CYCLIC VOLTAMMETRY, ^{13}C NMR AND MÖSSBAUER STUDY OF [m]-FERROCENOPHANE-1,n-DIONES

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Summary

Mössbauer parameters, redox potentials and ^{13}C NMR chemical shifts were measured in mono- and di-ketone derivatives of [3]-, [4]-, [5]-ferrocenophanes. Several comparisons were made of the results of the parent compounds and their derivatives. Correlations between the effect of the carbonyl group and the molecular structure are discussed in detail. The dipolar forms of the carbonyls are presumed on the basis of the ^{13}C NMR chemical shifts of [4]- and [5]-ferrocenophane-1-ones. Other possible relationships are also discussed.
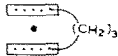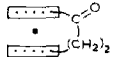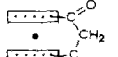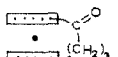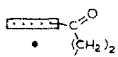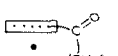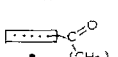
Introduction

The effect of a carbonyl group in the methylene bridge on the Mössbauer parameters have recently been shown in tri-, tetra- and penta-methylene bridged ferrocenes [1,2]. It was found that the decrease of the quadrupole splittings (QS) was accompanied by an increase of the isomer shifts (IS). These opposite changes have been interpreted as an increase in the electron population on the ϵ_1 molecular orbitals [1]. Some monoketoferrocenes have proved to be exceptions to the trend mentioned above. These exceptions belong to the trimethylene bridged ferrocene series (TMF) in which some changes of molecular geometry (MGC) were recently revealed [3–5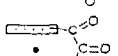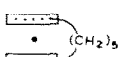]. In these ferrocene derivatives mentioned above the carbonyl groups cannot be coplanar with the cyclopentadienyl (Cp) ring, because of the MGC. As a continuation of this work, the effects of two carbonyl groups in the same methylene bridge of ferrocene derivatives are studied here by means of Mössbauer spectroscopy, cyclic voltammetry and ^{13}C NMR spectroscopy.

Results and discussion

The Mössbauer parameters of the ferrocene derivatives considered are listed in Tables 1–4. The schematic representations of the compounds under study are also shown. The Mössbauer spectra of these ferrocenes consist of single quadrupole splittings. The values of the oxidation potentials ($E_{1/2}$) are also listed in Tables 1 and 3. The differences between the oxidation potentials of mono- and di-keto bridged ferrocenes ($\Delta E_{1/2}$) are given in the last columns of the Tables. The ^{13}C NMR chemical shifts of the bridged ferrocenes and their mono- and di-ketone derivatives are presented in Table 5. It has been proved that electron-withdrawing groups such as carbonyls cause lowering of the QS values compared with ferrocene, and the effects of two carbonyl groups bonded to the different Cp rings are additive [6,7]. This is the case of 1,1'-diacetylferrocene and 1,1'-dibenzoylferrocene (see Table 4, and ref. 6), i.e.: ferrocene derivatives in which free rotation along the Cp–Fe–Cp axis is possible [6].

TABLE 1

MÖSSBAUER PARAMETERS AND OXIDATION POTENTIALS OF BRIDGED FERROCENYL KETONES

Compounds [a]		IS (mm/s)	QS (mm/s)	$E_{1/2}$ (mV)	$\Delta E_{1/2}$ ($>$CO) (mV)
$(CH_2)_3$	(I)	0.408(2)	2.256(3)	367	
$C=O$, $(CH_2)_2$	(VI)	0.416(1)	2.256(4)	660	293
$C=O$, CH_2, $C=O$	(VII)	0.407(1)	2.192(2)	921[*][b]	261
$(CH_2)_4$	(VIII)	0.421(2)	2.351(5)	345	
$C=O$, $(CH_2)_3$	(IX)	0.426(3)	2.180(2)	665	320
$C=O$, $(CH_2)_2$, $C=O$	(X)	0.436(1)	2.177(2)	960	295
$C=O$, $C=O$, $(CH_2)_2$	(XI)	0.427(1)	2.126(2)	865	200
$(CH_2)_5$	(XII)	0.430(4)	2.344(5)	296	
$C=O$, $(CH_2)_4$	(XIII)	0.429(2)	2.162(2)	640	344
$C=O$, $(CH_2)_3$, $C=O$	(XIV)	0.430(3)	2.134(4)	921	281

