

Cofacial interaction of ferrocenyl groups and metal atom motional anisotropy in [10]annulene organometallics

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Abstract

Two structurally related diferrocenyl [10]annulenes have been examined over the range $90 \leq T \leq 370$ K by temperature dependent ^{57}Fe Mössbauer effect (ME) spectroscopy. While the hyperfine interaction parameters [isomer shift (IS) and quadrupole splitting (QS)], and their temperature dependencies are very similar to those which have been reported earlier for similar ferrocenyl complexes, the vibrational anisotropy of the iron atom motion is diagnostic of a cofacial interaction of the two cyclopentadienyl rings in the 2,10-diferrocenyl compound, and absent in the 2,7-diferrocenyl homologue. These results are compared with the corresponding behavior of the 1,5- and 1,8-diferrocenylnaphthalene compounds reported earlier. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The significance of the co-facial interaction between two ferrocenyl groups attached to a common backbone structure has received considerable attention in the recent literature [1–6], and this interaction is of significant importance in the design of ferrocene-containing oligomers and polymers for a variety of optical solid state devices. In a recent study [7], it has been shown that temperature-dependent ^{57}Fe Mössbauer effect (ME) spectroscopy can be used to elucidate the presence of this interaction, and in addition to providing an insight into the motional behavior of the metal atom in a variety of iron-organometallics. In the present study, this technique has been used to examine the detailed behavior of the iron atom in two related ferrocenyl [10]annulenes. In one of these, 2,10-diferrocenyl-1,6-methano[10]annulene (**1**), the two ferrocenyl moieties are so located on the organic backbone that a π – π interaction between two cyclopentadienyl rings is readily

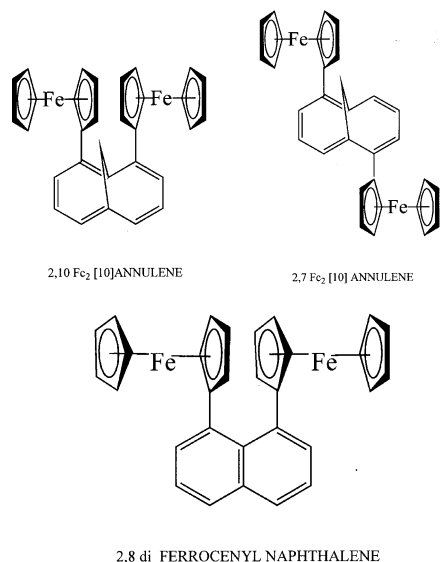
postulated. In the other, 2,7-diferrocenyl-1,6-methano[10]annulene, (**2**), such an intramolecular interaction can be ruled out on steric grounds. A comparison of the structures of **1** and **2**, as well as of 1,8 diferrocenyl naphthalene is given in Scheme 1.

2. Results and discussion

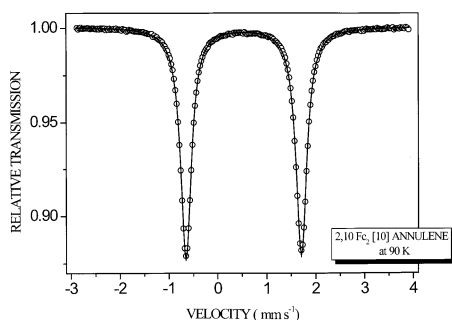
As has been repeatedly observed for a wide range of diamagnetic, covalent, ferrocene-related organometallic solids, the ME spectra of such solids consist of a single well resolved doublet, from which the hyperfine parameters (the isomer shift, IS; the Quadrupole splitting, QS and the recoil-free fraction, f) can be readily extracted by a least-squares fitting program suitably modified [8] to take into account sample thickness (line broadening) effects. A typical spectrum is shown in Fig. 1. The hyperfine parameters, the temperature dependencies of the IS and of the recoil-free fraction (as extracted from the temperature dependencies of the areas under the resonance curves, corrected for thickness effects at low temperatures), as well as M_{eff} (the effective vibrating mass) and Θ_{M} (the Mössbauer lattice

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Scheme 1. Structures of the compounds discussed in the text.

