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MÖSSBAUER STUDY OF BRIDGED FERROCENYL KETONES

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Summary

The effect of the carbonyl group on Mössbauer parameters can be seen in the keto-derivatives of methylene-bridged ferrocenes. The disturbing influence of ring tilt and bond shortness on the electron withdrawal of the carbonyl group is shown by some trimethylene-bridged ferrocenes. The results are interpreted by a change of electron population in ring-based orbitals and by the absence of coplanarity of the carbonyl group with the cyclopentadienyl ring.

Introduction

The Mössbauer studies of the early years of ferrocene chemistry revealed that the Mössbauer parameters of the ferrocene derivatives were fairly insensitive to the electronic character of the substituents in the cyclopentadienyl rings [1–3]. The ketoferrocenes, however, proved to be exceptions, i.e. their quadrupole splittings (QS) were found to be significantly lower than the QS of the ferrocene [4–6]. Further, the readiness of keto- and diketo-ferrocenes for protonation was pronounced large [7,8]. From the viewpoint of Mössbauer spectroscopy the protonated diketoferrocenes have been shown to be peculiar compounds since their QS values (1.78–1.85 mm s^{-1}) are the lowest yet reported for ferrocene derivatives [9]. It is noteworthy that the QS values of iron protonated ferrocenes are found among the highest QS values (2.6–2.8 mm s^{-1}) in ferrocene chemistry [10].

Here, we are concerned with the Mössbauer study of some ketoferrocenes, in particular the keto-derivatives of methylene-bridged ferrocenes.

Experimental

Ferrocene was purchased from BDH (England); acetylferrocene was prepared by the Rosenblum and Woodward method [11]. The keto-derivatives of the ferrocenes were prepared in Brookhaven National Laboratory by known procedures [12–18]. All solid compounds were purified by recrystallization and/or chromatography.

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TABLE 1

MOSSBAUER PARAMETERS OF BRIDGED FERROCENYL KETONES

No.	Compound	IS (mm/s)	$\Delta IS \times 10^3$	QS (mm/s)	$\Delta QS \times 10^3$
1	Ia	0.432 (2)	$+2 \pm 2$	2.367 (1)	-104 ± 4
	Ib	0.434 (1)		2.263 (4)	
2	IXb	0.421 (2)	$+5 \pm 4$	2.351 (5)	-171 ± 5
	Xb	0.426 (3)		2.180 (2)	
3	IIb	0.380 (2)	$+21 \pm 6$	2.297 (3)	-126 ± 6
	IVc	0.401 (6)		2.171 (5)	
4	III	0.378 (3)	$+15 \pm 3$	2.266 (1)	-138 ± 3
	XII	0.393 (1)		2.128 (3)	
5	IXc	0.430 (4)	-1 ± 4	2.344 (5)	-182 ± 5
	Xc	0.429 (2)		2.162 (2)	
6	IXc	0.430 (4)	0 ± 5	2.344 (5)	-210 ± 6
	XIII	0.430 (3)		2.134 (4)	
7	IXb	0.421 (2)	$+1 \pm 4$	2.351 (5)	-44 ± 6
	XI	0.422 (3)		2.307 (3)	
8 [a]	IIb	0.380 (2)	$+58 \pm 2$	2.297 (3)	-54 ± 4
	IVd	0.438 (1)		2.243 (2)	
9 [a]	IIb	0.380 (2)	$+29 \pm 3$	2.297 (3)	-33 ± 3
	Va	0.409 (2)		2.264 (1)	

[a] Reduced derivatives of Nos. 8 and 9 were not available

Their purity was checked with IR spectra, by TLC, and for some of them, by NMR. The Mössbauer spectra of these compounds were recorded at room temperature by means of a constant acceleration spectrometer using a ^{57}Co source in a rhodium matrix. The Mössbauer parameters were evaluated by the least squares method. The Mössbauer parameters given in Tables 1–3 are the average values of three to five runs. The errors recorded in the tables are the standard deviations of the average of the results for each sample. Systematic errors were not treated. Since the results presented and the interpretations of these results are based on the relative values of the QS and IS, only the relative errors are of importance.

TABLE 2

MÖSSBAUER PARAMETERS OF HOMOANNULARLY-BRIDGED FERROCENYL KETONES

No.	Compound	IS (mm/s)	$\Delta IS \times 10^3$	QS (mm/s)	$\Delta QS \times 10^3$
1 [a]	Ia	0.432 (2)	$+7 \pm 4$	2.367 (1)	-96 ± 1
	XIVa	0.439 (4)		2.271 (1)	
2 [a]	Ia	0.432 (2)	$+12 \pm 2$	2.367 (1)	-100 ± 1
	XIVb	0.444 (1)		2.267 (1)	
3	XVIa	0.321 (1)	$+16 \pm 6$	2.054 (2)	-78 ± 2
	XVIb	0.337 (6)		1.976 (1)	
4	VIa	0.344 (2)	$+13 \pm 9$	2.133 (2)	-159 ± 3
	VIb	0.357 (9)		1.974 (2)	
5 [a]	IXb	0.421 (2)	-2 ± 4	2.351 (5)	-88 ± 5
	XV	0.419 (4)		2.263 (2)	
6 [a]	IIb	0.380 (2)	$+20 \pm 6$	2.297 (3)	-59 ± 4
	XVIc	0.400 (6)		2.238 (2)	

[a] Reduced derivatives of Nos. 1,2,5 and 6 were not available.

