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Bridged Ferrocenes.V.[*] Moessbauer Spectra - Squeezing the Iron Ato

Manny Hillman
Division of Chemical Sciences, Dept. of Energy and Environment
Brookhaven National Laboratory
Upton, N. Y. 11973, USA
and
Agnes G. Nagy
Brookhaven National Laboratory and
Department of Chemistry, Central Research Insitute for Physics
1121 Budapest, Hungary

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Summary

New Moessbauer measurements were made for an assortment of bridged ferrocenes containing one tetramethylene or pentamethylene bridge, and ferrocenes containing two bridges, one trimethylene and one tetramethylene, or both tetramethylene. The results for compounds containing four- and five-carbon bridges demonstrate that the trends reported earlier [1] for compounds with only three-carbon bridges were indeed due to strain caused by the short three-carbon bridge. Moessbauer results for four compounds for which the crystal structures had been established show a linear correlation between the change of the iron to ring distances and the change of the Moessbauer parameters. Ring tilt is important only to the extent that it causes the iron to ring distances to change.

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[*] See Ref. 7 for Part IV.

Experimental

All of the trimethylene ferrocenes (see Fig. 1 for all of the structures) were prepared by the method of Rinehart et al. [9] except for VII which was prepared by the method of Vigo [10], and IX which was prepared by $LiAlH_4$-$AlCl_3$ reduction of the precursor ketone which had been prepared by the method of Rinehart et al. [9]. Tetramethyleneferrocene (IIb) was prepared by the method of Rosenblum [11], and pentamethyleneferrocene (IIc) by the method of Barr and Watts [12]. The 1,1',3,3'-bis(tetramethylene)ferrocene (IVc) and the mixed tri- and tetramethyleneferrocenes (IIIb, IVb) were prepared by the methods of Hisatome et al. [13,14].

The Moessbauer Spectra of many of these compounds had been obtained [1] in Budapest on a constant acceleration spectrometer. For consistency the spectra of all of the compounds were determined at Brookhaven National Laboratory on a constant velocity spectrometer described by Kistner [15]. The results obtained with the two spectrometers were in excellent agreement.

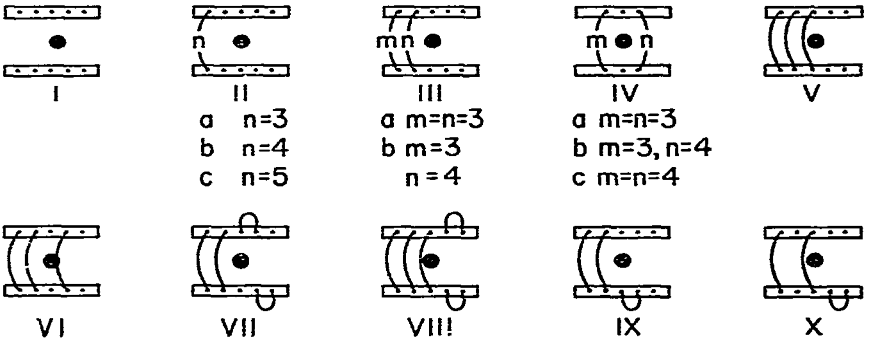

Fig. 1. Ferrocene derivatives. In each case the rectangles represent the cyclopentadienyl rings, the small solid circles the carbon atoms of the ring, the larger circles the iron atoms, and the arcs the bridges. The values for n and m are the numbers of methylene groups in the bridges. The unlabeled arcs are trimethylene bridges.

In Budapest ^{57}Co in a chromium matrix was used as a source and at Brookhaven ^{57}Co in a copper matrix was used. Metallic iron enriched in ^{57}Fe was used for the calibration of the velocity scale. All measurements were made at room temperature. Because of its rarity, V was no longer available for remeasurement, and the value previously reported [1] was used in the ensuing analysis.

From two to seven measurements were made for each sample. The instrument was recalibrated using the ^{57}Fe between each successive pair of measurements, which were rarely of the same compound. Correlation of all of the standard measurements was used to correct for drift of the instrument. In addition, potassium ferrocyanide was measured simultaneously with the standard. The average of 40 standard measurements showed that the QS could be determined to within a relative error of 0.1% and that the IS could be determined with a relative error of 0.001 mm/sec.

