

THE STRUCTURE OF BIS(AS-INDACENYLIRON)

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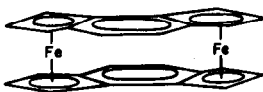
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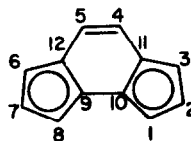
Dilithium as-indacene in tetrahydrofuran reacts with ferrous chloride to give bis-(as-indacenyliiron), $(C_{12}H_8Fe)_2$,¹ one of only four compounds known in which two metal atoms are sandwiched between a pair of aromatic rings. (The related substances are two complexes of benzene with palladium chloride plus aluminum chloride² and 1,1'-biferrocenylene.³) Bis-(as-indacenyliiron) is believed to have structure I or II on the basis of its analysis, its mass spectrum, and its method of preparation which is analogous to that for ferrocene.⁴ However, the nmr spectrum of the compound is unusual for a ferrocene and we are reporting it below. We are also reporting the results of an X-ray analysis, which indicate the structure of the compound and show that the double bonds in the ligand are localized⁵ at least to the extent suggested by structure III.



I



II



III

Crystal data: dark-red prisms from toluene, $C_{24}H_{16}Fe_2$, $M_w = 416.1$, monoclinic, $a = 7.568(7)$, $b = 11.337(12)$, $c = 9.923(8)\text{\AA}$, and $\beta = 106^\circ 35'(5')$, $V = 816 \times 10^{-24}\text{cm}^3$, $\rho_{\text{meas}}(\text{aq. KI}) = 1.71\text{ g cm}^{-3}$, $Z = 2$, $\rho_{\text{calcd}} = 1.69\text{ g cm}^{-3}$, space group $P2_1/c$. Cell dimensions were determined by a least squares analysis of the diffractometer settings for eleven reflections ($Mo K_\alpha$ radiation, $\lambda = 0.71073\text{\AA}$). A total of 1657 independent non-zero structure amplitudes was obtained on a computer-controlled Picker FACS-1 diffractometer ($Mo K_\alpha$).

The space group information requires C_1 molecular symmetry which suggested that the

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molecular structure was that of the trans isomer (II). However, a difference map calculated after isotropic refinement of this model ($R_1 = 0.144$, $R_2 = 0.134$)* revealed maxima corresponding to alternative sites for all the carbon atoms. These peaks and the nmr spectrum (described below) can be accounted for if the cis isomer, I, is also present, but, to satisfy the symmetry requirements of the space group, present in two orientations equally populated. If this hypothesis is correct and if x is the fraction of trans isomer, then the heights of the peaks corresponding to the major site for the ligand and the peaks corresponding to the minor site should be in the ratio $\frac{1+x}{2} : \frac{1-x}{2}$. The peak heights from both the difference map and the least squares results indicate that x is approximately 0.5. Isotropic refinement of this model gave $R_1 = 0.129$ and $R_2 = 0.119$, which by Hamilton's test⁶ allows us to reject at the 0.005 level of significance the original hypothesis that the bis(as-indacenyliron) molecules occupy only one site in the crystal. Subsequent refinement of anisotropic temperature factors for the iron atom and the carbon atoms of the major site and of isotropic temperature factors for the atoms of the minor site gave $R_1 = 0.065$ and $R_2 = 0.071$.

In the ligand occupying the major crystal sites the C-C distances in the cyclopentadienyl rings range from 1.387-1.430 Å, the C₉-C₁₀ length is 1.451 Å, the C₄-C₁₁ and C₅-C₁₂ lengths are both 1.453 Å, and the C₄-C₅ length is 1.348 Å. (The spread of the C-C lengths from the least squares results are between 0.010 and 0.011 Å.) Thus the lengths of the C-C bonds are those associated with the electronic structure III. The Fe-C distances (avg. 2.045 Å) are similar to those in other ferrocenes,^{3c,4,7} but the iron atom is significantly displaced toward C₃. [The distance from Fe to C₃ is 2.011(7) Å, while from Fe to C₁ or C₁₀ is 2.071(7) Å.] The Fe-Fe distance is 3.887(1) Å.

