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MÖSSBAUER STUDY OF BRIDGED FERROCENE DERIVATIVES

ÁGNES G. NAGY *, I. DÉZSI
Central Research Institute for Physics, Budapest (Hungary)
M. HILLMAN
Brookhaven National Laboratory, Upton, N.Y. (U.S.A.)
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Summary

The molecular geometry of a series of trimethylene bridged ferrocene derivatives has been studied by means of Mössbauer techniques. The differences in quadrupole splitting and isomer shift among the various derivatives can best be explained as being due to differences in the planarity of the cyclopentadienyl rings.

The structural characteristics of metallocenes have been much studied [1—7]. The studies have included the effects of tilting the rings so that they are no longer parallel [5,7]. Many metallocenes are normally of this form, e.g. titanocene dichloride, others are forced to have non-planar rings by means of bridges across the rings which are too short to permit parallel rings. Among the latter are the di- and tri-methylene bridged derivatives of ferrocene and of the monomethylene bridged titanocene [5,6].

Mössbauer data for the ferrocene system were first reported in 1962 [8,9]. A large quadrupole splitting was observed in the Mössbauer spectrum of the ferrocene and the reduction of this quadrupole splitting to almost zero in the ferricinum $[(C_5H_5)_2Fe]^+$ spectrum. The vanishing of quadrupole splitting can be explained by Ballhausens' molecular orbital model and by the results of Collins' magnetically perturbed Mössbauer experiment [10,11]. In these explanations the major splitting is assumed to be caused by the $3d$ electrons, the removal of one electron from the $3d_0$ molecular orbital causing the splitting to vanish. This delocalization has only a small effect, however, on the isomer shift.

Interannularly bridged ferrocene derivatives include poly-bridged trimethyleneferrocenes [12,13]. In these the cyclopentadienyl rings are linked by one or more bridges of three methylene groups. Linking of the rings by one trimethylene bridge apparently has little or no effect on the iron—ring bonding [7,14,15]. In-

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* Author to whom correspondence should be addressed.

creasing the number of bridges could possibly introduce an effect because of some property other than ring tilting. The strain introduced by the trimethylene bridge may be relieved in several ways, e.g., the rings may be tilted, ring—ring distances may be shortened, or the rings may become non-planar. The purpose of our investigation was to study the effect of the introduction of more than one bridge.

Experimental

The bridged ferrocene derivatives were prepared by published methods [13] with minor modification. In the bridged ferrocenes the cyclopentadiene rings were linked by one or more trimethylene bridges (Fig. 1). There are two possible isomers with two or three bridges. For example, in the case of 12BTMF the cyclopentadiene rings were linked at adjacent positions, but in the 13BTMF the bridges were nonadjacent.

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 chromium matrix. Metallic iron was used for the calibration. The Mössbauer parameters were evaluated by least squares method. The isomer shifts refer to the centroid of the spectrum of metallic iron at room temperature.

Results and discussion

The results of the measurements on ferrocene and various bridged derivatives are summarized in Fig. 2 and 3. They all have doublets due to quadrupole splitting. Except for TKTMF significant decrease in values of the quadrupole splittings (*QS*) and of the isomer shifts (*IS*) are observed as the number of bridges increases. Differences are observed between the isomers of both isomeric pairs, with larger decreases in *QS* and *IS* for the isomers with nonadjacent bridges 13BTMF and 124TTMF. For the TKTMF the *QS* and *IS* are higher than the *QS*

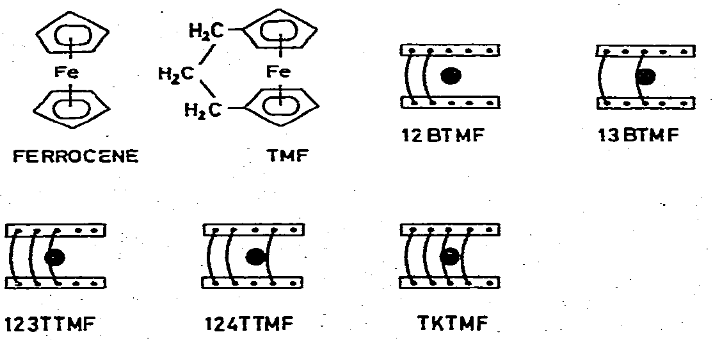

Fig. 1. Ferrocene and its poly-bridged trimethylene derivatives. In each case the rectangles represent the cyclopentadienyl rings, the small solid circles the carbon atoms of the ring, the large solid circles the iron atoms and the arcs the carbon bridges. TMF, 1,1′-trimethyleneferrocene; 12BTMF, 1,1′, 2,2′-bis(trimethylene)ferrocene; 13BTMF, 1,1′, 3,3′-bis(trimethylene)ferrocene; 123TTMF, 1,1′, 2,2′, 3,3′-tris(trimethylene)ferrocene; 124TTMF, 1,1′, 2,2′, 4,4′-tris(trimethylene)ferrocene; TKTMF, 1,1′, 2,2′, 3,3′, 4,4′-tetrakis(trimethylene)ferrocene.