[a] In each case the rectangles represent the cyclopentadienyl rings, the small dots the carbon atoms of the ring, the larger dots the iron atoms. [b] See text for the meaning of *.
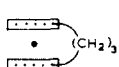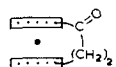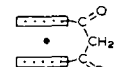
The electron withdrawal of the carbonyl is the greatest in that compound in which $>CO$ is coplanar with the Cp-ring thus enabling the $>CO$ group to manifest its $-M$ effect. This was well demonstrated by the QS values of different acylferrocenes, viz. Fc–CO–R where R $= CH_3$ (QS 2.263 mm/s); R $=$ phenyl (2.262 mm/s); R $=$ t-butyl (2.281 mm/s); and R $=$ mesityl (2.341 mm/s) [9]. In the first two cases the $>CO$ group is coplanar with the Cp ring whereas, with the t-butyl group the angle between the carbonyl and Cp ring is 40°; it should be higher for mesityl. The QS values are not sensitive to the electronic effects of substituents on the benzene ring of benzoylferrocenes because the benzene ring in these derivatives is not coplanar with the carbonyl group [10]. From a comparison of the QS values of ferrocene (2.367 mm/s, ref. 2), [5]ferrocenophane (2.344 mm/s), [4]ferrocenophane (2.351 mm/s) and [3]ferrocenophane (2.256 mm/s), it can be seen that the QS values are also an indication for the various ferrocene moiety conformations. The Mössbauer parameters of the dicarbonyl derivatives of [m]ferrocenophanes given in Tables 1 and 2 reveal that the effects of the first and the second carbonyl group are not additive. From this observation it follows that nearly the same QS values of [3]ferrocenophane and [3]ferrocenophane-1-one can be explained by the fact that the $>CO$ group cannot apply its $-M$ effect because of the ring tilt (8.8°) and the angle between the carbonyl and Cp-ring (42°) [3,11]. The second carbonyl group in [3]ferrocenophane-1,3-dione causes the higher rigidity of the derivatives. The ring-tilt is 9.8° and the angles between the carbonyl and the ring are 38.6° and 45.2°, respectively [12]. The second $>CO$ thus causes a small decrease in the QS value, (see Table 2). The decrease of QS in [4]ferrocenophane-1-one is considerable since the position of the carbonyl is near to being coplanar with the Cp ring. The angle between them is 18.3° and the ring-tilt is 4.4° [13]. For [4]ferrocenophane-1,4-dione an analogy with the [3]ferrocenophane-1,3-dione is assumed: i.e., the second carbonyl cannot attain coplanarity with the Cp ring so its influence reflected in QS is poor. With [5]ferrocenophane-1,5-dione the effect of a second carbonyl on the QS is more pronounced than in [4]ferrocenophane-1,4-dione because of the high flexibility of the five-membered bridge (see Tables 1,2). These Mössbauer measurements confirm the conclusions drawn from UV and visible absorption spectra of these diketones [14,15].

The Mössbauer parameters of two additional [3]ferrocenophane derivatives (XV and XVI) are also listed in Table 3. In these compounds all three carbon atoms of the bridge are in an sp^2 hybride state. In both cases the rigidity of the system should be higher than for [3]ferrocenophane-1,3-dione. For XV the great rigidity has recently been proved by X-ray crystallography [16]. By this measurement the ring tilt is 13.6° and the angles between the $>CO$ groups and the Cp rings are near to 80°. Possibly the high rigidity and direct interaction between the Fe orbitals and the conjugated double bond system of the bridge cause both the low QS value of XV in relation to the QS of VII and the low QS of XVI in relation to the QS value of VI. However, this explanation needs additional support.

For the [4]ferrocenophane-1,2-dione (XI), in which the second carbonyl cannot possibly cause additional rigidity to the system, the ΔQS is proved to be additive, that is, ΔQS is near to the sum of ΔQS_α and ΔQS_β (Table 1 in ref. 1, where $\Delta QS_\alpha = -171 \times 10^{-3}$ mm/s and $\Delta QS_\beta = -44 \times 10^{-3}$ mm/s). The oxidation potential values ($E_{1/2}$) of these compounds and the $\Delta E_{1/2}$ values are also listed in Tables 1 and 3. It is known that the carbonyl of a methylene-bridge in the α-position
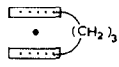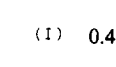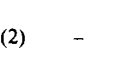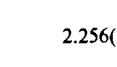
TABLE 2