TABLE 3

BRIDGED FERROCENYL KETONES WHOSE MÖSSBAUER PARAMETERS ARE UNUSUAL

No.	Compound	IS (mm/s)	$\Delta IS \times 10^3$	QS (mm/s)	$\Delta QS \times 10^3$
1	IXa	0.408 (2)	$+8 \pm 2$	2.256 (3)	0 ± 5
	Xa	0.416 (1)		2.256 (4)	
2	VIIa	0.385 (1)	$+13 \pm 5$	2.169 (3)	$+11 \pm 3$
	VIIIa	0.398 (5)		2.180 (1)	
3	IIa	0.330 (2)	$+26 \pm 8$	2.020 (1)	$+22 \pm 1$
	IVa	0.356 (8)		2.042 (1)	
4	VIIb	0.391 (1)	$+16 \pm 2$	2.213 (2)	$+34 \pm 4$
	VIIIb	0.407 (2)		2.247 (3)	
5	IIc	0.385 (2)	$+26 \pm 5$	2.236 (5)	-9 ± 5
	IVb	0.411 (5)		2.227 (1)	
6	IIb	0.380 (2)	$+29 \pm 4$	2.297 (3)	$+37 \pm 5$
	Vb	0.409 (3)		2.334 (4)	

Results and discussion

The schematic representations of the keto-derivatives of the bridged ferrocenes studied in this work are shown in Fig. 1. The Mössbauer spectra of these compounds, measured at room temperature, are found to contain single quadrupole splitting. The Mössbauer parameters of hetero- and homo-annularly bridged ketoferrocenes are presented in Tables 1 and 2, and the QS and IS values of the ketoferrocenes whose QS values are not decreased by the presence of the carbonyl group are listed in Table 3. If the QS values of the bridged ferrocenyl ketones in Table 1 are compared with those of bridged ferrocenes without a carbonyl group * (also in Table 1) it seems that the QSs for all of the keto-derivatives are smaller than those of their parent compounds. These results tend to correlate well with the Mössbauer parameters of unbridged ferrocenyl ketones, for example, with the QS of monoacetyl ferrocene (Table 1) [4,9,19].

The interpretation of the QS change in these derivatives would be possible in two ways: one of them is the population change in iron-based orbitals $\epsilon_2(d_{xy},d_{x^2-y^2})$, the other is the population change in ring-based orbitals $\epsilon_1(d_{xz},d_{yz})$, [6,20–24]. In view of the lower QS values observed, withdrawal of the electron density is unlikely to occur via ϵ_2-orbitals since it has been amply demonstrated that such withdrawal results in substantial increases in QS values, e.g. in ferrocene–$HgCl_2$ complexes (QS 3.09 mm/s) or in iron-protonated ferrocenes (2.6–2.8 mm/s) [25,10]. Electron-withdrawal therefore seem to occur mainly via the ring-based orbitals ϵ_1 in these cases. This interpretation is also supported by the trend of the IS change. MO calculations for ferrocene show that the contribution of the electrons on ϵ_1 orbitals to the QS value is -2.4 mm/s; the contribution of the electrons on ϵ_2 is $+5.4$ mm/s [20,21]. Consequently a decrease in the ϵ_2 population should be accompanied by a decrease of IS because of the decreased shielding effect of "*d*" electrons on the

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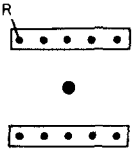
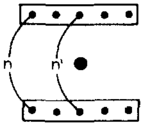
* For purposes of comparison, it is suggested that the Mössbauer parameters of the reduced pairs of the bridged ferrocenyl ketones be used instead of the data for the ferrocene; this enables perturbing effects to be avoided. In reality, such a treatment of the results is not possible in every case because the reduced pair of ketoferrocenes is not always available.