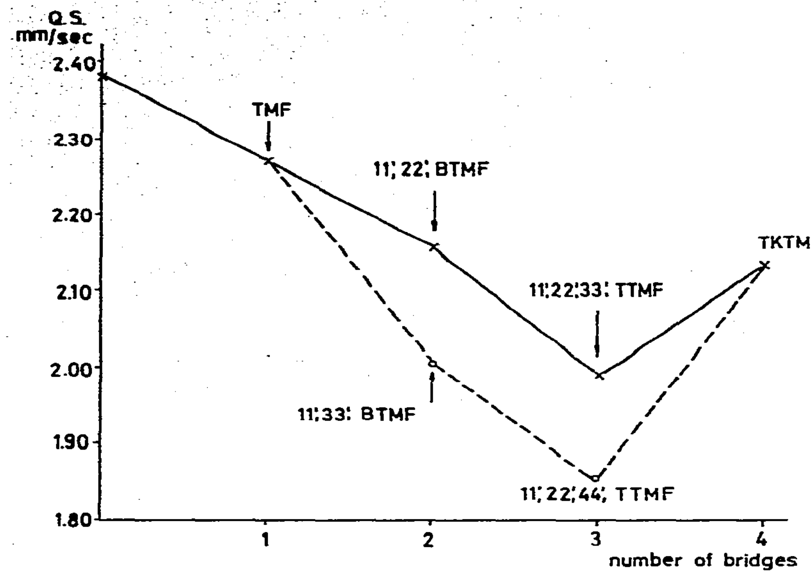

Fig. 2. Values of quadrupole splittings in the Mössbauer spectra of poly-bridged trimethyleneferrocenes as a function of the number of the bridges (values of *QS* are ±0.01 mm/sec).

and *IS* of the three-bridged isomers and between the *QS* and *IS* of two-bridged isomers.

It has been observed that the bonding of the iron atom to the rings is not affected by alkyl substituents in the cyclopentadiene rings (Table 1) [14,15]. However, in the bridged alkyl derivatives it seems that the linkage of the cyclopentadiene rings by trimethylene bridges causes a significant increase in the electron delocalization for two and three bridges and then a decrease for four bridges. It should be noted that if only values of *QS* and *IS* for ferrocene and TMF were available, it would be difficult to assert that there is significant delocalization of electrons from the iron, and the conclusions of Good [14] would not be questioned.

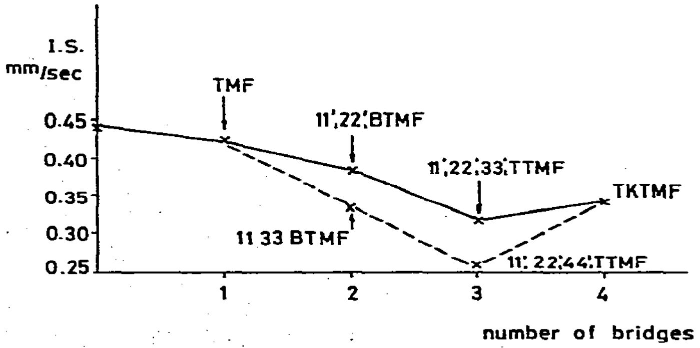

Fig. 3. Values of the isomer shifts of poly-bridged trimethyleneferrocenes as a function of number of bridges (values of *IS* are ±0.01 mm/sec).

TABLE 1

ISOMER SHIFT (*IS*), QUADRUPOLE SPLITTING (*QS*) VALUES AND STRUCTURAL FEATURES OF SUBSTITUTED FERROCENES [a]

Compound	Temperature (K)	*IS* (mm/sec)	*QS* (mm/sec)	Structural data
$(C_5H_5)_2Fe$	78	0.52	2.41	Rings are planar and parallel in staggered configuration
$(C_5H_5)Fe(C_5H_4CH_3)$	77	0.53	2.39	*b*
$(C_5H_5)Fe[C_5H_4C(H)(OH)(C_6H_5)]$	78	0.51	2.41	*b*
$(C_5H_4Cl)_2Fe$	80	0.48	2.35	*b*
$(C_5H_5)Fe(C_5H_4Cl)$	80	0.50	2.42	*b*

[a] Ref. 14. [b] Ferrocene structure expected.

Molecular models suggest that the preferred inter-ring separation of ca. 3.3 Å in ferrocene cannot be spanned by a chain of three C atoms unless the rings become mutually inclined [16,17]. In the trimethyleneferrocene the angle between rings planes in ca. 9° [3]. Ballhausen and Dahl have concluded that splaying of the rings about the metal atom can occur in principle without significant loss in metal—ring bond strength [7]. However, linkage of the rings by two or more bridges could not only cause tilting of the rings but may also cause a change in the planarity of rings. If the rings become non-planar the π-orbitals and consequently the metal—ring bond strength are expected to become weaker. The *d* orbital electron density on the iron would be lower and the *QS* and *IS* reduced. The nonadjacent bridges to the cyclopentadiene rings would be expected to cause larger perturbations in the planarity of the rings than would the adjacent bridges, and ultimately cause an even greater reduction in the *QS* and *IS*.

In the case of TKTMF it seems likely that the degree of planarity of the rings associated with the three bridged derivatives is increased on introduction of the fourth bridge because of increased equivalence of the strain on all the ring carbon atoms. In this case the ring—ring distance would also be decreased and the ring—iron bond strengthened. The Mössbauer study of the five-bridged member in this series may provide further evidence on this hypothesis, since symmetry considerations demand planarity and a probable shortening of the ring—ring distance. This compound has been prepared but not in sufficient quantity and purity for a Mössbauer measurement [18].

The Mössbauer results reported here are explained by a hypothesis of the non-planarity of the rings. Additional studies necessary to confirm the hypothesis involve a direct structural determination by X-ray crystallography. A preliminary report has been given of the structure of 13 BTMF and the structure of a keto derivative of TMF has been more thoroughly investigated [19].

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