DIFFERENCES BETWEEN MÖSSBAUER PARAMETERS OF MONO- AND DI-KETO DERIVATIVES OF BRIDGED FERROCENES

Compounds			ΔQS (1st CO) (mm/s) [a]	ΔQS (2nd CO) (mm/s)	ΔIS (1st CO) (mm/s)	ΔIS (2nd CO) (mm/s)
ferrocene-$(CH_2)_3$	ferrocene-C=O-$(CH_2)_2$	ferrocene-C=O-CH_2-C=O	0	−64	8	−1
ferrocene-$(CH_2)_4$	ferrocene-C=O-$(CH_2)_3$	ferrocene-C=O-$(CH_2)_2$-C=O	−171	−3	19	15
ferrocene-$(CH_2)_5$	ferrocene-C=O-$(CH_2)_4$	ferrocene-C=O-$(CH_2)_3$-C=O	−182	−28	−1	0

[a] All values to be multiplied by 10^{-3}.

TABLE 3

MÖSSBAUER PARAMETERS OF TRIMETHYLENE BRIDGED FERROCENYL KETONES

| Compounds		IS (mm/s)	ΔIS (10^3 mm/s)	QS (mm/s)	ΔQS (10^3 mm/s)	$E_{1/2}$ (mV)	$\Delta E_{1/2}$ ($>$CO) (mV)
ferrocene-$(CH_2)_3$	(I)	0.408(2)	–	2.256(3)	–	367	–
ferrocene-C=O-$(CH_2)_2$	(VI)	0.416(1)	+8	2.256(4)	0	660	293
ferrocene-C=O-CH_2-C=O	(VII)	0.407(1)	−1	2.192(2)	−64	921★ [a]	(261) [b]
ferrocene-C=O-C=CHPh-C=O	(XV)	0.413(2)	+5	2.127(1)	−129	916★ [a]	(256) [b]
ferrocene-C(O-CH_2-Ph)=CH-C=O	(XVI)	0.406(1)	−2	2.234(2)	−22	771★ [a]	(111) [b]

[a] See text for meaning of ★. [b] $E_{1/2}$ (VII or XV or XVI)$- E_{1/2}$ (VI).

TABLE 4

MÖSSBAUER PARAMETERS AND OXIDATION POTENTIALS OF DIKETO DERIVATIVES OF FERROCENE

Compounds	IS (mm/s)	ΔIS [a] (10^3 mm/s)	QS (mm/s)	ΔQS ($>$CO) (10^3 mm/s)	$E_{1/2}$ (mV)	$\Delta E_{1/2}$ ($>$CO) [b] (mV)
Monoacetylferrocene	0.434±2	+2	2.263±4	−104	682	242
1,1′-Diacetylferrocene	0.422±1	−10	2.151±2	−108	910	235
Benzoylferrocene	0.450±1	+18	2.251±1	−116	689	249
1,1′-Dibenzoylferrocene	0.433±2	+1	2.170±3	−99	908	234
Ferrocene	0.432±2	–	2.367±2	–	440	0

[a] IS(compound)$- IS$(ferrocene). [b] $E_{1/2}$(compound)$- E_{1/2}$(ferrocene). The oxidation potential and the Mössbauer parameters of the ferrocene are considered here, instead of the $E_{1/2}$ and QS and IS values of the reduced pair of these ketoferrocenes.

TABLE 5

## ^{13}C NMR CHEMICAL SHIFTS OF THE BRIDGED FERROCENE DERIVATIVES
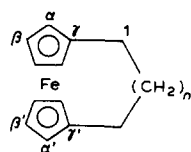
Compounds	C(γ/γ')	C(α/α')	C(β/β')	C(1)	C(2)	C(3)	C(4)	C(5)
	85.5	69.3	68.1	24.5	35.1	24.5		
	88.1 74.1	71.2 69.3	72.7 70.3	211.9	44.2	31.8		
	87.2	72.4	74.4	192.1	59.6	192.1		
	88.2	68.5	67.9	29.4	27.0	27.0	29.0	
	90.0	69.3	70.9 70.8	205.8	39.3	21.8	21.8	
	91.9	73.4	75.2	204.3	37.9	37.9	204.3	
	86.6 76.6	68.2	68.4 69.0	41.4	207.3	41.3	25.7	
	90.0	69.3	70.9 70.8	205.8	211.7	39.3	21.8	
	89.8	68.2	66.7	25.2	24.8	24.9	24.8	25.2
	88.3 79.7	68.9 68.4	72.6 70.2	205.3	41.0	22.5	25.1	25.1
	81.6	73.9	70.6	202.4	37.2	27.9	37.2	202.4
[a]	79.4 78.8	72.1 72.0	73.3 72.4	195.2	110.8	168.8		
[b]	79.2 86.4	73.3 74.0	77.2 74.9	192.6	139.8	189.0		