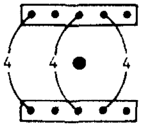
I

a) R = H
b) R = CO-CH$_3$

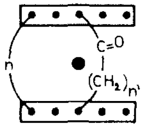


II

a) n = n' = 3
b) n = n' = 4
c) n = 4 , n' = 3

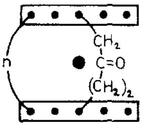


III



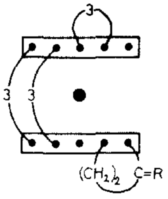
IV

a) n = 3, n' = 2
b) n = 4, n' = 2
c) n = 4, n' = 3
d) n = 5, n' = 3



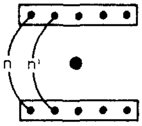
V

a) n = 5
b) n = 4



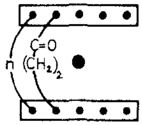
VI

a) R = H$_2$
b) R = O



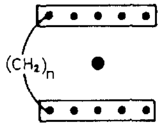
VII

a) n = n' = 3
b) n = 4 , n' = 3



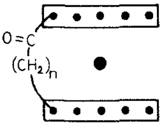
VIII

a) n = 3
b) n = 4



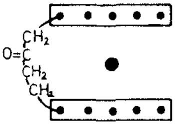
IX

a) n = 3
b) n = 4
c) n = 5

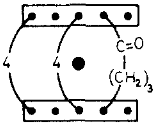


X

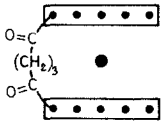
a) n = 2
b) n = 3
c) n = 4



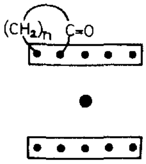
XI



XII

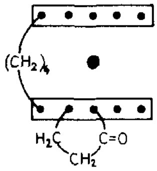


XIII

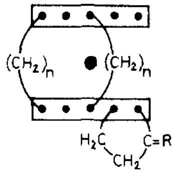


XIV

a) n = 3
b) n = 4



XV



XVI

a) n = 3 , R = H$_2$
b) n = 3 , R = O
c) n = 4 , R = O

Fig. 1. Schematic representations of bridged ferrocenes and ketoferrocenes. The rectangles represent the cyclopentadienyl rings, the small solid circles the carbon atoms of the ring, the large solid circles the iron atoms, and the arcs the bridges. The values for *n* and *n'* are the numbers of methylene groups in the bridges

"*s*" electron density at the nucleus. Since the IS values of these compounds are higher than those of their pendants it is probable that the ϵ_2 is not involved in the effect of the carbonyl group. It should be noted, however, that these ΔIS values are extremely small but the effect is significant because the same trend can be seen in a number of other samples.

The effect of the keto group on the electron distribution is also observable in the case of the homoannularly-bridged ferrocenes (Fig.1, Table 2). The change of the Mössbauer parameters shows the same tendency as observed in the keto-derivatives of the heteroannularly-bridged ferrocenes. With regard to Table 2 it should be mentioned that the compounds for comparison, i.e. the carbonyl-free parent-compounds, are available only for Nos. 3 and 4. For estimating ΔQS and ΔIS values for Nos. 1,2,5–7 the Mössbauer parameters of bridged ferrocenes without a homoannular bridge are listed in Table 2.

Some compounds are found not to follow the tendency mentioned above: their Mössbauer parameters are listed in Table 3. As shown, the QS values of these derivatives are not decreased by the carbonyl, or the decrease is extremely small. All of them, except β-keto-1,1′,3,3′-bistetramethyleneferrocene (Vb), are members of the trimethylene-bridged ferrocene (TMF) series in which the cyclopentadienyl rings are linked by one or more trimethylene bridges. In the TMF series, significant molecular geometry changes (MGC) (e.g. ring-tilt and bond-shortness) were observed, especially in the polybridged derivatives [26–30]. The MGC found in these compounds * were caused by the shortness of the trimethylene bridges. In VIIIb and IVb the MGC (tilt) may be assumed, though there is no experimental evidence for it.

On the basis of these observations it seems possible that in all of these trimethylene-bridged ferrocenes the coplanarity of the carbonyl group with the cp ring is hindered by MGC. It is known that a carbonyl group in a non-planar position with the cp ring shows a reduced electron-withdrawal effect on the ferrocenyl moiety [6,12,35]. The dominant role of carbonyl-coplanarity is supported by the Mössbauer data for the mixed, homo- and hetero-annularly-bridged ferrocenes as well as for those in which the carbonyl is built into the homoannular bridge (Table 2). With XVIb and VIb, strong MGC can be assumed ** and yet the QS values are decreased by the carbonyl of the homoannular bridge. This means that a carbonyl in a position coplanar with the cp ring can affect even a perturbed molecular orbital as well.

From the QS value of the single diketone examined, α,α′-diketo-1,1′-pentamethyleneferrocene (XIII), it would appear that the effect of two carbonyls in the same bridge is not additive; nevertheless, for some unbridged diketone derivatives of ferrocene the effect has proved to be roughly additive [9]. It is likely that the coplanarity of the second α′-carbonyl is also hindered in the conformational forms of the pentamethylene bridge. To obtain evidence on this requires further investigation on diketone derivatives of bridged ferrocene.

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* The conformational demands of tetra- and penta-methylene bridges in ferrocene derivatives are discussed in Refs. 13,31–34.

** In the reduced parents of these compounds (XVIa, VI) ring tilt and bond-shortness were found [29,30].

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