Results and Discussion

All of the results are summarized in Table 1. The errors recorded are the standard deviations of the average of the results for each sample, but no lower than the error obtained for the standard. These are relative errors. Systematic errors were not treated but are reasonably assumed to be the same for each sample. 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.

There are a number of conditions which may affect the QS or IS values which we shall eliminate at the outset. The first is the effect of axial symmetry on the QS values. Trautwein et al. [2] calculated the values of η for some of these compounds, IIIa, IVa, V, and VI. They ranged from 0.04 to 0.26. The effect

Introduction

Recently [1], Moessbauer spectra of ferrocene derivatives with one or more trimethylene bridges were reported. As the number of bridges increased, decreases were observed in the values of the quadrupole splitting, QS, and in the values of the isomer shift, IS. Differences were also found between the isomers of two isomeric pairs. The interpretation of these results was based on the assumption that bridging the two cyclopentadienyl rings by trimethylene groups causes significant changes in the configurations of the molecules. This arises since the trimethylene group is too short to span the distance between the two rings without causing the rings to become mutually inclined or closer together and consequently closer to the iron atom. In some cases, particularly with three or more bridges, the rings may become non-planar. All of these properties were expected [1] to contribute to the changes in the Moessbauer parameters, and indeed, all of these properties have been observed in the crystal structures of various bridged ferrocenes [3-7].

To confirm that the changes in the Moessbauer parameters were due to the constricting effect of the trimethylene groups, bridged ferrocenes were investigated containing tetramethylene and pentamethylene bridges, pairs of tetramethylene bridges and both tri- and tetra-methylene bridges. X-ray crystallography of a ferrocene derivative with three not-all-adjacent tetramethylene bridges showed that the tetramethylene bridge is long enough to span the rings, but that a conformation is preferred with the rings rotated 10° from eclipsed and 0.02Å closer to the iron in ferrocene [8]. It is assumed that the pentamethylene bridge is of sufficient length to span the gap between the two cycopentadienyl rings without strain.

on the QS values ranges from 0.02 to 1.1%, which is considerably smaller than the differences of QS values we observed among the compounds.

The second is the effect of molecular dynamics. Ferrocene can have virtually freely rotating rings [16], while the other compounds, because of the bridges, cannot. However, in the solid state, ferrocene's rings do not freely rotate, but in fact are rotationally disordered with a most probable deviation of about 10^{o} from the eclipsed configuration observed for the trimethylene bridged derivatives [17]. The configurations for the tetramethylene and the pentamethylene bridged derivatives have not been determined, but, as was found with the tris(tetramethylene)ferrocene [8], they are most likely close to that of ferrocene. At any rate, Trautwein et al. [2] calculated that the QS values for eclipsed and fully staggered configurations of ferrocene may differ by 0.05 mm/sec. This is already lower than the differences we observed, and the real effect on our results may be even less than that since the fully staggered configuration is unobserved for the trimethylene bridged ferrocenes and unlikely for the rest.

The third is the effect of temperature which must be considered if the differences of the QS or IS measured at different temperatures differ greatly from compound to compound. The effect of temperature is a second order effect. When two similar compounds are compared, the second order difference between the temperature effects of the different compounds gives some information about differences between the similar compounds. For very similar compounds, the second order difference is expected to be very small. For widely differing ferrocene derivatives measured by Stukan et al. [18] at 80^{o} and 300^{o} K, the average ΔQS was 0.014 ± 0.013 which is much lower than the range of the quadrupole splittings we measured. For very similar compounds, these averages would be lower still, and the second order temperature effect for the quadrupole splittings of the compounds discussed in this paper is considered to be negligible. the average ΔIS for the compounds measured by Stukan et al. [18] was 0.066 ± 0.009 which is comparable to the range of the isomer shift values we have measured. However, since the trends of the isomer shifts follow those of the quadrupole splittings quite closely, the second order temperature effect for the isomer shifts of the compounds discussed in this paper must also be considered to be negligible.