[a] Aromatic 135.3, 128.7, 128.4, 127.7 and $-CH_2-Ph$ 71.8. [b] Aromatic 133.3, 131.3, 130.9, 128.7 and $=CH-Ph$ 145.7.

to the Cp ring increases the oxidation potential by 280–300 mV and the $>$CO in the β-position increases the $E_{1/2}$ by ~ 150 mV [17,18,4]. The $\Delta E_{1/2}$ values of the second carbonyl in X and XIV are found to be near to the average increase. The $\Delta E_{1/2}$ values given by the first carbonyl groups in IX and XIII, however, are not in the range given above: they are a little higher than the average increase. This seems to reflect the increasing conformational flexibility of the tetra- and penta-methylene bridges. The $\Delta E_{1/2}$ caused by the β-carbonyl in the single α,β-diketone is slightly higher than the $\Delta E_{1/2}$ of the analogous β-monoketone which was found to be 150 mV [18,4]; this may be due to the carbonyl in β-monoketones being separated from the Cp ring by an electron-donating methylene group which may decrease the effect of the $>$CO group on the ferrocenyl moiety.

The $E_{1/2}$ values marked by asterisks are given by estimation from the position of the anode peak (Tables 1,3). It would appear that all these compounds belong to the TMF series. On the cyclic voltammograms of these derivatives only the anode peak characterizing the oxidation of the ferrocenyl moiety can be found, the cathode peak is absent *. It means that there is no oxidized form to be reduced in the solution. A number of chemical experiments [20] show the decompositions of these oxidized forms:
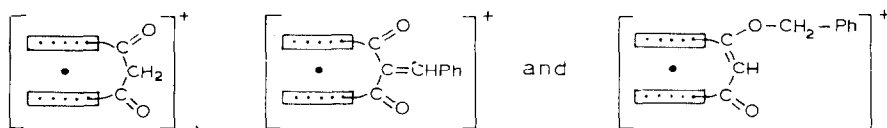
It is likely that these diketo derivatives, which have ϵ_2 molecular orbitals rehybridized by the MGC and their ϵ_1 molecular orbitals, strongly perturbed by the two carbonyl groups, are not able to withstand the full delocalization of an electron without decomposition.

To gain some additional information about these compounds, more precisely about the dihedral interplanar angles between the carbonyl and the Cp ring, some ^{13}C NMR measurements were obtained. The chemical shift values ($\delta(^{13}C)$) of the bridged ketones, as well as of the parent [m]ferrocenophanes are listed in Table 5. From a comparison of the spectra of the parent ([m]ferrocenophane) and the corresponding mono- and di-keto derivatives it seems that the δ values of the carbon atoms in the Cp rings are not too sensitive to the insertions of carbonyl groups into the bridge. The δ values of the neighbouring methylene groups are shifted considerably to the lower field (from ~ 25 to ~ 40 ppm). The effect of the carbonyl on the $\delta(>CH_2)$ values of the further methylene groups is rather small. However, great differences can be found among the δ values of the carbonyl groups (see Table 5). These differences are connected with structures A or B of the molecules.

It has recently been found in the ferrocene derivatives that the δ value of the carbon atom in the carbonyl group depends numerically on the dihedral angle between the planes of the carbonyl and the adjacent Cp ring (Φ). Acetylferrocene (Φ 0°) and [3]ferrocenophane-1-one ($\Phi 42°$) were used as reference compounds [9]. It was reasoned that the dependence of $\delta(>CO)$ on coplanarity infers the possibility of

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* The difference between the anode and cathode peaks is usually 58 mV, so a hypothetical $E_{1/2}$ value may be estimated from the position of the anode peak [19].

the $>$CO being able to apply its $-M$ effect (eq. 1, ref. 9, eq. 10).

$$\cos^2 \Phi_{\text{calc}} = 1 - 0.0457\Delta_x \tag{1}$$

We attempted to use this method to evaluate the dihedral angle between the carbonyl group and the Cp ring, and have found that this method gave a false Φ value for [4]ferrocenophane-1-one, i.e. 25.2° was obtained instead of the measured 18.3° [13]. Concerning this method, it is believed that [3]ferrocenophane-1-one is not the appropriate reference compound for this purpose. The authors [9] did not take into account that the carbon atom of the carbonyl in this compound tilts out from the plane of the Cp ring by 0.30 Å towards the iron atom, which is another hindrance for application of $-M$ effect of the carbonyl groups, in addition to the nonplanarity of the carbonyl group and the Cp ring [21,11,3]. Thus, all Φ values obtained with this reference compound contain a systematic error.