The nmr spectrum (Figure 1) of bis(as-indacenyliron) is unusual in two respects. One is that it exhibits six groups of peaks and is therefore inconsistent with the compound's having only structure (I) or (II). It can be accounted for if the compound is a mixture of comparable amounts of both, since of the triplet, two doublets and singlet expected of (I) or (II), all are observed except two doublets, presumably superimposed at τ 5.99, and both singlets, presumably superimposed at τ 2.39.^{††} The second unusual feature is that the range of chemical

* Defined as $R_1 = \frac{\sum |F_{obs}| - |F_{calc}|}{\sum |F_{obs}|}$; $R_2 = \left[\frac{\sum (|F_{obs}| - |F_{calc}|)^2}{\sum |F_{obs}|^2} \right]^{1/2}$.

†† A similar spectrum was recorded in toluene-d₈ solvent at 100°. The low field singlet was split into two singlets separated by 0.06 ppm. Some samples contained about twice as much of one isomer as of the other, and the intensities in the proton nmr spectra showed that the peaks at τ 3.92 and 6.84 originated from one isomer while those at τ 4.72 and 6.39 from the other.

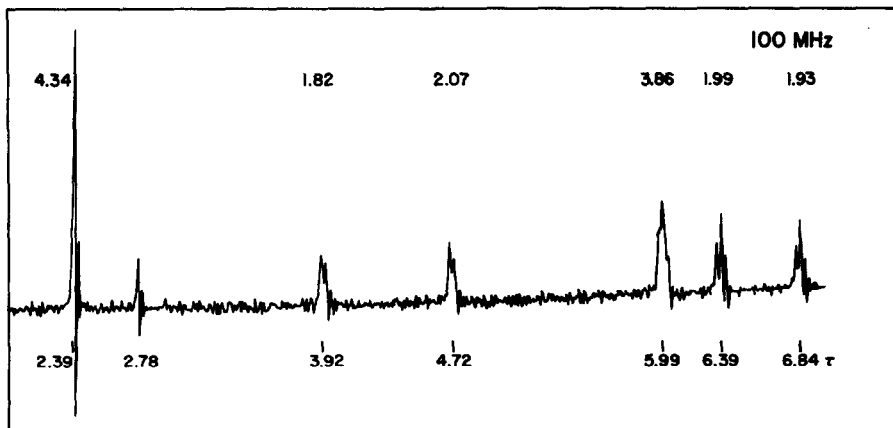
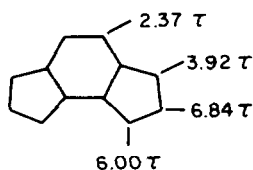


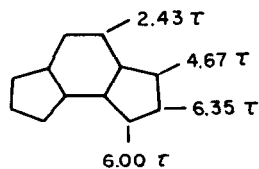
Figure 1: Nmr spectrum of bis(as-indacenyliron) in CS_2 at 100 MHz after 50 sweeps with a CAT. Intensities are above the peaks. ²The peak at τ 2.78 is probably spurious.

shifts of the metallocene resonances is very large. In bis(indenyl) iron, for example, the two metallocene protons resonate only 0.5 ppm apart.^{8b,c,d} The 0.5 ppm chemical shift in that compound has been accounted for with two assumptions: 1) that the central proton in one indenyl residue is shielded by the ring current in the other, and 2) that the indenyl residues are disposed trans.^{8b,9} However, these seem inadequate to account for the high field position of the triplets and for the range of chemical shifts in bis(as-indacenyliron). A similar but smaller spread of chemical shifts was recently found for the related compound 1,1'-biferrocenylene.³

The protons accounting for each of bis(as-indacenyliron)'s resonances are identified in the structural formulas below. (The data are for toluene- d_8 solutions.) These assignments are made because in some samples one isomer is predominant,[#] and because there is a small



IV



V

[‡]The magnitudes of the splittings are 2.6Hz, cf. other ferrocenes.⁸

[#]See footnote on the previous page.

coupling between the (presumably proximate) protons resonating at τ 2.37 and 3.92 and those at 2.43 and 4.67. Thus irradiation at τ 2.37 resolves the resonance at 3.92 into a clean doublet of doublets and irradiation at 2.43 similarly resolves the resonance at 4.67. Whether IV or V is to be associated with the trans structure is uncertain, but refinement of the X-ray data for a fractionated sample of bis(as-indacenyliron) and application of Hamilton's test implies the latter. It is evident that the differences in the chemical shifts of similar protons in the two isomers are not large, while those within each isomer are.

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