The results for compounds with up to two bridges and with three- to five-carbon bridges are compared graphically in Fig. 2. It is quite evident from Fig. 2 that the QS and IS are not as greatly reduced in the compounds containing tetra- and penta-methylene bridges. This is consistent with the hypothesis that the effect was due to a change in the configuration of the molecule and not, for example, to an interaction of the iron electrons with the carbons and protons of the bridges. The

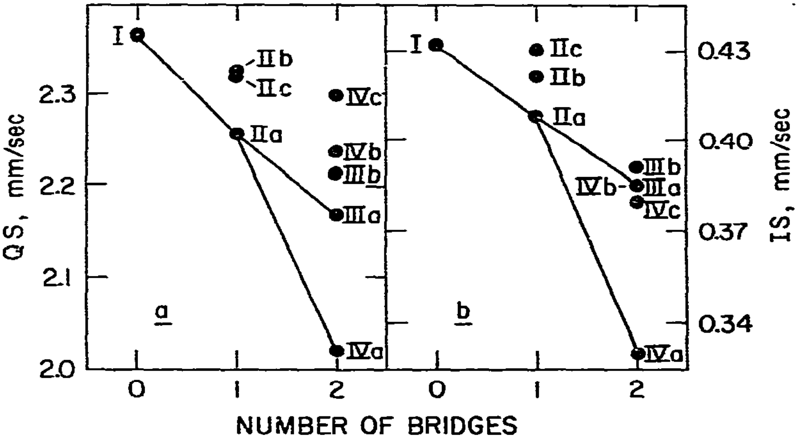

Fig. 2. Values of a) quadrupole splittings, QS, and b) isomer shifts, IS, in the Moessbauer spectra of polybridged ferrocenes as a function of the number of bridges. The errors are smaller than the circles.

latter effect would have been expected to be the same or even greater for the tetra- and penta-methylene bridges than for the trimethylene bridges. One measurement is somewhat out of line with this conclusion. The IS of IVc which has two non-adjacent tetramethylene bridges is lower than the IS of IVb which has correspondingly one four-carbon bridge and one three-carbon bridge. The QS's on the other hand are in the order expected.

Having established that the effect on the Moessbauer parameters is due to changes in the configurations of the molecules, there remains the problem of assigning a degree of significance to the various possible changes in configuration: ring-tilting, iron-ring distance and non-planarity of the rings.

Ring tilting can be described in various ways. Three examples are given in Fig. 3.

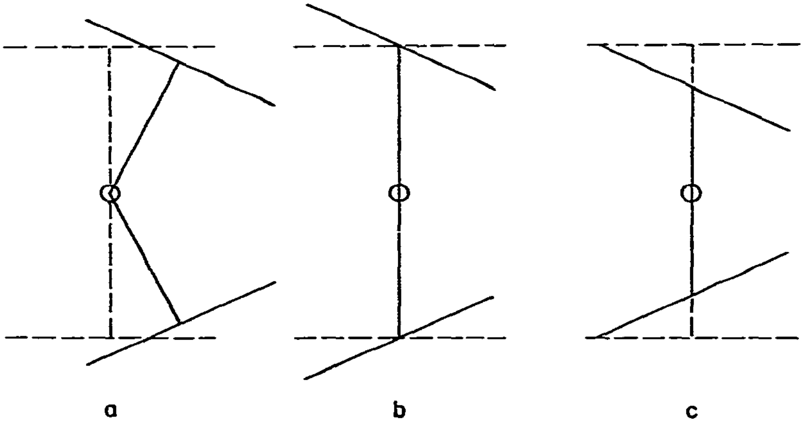

Fig. 3. Examples of ring tilting: a) iron as fulcrum; b) centroid of the cyclopentadienyl ring as fulcrum; c) resembles experimental results. The dashed horizontal lines represent the position of the cyclopentadienyl rings in ferrocene; the central circle is the iron atom.

Ballhausen and Dahl [19] have discussed the effect of ring tilting and have concluded that tilts of 30° can occur without decreasing the strength of the iron-ring bonds. There is also an accompanying change in population of the molecular orbitals. The latter could explain the changes in Moessbauer parameters, but this effect has not been investigated. The type of tilt that these authors discuss, however, involves a pivoting of the cyclopentadienyl rings about the center of the iron atom (Fig. 3a). No change in iron to ring distances or for that matter iron to ring-carbon distances take place. Although this may be a correct description for titanocene type compounds where the metal's bonding is tetrahedral, and the rings are normally tilted, this is not what occurs in polymethylene bridged ferrocenes.