Concerning the ^{13}C NMR measurements of the compounds under discussion three points have to be mentioned.
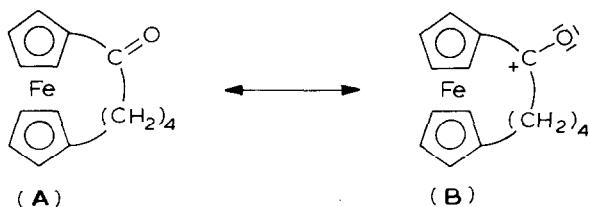
1. The $\delta(>$CO) values for [3]ferrocenophane-1-one, [4]ferrocenophane-1-one and [5]ferrocenophane-1-one are 211.9, 205.8 and 205.3, respectively. Since the δ value can be considered as a measure of the electron density at the carbon atom it seems that this trend can be explained by the canonical forms **A** and **B** of the carbonyl groups.

The canonical form **B** may have a considerable weight if the ferrocenyl moiety can stabilize the adjacent carbonium ion. This stabilization is possible for [5]- and [4]-ferrocenophane-1-one in which the $>$CO groups are nearly coplanar with the Cp rings *. This is not the case in the [3]ferrocenophane-1-one where the Φ is 42°. The $\delta(>$CO) of 211.9 ppm of [3]ferrocenophane-1-one is rather close to that found in cyclic and acyclic aliphatic ketones [22].

2. The $\delta(>$CO) value in [3]ferrocenophane-1,3-dione is exceptionally low (192.1 ppm). A similar value was found for the ferrocene analogues of chalcones in which the carbonyl was conjugated with the Cp ring as well as with the CH=CH group. In the [3]ferrocenophane-1,3-dione, however, the carbonyl groups are not coplanar with Cp rings (see above) and the enol form of this diketone is excluded by ^{1}H NMR measurements in CDCl$_3$. This rather low δ value can be explained if we assume that carbon atoms of the carbonyl groups are so close to the iron atom that interaction between the Fe d-orbitals and the carbon atom px orbitals is possible. The X-ray measurements support this idea [12]. The Fe–carbonyl distance in this compound was found to be 2.99 Å, a value which is close to the values of 2.71 and 2.85 Å found for the ferrocenylcarbenium ions [24,25].

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* The explanation given in ref. 23 is misleading because it assumes that the Φ is higher in [4]ferro-cenophane-1-one than in [3]ferrocenophane-1-one.

3. As can be seen in Table 5, indentical $\delta(>CO)$ values of the carbon atoms of two carbonyl groups are found for [3]ferrocenophane-1,3-dione, [4]ferrocenophane-1,4-dione and [5]ferrocenophane-1,5-dione. However the first and the second carbonyl group exert different effects on the QS values in these compounds (see Table 3). It follows that the carbonyls are equivalent in the solution because of the twisting of the bridge. However, the carbonyl groups are not equivalent in Mössbauer and X-ray measurements since in the solid state the twisting of the bridge is not possible therefore ΔQS by the first carbonyl and ΔQS by the second $>CO$ are different. The non-equivalence of the carbonyl groups in [3]ferrocenophane-1,3-dione has also been proved by X-ray measurement [12]. It is assumed that ongoing X-ray measurements will prove the non-equivalence in [4]ferrocenophane-1,4-dione and in [5]ferrocenophane-1,5-dione.

Experimental

The oxidation potentials $(E_{1/2})$ and the Mössbauer parameters of these compounds were measured by cyclic voltammetry and a constant acceleration Mössbauer spectrometer (for details see refs. 1 and 20). The ^{13}C NMR spectra were run on a JEOL FX-100FT spectrometer with proton noise decoupling at 25 MHz. Details of the measurements were the same as in ref. 26. The [3]-, [4]-, and [5]-ferrocenophane-1-one were prepared in accordance with refs. 27, 28 and 29, respectively. The [3]-, [4]- and [5]-ferrocenophane-1,n-diones ($n = 3,4,5$) were prepared as in refs. 30–32 and the 2-benzylidene [3]ferrocenophane-1,3-dione and the 3-benzyloxy [3]ferrocenophane-2-en-1-one as in ref. 30. The [4]ferrocenophane-1,2-dione was prepared by the Kreidlin and Rubinskaja method [33].

Acknowledgements

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