds **I** and **II**. The crystal structure of the S-benzyl ferrocenothioate (**I**) shows a synperiplanar conformation around the sulfenyl carbonyl moiety with a dihedral angle τ O–C–S–Y = 14.5°. This marked deviation from the predicted planarity (τ = 0°) is attributed to the establishment of a new plane due to an intramolecular hydrogen bond interaction: C=O···H–C7.

Acknowledgments

The authors acknowledge the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC), Facultad de Ciencias Exactas (UNLP), Agencia Nacional de Promoción Científica y Técnica (ANPCYT), Fundación Antorchas, Alexander von Humboldt Foundation, DAAD (Deutscher Akademischer Austauschdienst, Germany). ICHC specially acknowledges the CONICET for the doctoral scholarship to Latin-American students.

CODV specially acknowledges the DAAD, which generously sponsors the DAAD Regional Program of Chemistry of the Republic

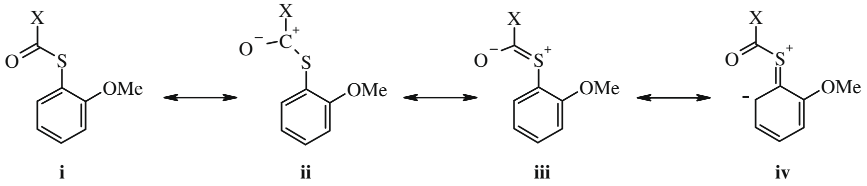


Fig. 5. Resonance forms in S-aryl thioesters.

Argentina supporting Latin-American students to make their Ph.D. in La Plata. JLJ acknowledge the WUS organization for the provision of an FT-IR 200 equipment. OEP is a Research Fellow of CONICET. The X-ray diffraction data were collected at LANADI (CONICET).

Appendix A. Supplementary data

CCDC 722639 contains the supplementary crystallographic data for S-(2-methoxyphenyl)ferrocenecarbothioate. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2009.11.006.

References

[1] I.C. Henao Castañeda, J.L. Jios, O.E. Piro, G.E. Tobón, C.O. Della Védova, J. Mol. Struct. 842 (2007) 46.

[2] (a) C. Amatore, S. Gazard, E. Maisonhaute, C. Pebay, B. Schollhorn, J.-L. Syssa-Magale, J. Wadhawan, Eur. J. Inorg. Chem. (2007) 4035;
(b) A.N. Nesmeyanov, E.G. Perevalova, L.I. Leont'eva, Yu.A. Ustynyuk, Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, 1965, pp. 1696–1697 (CA: 63:98558);
(c) G. Paiaro, A. Musco, G. Diana, J. Organomet. Chem. 4 (1965) 466.

[3] C.G. Rodriguez-Cendejas, L.S. Liebeskind, E. Peña-Cabrera, ARKIVOC 6 (2005) 250.

[4] L. Courtney Smith, Dev. Comp. Immunol. 26 (2002) 603.

[5] J.S. Boschwitz, J.F. Timoney, Vet. Immunol. Immunopathol. 38 (1993) 139.

[6] D. Raimondo, A. Giorgetti, F. Bernassola, G. Melino, A. Tramontano, Biochem. Pharmacol. 76 (2008) 1620.

[7] S. Patterson, P.R. Flatt, N.H. McCleneghan, Arch. Biochem. Biophys. 461 (2007) 287.

[8] S. Budavari, M.J. O'Neal, A. Smith, P.E. Heckelman (Eds.), The Merck Index, 13th ed., Merck & Co., Whitehouse Station, NJ, 2001.

[9] Y. Song, A. Goel, V. Basrur, P.E.A. Roberts, J.A. Mikovits, J.K. Inman, J.A. Turpin, W.G. Rice, E. Appella, Bioorg. Med. Chem. 10 (2002) 1263.

[10] P. Srivastava, M. Schito, R.J. Fattah, T. Hara, T. Hartman, R.W. Buckheit Jr., J.A. Turpin, J.K. Inman, E. Appella, Bioorg. Med. Chem. 12 (2004) 6437.

[11] E.F.A. Brandon, R.W. Sparidans, I. Meijerman, I. Manzanares, J.H. Beijnen, J.H.M. Schellens, Invest. New Drugs 22 (2004) 241.

[12] K.A. Reed, R.R. Manam, S.S. Mitchell, J. Xu, S. Teysan, T.-H. Chao, G. Deyanat-Yazdi, S.T.C. Neuteboom, K.S. Lam, B.C.M. Potts, J. Nat. Prod. 70 (2007) 269.

[13] C. Courvoisier, M.J. Paret, J. Chantepie, J. Goré, G. Fournet, G. Quash, Bioorg. Chem. 34 (2006) 49.

[14] G. Quash, G. Fournet, C. Courvoisier, R.M. Martinez, J. Chantepie, M.J. Paret, J. Pharaboz, M.O. Joly-Pharaboz, J. Goré, J. André, U. Reichert, Eur. J. Med. Chem. 43 (2008) 906.

[15] (a) D.R. van Staveren, N. Metzler-Nolte, Chem. Rev. 104 (2004) 5931;
(b) C. Biot, G. Glorian, L.A. Maciejewski, J.S. Brocard, O. Domarle, G. Blampain, P. Millet, A.J. Georges, H. Abessolo, D. Dive, J. Lebibi, J. Med. Chem. 40 (23) (1997) 3715;
(c) O. Domarle, G. Blampain, H. Agnaniet, T. Nzadiyabi, J. Lebibi, J. Brocard, L. Maciejewski, C. Biot, A.J. Georges, P. Millet, Antimicrob. Agents Chemother. 42 (1998) 540.

[16] M.F. Erben, C.O. Della Védova, Asian Chem. Lett. 8 (2004) 219.

[17] J.L. Jios, S.I. Kirin, T. Weyhermüller, N. Metzler-Nolte, C.O. Della Védova, J. Mol. Struct. 825 (2006) 53.

[18] CAD4 EXPRESS Software, Enraf-Nonius, Delft, The Netherlands, 1994.

[19] K. Harms, S. Wocadlo, XCAD4-CAD4 Data Reduction, University of Marburg, Marburg, Germany, 1995.

[20] A.L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 1998.

[21] G.M. Sheldrick, SHELXS-97. Program for Crystal Structure Resolution, University of Göttingen, Göttingen, Germany, 1997.

[22] G.M. Sheldrick, SHELXL-97. Program for Crystal Structures Analysis, University of Göttingen, Göttingen, Germany, 1997.

[23] GAUSSIAN 03, Revision B.05, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara., M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.

[24] C.O. Della Védova, Spectrochim. Acta 47A (1991) 1619.

[25] S. Naveen, B. Dinesh, K. Abiraj, D. Channe Gowda, M.A. Sridhar, J. Shashidhara Prasad, J. Chem. Crystallogr. 37 (2007) 721.

[26] M.F. Erben, C.O. Della Védova, R.M. Romano, R. Boese, H. Oberhammer, H. Willner, O. Sala, Inorg. Chem. 41 (2002) 1064.

[27] K. Kößler, T. Rüffer, B. Walfort, R. Packheiser, R. Holze, M. Zharnikov, H. Lang, J. Organomet. Chem. 692 (2007) 1530.