Trautwein et al. [2] have calculated the Moessbauer parameters for bridged ferrocenes as a function of ring-tilt and found that a ring-tilt of 6^o will have no effect on the Moessbauer parameters. This is due to the fact, they state, that tilting brings some carbons closer to the iron atom and others more remote from the iron causing an average effect of zero. The type of tilting one must assume that they are discussing is about a fulcrum at the center of the cyclopentadienyl rings (Fig. 3b). This differs from the type of tilting described by Ballhausen and Dahl [19]. It is not, however, a generally applicable description of tilting in bridged ferrocenes.

With the increase in availability of crystallographic data (Table 1) for some of these and other related compounds, it can be shown that a simple description of tilting is difficult. For singly bridged ferrocenes, tilting appears to resemble Fig. 3b with some admixture of Fig. 3c. Some transposition of the iron must also take place to account for its position nearly normal to the ring centroid. For polybridged ferrocenes, the tilting occurs as in Fig. 3c (see Table 6, Ref. 4 for a list of compounds and references).

Trautwein et al. [2] presented a model of bridged ferrocenes for which they calculated the Moessbauer parameters (Table 1). Their agreement with the experimental results reported in [1] was sufficiently good to be able to intimate that something was amiss with the four-bridged derivative (XI, Fig. 4). Since the appearance of their work, it has been shown [6] that the compound

Table 1. Moessbauer and Molecular Parameters of Bridged Ferrocenes

	IS mm/sec	QS mm/sec	Calc. QS[a]	Ring Tilt(°)	Fe-R Dist(Å)
I	0.432(2)	2.367(1)	---	0.0[b]	1.66[b]
IIa	0.408(2)	2.256(3)	2.285	8.8[c]	1.64[c]
IIb	0.421(2)	2.351(5)	---	---	---
IIc	0.430(4)	2.344(5)	---	---	---
IIIa	0.385(1)	2.169(3)	2.159	---	---
IIIb	0.391(1)	2.213(2)	---	---	---
IVa	0.330(2)	2.020(1)	2.040	---	---
IVb	0.385(2)	2.236(5)	---	---	---
IVc	0.380(2)	2.297(3)	---	---	---
V[d]	0.320(10)	1.980(10)	2.030	---	---
VI	0.260(1)	1.825(3)	1.875	2.4[e]	1.573[e]
VII	0.344(2)	2.133(2)	---	11.1[f]	1.616[f]
VIII	---	---	---	12.5[g]	1.60[g]
IX	0.367(3)	2.164(4)	---	---	---
X	0.321(1)	2.054(2)	---	9.0[h]	1.60[h]

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a) Ref. 15

b) Ref. 20

c) for α-keto-1,1'-trimethyleneferrocene, Ref. 2

d) Moessbauer results from Ref. 1

e) Ref. 4

f) Ref. 5

g) Ref. 6

h) unpublished results of E. Fujita and S. Takagi

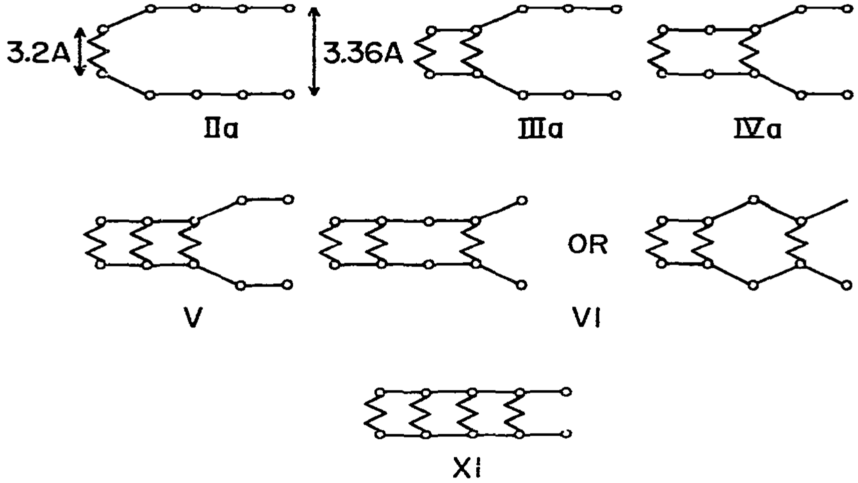

Fig. 4. The Trautwein et al. model.

considered to be XI in reality contained two adjacent bridges and two homoannular trimethylene groups, VII. For the sake of clarity, a description of their model is included here (Fig. 4).