Fig. 1. Mössbauer spectrum of **1** at 90 K.Table 1
Mössbauer parameters for **1** and **2**

Parameter	1	2	Units
	2,10 Fc ₂ [10]An- nulene	2,7 Fc ₂ [10]An- nulene	
IS(90)	0.5273(4)	0.5169(4)	mm s ⁻¹
QS(90)	2.362(1)	2.343(1)	mm s ⁻¹
-dIS/dT	5.42(8) ^a	5.17(3) ^b	mm s ⁻¹
-d ln A/dT	9.45(2) ^a	7.53(6) ^b	K ⁻¹ × 10 ⁻⁴
M _{eff}	73 ^c	80 ^c	Da
Θ _M	103.4 ^d	113 ^d	K

^a 230 ≤ T ≤ 370 K.^b 230 ≤ T ≤ 380 K.^c From the high temperature limiting slope of IS(T).^d From the high temperature limiting slopes of IS(T) and ln A(T).

temperature) [9], are summarized in Table 1 and are, by and large, unremarkable in terms of the values reported earlier [10] for a variety of ferrocenyl organometallics. The latter two parameters have been extracted from the high temperature (230 ≤ T ≤ 370 K) data of the IS and

In A values, and are well represented by a linear regression fit. Moreover, the Θ_M values clearly justify characterizing the above temperature intervals as lying in the T > Θ_M/2 domain.

The temperature-dependence of the QS (which is related to the electric field gradient tensor V_{zz} which is presumed to be negative as in the case of the parent ferrocene [11]) is negative in both **1** and **2** as expected on the basis of simple thermal expansion considerations, but this dependence is barely outside of experimental error, the difference between the 90 and 370 K values amounting to only 0.026 and 0.015 mm s⁻¹, respectively.

Of more significance with respect to the present discussion are the temperature dependencies of the area ratio, R [R = A(+)/A(-), with the signs indicating the component of the doublet at velocities more positive or more negative than the spectrum centroid, respectively] for **1** and **2**, which are summarized graphically in Fig. 2. It is readily seen from this figure, which pertains only to the temperature-dependent part of R, and hence corrects for a (minor) texture effect [12], that while the data for **2** show no significant departure of R from unity, there is a pronounced deviation from this value for **1**, especially at temperatures above ~220 K. The large error bars associated with the high temperature data are, of course, a consequence of the rapidly decreasing recoil-free fraction as the temperature is raised. Moreover, it is also worth noting that the Mössbauer data for both **1** and **2** were acquired both in warming and cooling regimes, and these data clearly show that the observed R(T) behavior is reversible after reaching (and remaining at) the highest temperature sampled (380 K in the case of **1**) during the time of data acquisition ~24 h to accumulate in excess of 18 × 10⁶ counts per channel.

The R data for **1** summarized in Fig. 2 can be readily understood in terms of an anisotropy of the metal atom motion with respect to the (local) molecular symmetry

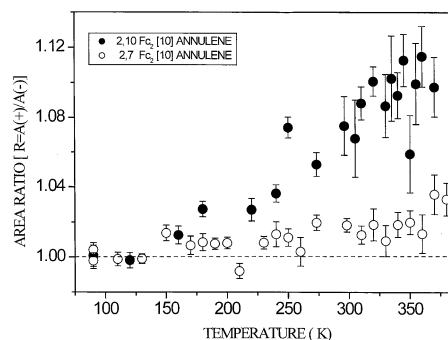


Fig. 2. Temperature dependence of the area ratio, R, as defined in the text for **1** (filled circles) and **2** (open circles). A small, temperature-independent anisotropy, presumably due to a 'texture' effect, extracted from the low temperature data, has been subtracted from both data sets.

axis which is presumed to run through the metal atom and the centers of the two cyclopentadienyl rings. This motional anisotropy is referred to as the Gol'danskii–Karyagin effect (GKE) [13], and has been previously observed in related ferrocenyl systems, including 1,8-diferrocenyl naphthalene [7] and 1,8 bis (ethynyl ferrocenyl) naphthalene [5,14]. In contrast to the naphthalene complexes, however, in which the two carbon atoms anchoring the ferrocenyl groups are part of a coplanar framework including both aromatic C₆ rings, in **1** and **2** this geometric requirement is no longer imposed on the structure. In fact the crystal structure reported by Iyoda et al. [15] clearly shows the puckering of the severely strained [10]annulene framework. Nonetheless, two cyclopentadienyl rings are fixed face-to-face in **1** and are rotated by 30.4 and 50.9° with respect to the least squares plane of the annulene ring, comparable with the corresponding value (45–47° from a conformation which would place them perpendicular to the naphthalene best plane) reported [1–3] in the case of 1,8-diferrocenyl naphthalene. The dihedral angle between the two cyclopentadienyl rings is 33.6°, which is slightly larger than that (29.1°) observed in 1,8-diferrocenyl naphthalene.

The observed $R(T)$ values, together with the mean-square-amplitude of vibration (msav) of the metal atom, extracted from the $\ln A(T)$ data, permit a calculation [16] of the msav parallel and perpendicular to the local molecular symmetry axis referred to, above. The results of these calculations for **1** are summarized graphically in Fig. 3, in which the parameter $k^2 \langle x^2 \rangle$ is shown as a function of T . Here, k is the wave vector of the emitted ⁵⁷Fe gamma ray and corresponds to $7.304 \times 10^8 \text{ cm}^{-1}$. It should be noted in this context that the value of $k^2 \langle x_{\text{ave}}^2 \rangle$ extracted from the X-ray diffraction (U_{ij}) data of Iyoda et al. [15] at 296 K is 2.28, whereas the value at this temperature extracted from the present Mössbauer data is 2.63. However, the difference between the X-ray and Mössbauer $k^2 \langle x^2 \rangle$ values is only slightly larger than that noted [17] for six other ferrocenyl systems for

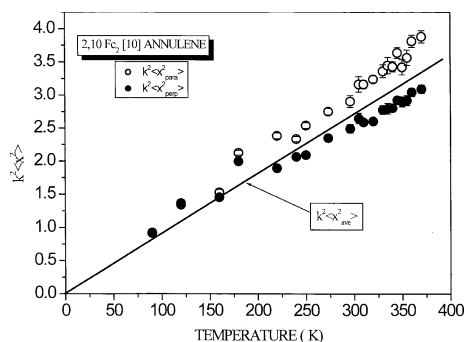


Fig. 3. Temperature dependence of $k^2 \langle x^2 \rangle$ parallel (open circles) and perpendicular (closed circles) to the local molecular symmetry axis for **1**. The solid line represents the temperature dependence of $k^2 \langle x_{\text{ave}}^2 \rangle = 1/3 k^2 \langle x_{\text{para}}^2 \rangle + 2/3 k^2 \langle x_{\text{perp}}^2 \rangle$.

which this comparison has been effected. The origin of this difference, which is significant with respect to the individual quoted errors in the two types of data, is not well understood at the present time. The differences in the root-mean-square (rms) amplitudes of vibration parallel and perpendicular to the molecular symmetry axis are 0.0125, 0.0173 and 0.0289 Å at 240, 296, and 370 K, respectively, with the vibrational amplitude perpendicular to the molecular symmetry axis smaller than the corresponding parallel value.

3. Experimental

Samples of **1** and **2** were generously made available to us by the Tokyo Metropolitan University group [15], ground with quartz glass powder to reduce crystallite size, mixed with boron nitride to ensure random sample orientation with respect to the optical axis of the experiment, and mounted in the Mössbauer cryostat. Details of spectrometer calibration, temperature control and data reduction have been given previously [7,10]. The low-temperature data, for which the ‘thin absorber’ approximation is no longer valid, were analyzed using a transmission integral procedure describe earlier [8]. All IS refer to the centroid of a room temperature α -Fe spectrum which was also used for spectrometer calibration. Data were acquired in both a temperature increasing and decreasing regime to ensure reversibility of the observed dynamical parameters.

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