They assumed, apparently, that the bridges pull the bridged ring-carbons closer together while the other corresponding ring-carbons remain at the original distances. Such a simplified model causes three effects simultaneously: 1) the average planes of the two cyclopentadenyl rings are tilted with respect to each other; 2) the average planes of the cyclopentadienyl rings are closer to the iron atom; and 3) the cyclopentadienyl rings are non-planar. This type of tilt is that of Fig. 3c; the decrease of the iron to ring distance is concommitant with this type of tilt and cannot really be separated from it. The fact that only two of the compounds (VI and VIII) whose structures have been determined [6,7] have non-planar cyclopentadienyl rings, while those in the model all have non-planar cyclopentadienyl rings is probably of little importance since the deviation from planarity in all cases is very small.

The existence of crystal structures of four of the compounds for which Moessbauer parameters have been measured and of two other closely related compounds makes it possible to relate the Moessbauer parameters to the structural properties in the calculations. The pertinent parameters are given in Table 1. It is apparent that a correlation exists between the iron-to-ring distances and the Moessbauer parameters. The angle of ring-tilt *per se* is of no importance.

In Fig. 5 are plotted the changes in Moessbauer parameters *vs* the changes in iron-ring distances for all of the trimethylene ferrocene derivatives measured. The changes in iron to ring distances for the compounds for which no crystal structures had been determined were assumed to be the same as for the measured compounds with the same number and arrangement of bridges. A linear correlation is evident.

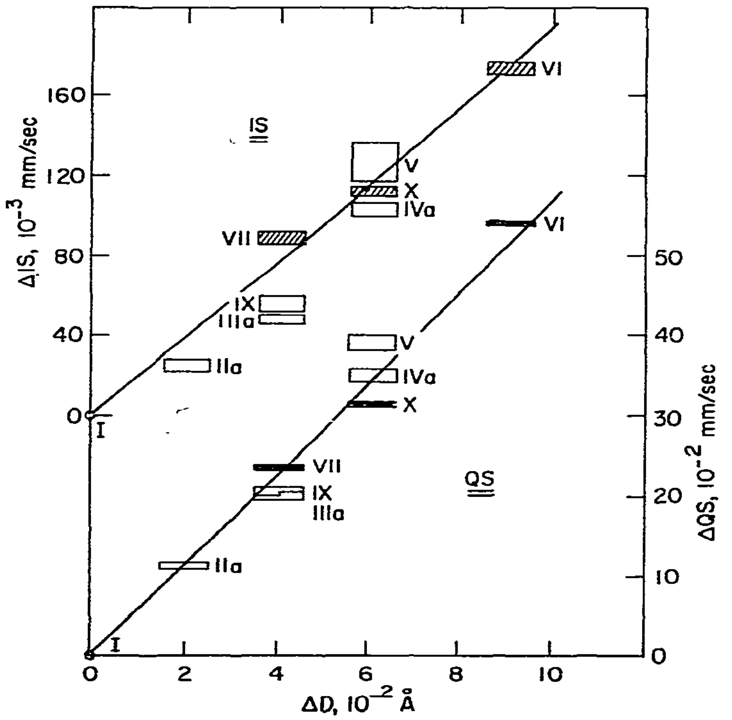

Fig. 5. Change in iron-to-ring distances vs change in IS or QS relative to ferrocene. Filled points have measured distances Open points have related compounds with measured distances.

It is of interest to note that the experimental iron to ring distance for compound VI (1.573 Å) is smaller than that assumed in Trautwein's model (1.61 Å). The actual distance is even smaller that that assumed for XI (Fig. 4). Since this distance is apparently the most sensitive factor, the agreement of experiment and theory is not as good as previously supposed. It would be of value if The Trautwein [2] calculation of the Moessbauer parameters of all the compounds were redone with a model using experimental distances wherever available or reasonable estimates based on available data. The combination of crystallographic data and Moessbauer results may serve to improve the input parameters for the molecular orbital calculations, and in turn an improved calculation of the charge on the iron atom.

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