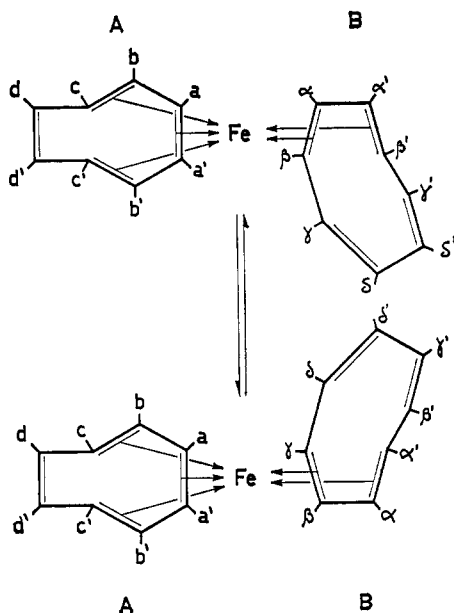


Scheme I



same intensity and the four pairs of protons of this ring can be made on the basis of the above spin-decoupling experiments. The decoupling of two pairs of protons observed when irradiating the signal at  $\tau$  5.02 suggests that this signal be attributed to the most coupled protons, *i.e.*, to  $H_{b,b'}$ . The signal at  $\tau$  5.42, which remains unchanged in this case, should be due to the protons having minimum interaction with  $H_{b,b'}$ , and hence to  $H_{d,d'}$ . With regard to the two signals at  $\tau$  4.60 and 5.50 the multiplet structure of the former induces us to attribute it to  $H_{a,a'}$  and the latter to  $H_{c,c'}$ .

The uv spectrum of **1** (Unicam SP.800, room temperature, cyclohexane solution, 210–700-nm range) shows one broad absorption at 295 nm ( $\log \epsilon$  3.2) and a flat one at 343 nm ( $\log \epsilon$  3.1).

The assigned structure has been confirmed by the X-ray study of **1** carried out by Allegra, *et al.*, of the Politecnico of Milan in collaboration with our laboratory. Preliminary results are reported in this issue.<sup>11</sup> In the crystalline state the molecules in general position contain one COT ring that is tri- and one that is 1,3-bicoordinated to the iron. Unlike the situation in solution at  $-84^\circ$ , the latter ring is also frozen, presenting localized bonds and fixed conformations.

A third situation is that existing in solution down to  $-35^\circ$ . In this case, in addition to the cited intranuclear bond rearrangement in the B ring, the equivalence of all protons implies a steady internuclear rearrangement, which transforms the tricoordinated ring to a 1,3-bicoordinated one and *vice versa*, with consequent interconversion of the conformation of the two rings and interchange of all bonds.

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Received February 19, 1968

## The Crystal Structure of Bis(cyclooctatetraene)iron

Sir:

In connection with the studies carried out in our laboratory on the structure of organometallic complexes containing transition metals and unsaturated ligands,<sup>1–4</sup> we performed the three-dimensional structural analysis of bis(cyclooctatetraene)iron(0).<sup>5,6</sup>

The complex crystallizes in the monoclinic system; the unit cell parameters are  $a = 25.13 \pm 0.09$ ,  $b = 10.68 \pm 0.03$ ,  $c = 13.98 \pm 0.04$  Å;  $\beta = 99.5 \pm 0.2^\circ$ . The density, calculated on the basis of 12 molecules per unit cell, is  $d$  1.42 g/cm<sup>3</sup> (exptl, 1.38 g/cm<sup>3</sup>); the space group is Cc or C2/c. Spectra were recorded using the equiinclination, multiple-film Weissenberg technique (Cu K $\alpha$  radiation) on a crystal rotating around its  $b$  axis. Nine layers were collected at room temperature; 1003 nonzero independent intensities were visually estimated, out of 2380 reflections investigated. In order to prevent decomposition of the crystal, it was maintained in an inert atmosphere. A consistent array of Fe–Fe vectors was found in the three-dimensional Patterson synthesis, and this is in accord with the centrosymmetrical C2/c space group. Two crystallographically different Fe atoms were found in the unit cell: one in general position, and the other on the twofold axis. The structure was then elucidated by Fourier methods, assuming C2/c as the correct space group. The molecule containing the Fe atom in the twofold axis position was found to be strongly affected by structural disorder. On the basis of the assumption that the actual Fourier image of the molecule is due to the superposition of two molecules, the atomic coordinates were first derived by conformational considerations, the structure being then refined through 14 cycles of full-matrix least squares.

Figures 1 and 2 show the images of the two non-equivalent molecules; the differences between them are within the limits of experimental error. This conclusion and the fairly good degree of convergence found in the least-square refinement substantiate the correctness of the above assumption of structural disorder. Because of the limitations in the computer storage, either the ordered molecule (I, Figure 1) or that resulting from the splitting of the intertwined pair (molecule II, Figure 2) was maintained fixed in each least-square cycle. Anisotropic thermal parameters were assigned only to the Fe atoms; furthermore, in order to remove the indetermination in the refinement of the parameters, the  $B$  factors of the badly resolved C atoms of molecule II were maintained equal in corresponding pairs. The final  $R$  value ( $= \sum |\Delta F| / \sum |F_o|$ ) is 0.148 for the reflections observed.

As might be expected, the two COT rings in each molecule differ in their geometrical conformation as well as in their mode of coordination to the central Fe

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(4) G. Allegra, F. Logiudice, G. Natta, U. Giannini, G. Fagherazzi, and P. Pino, *Chem. Commun.*, 1263 (1967).

(5) A. Carbonaro, A. Greco, and G. Dall'Asta, *Tetrahedron Lett.*, 2037 (1967).

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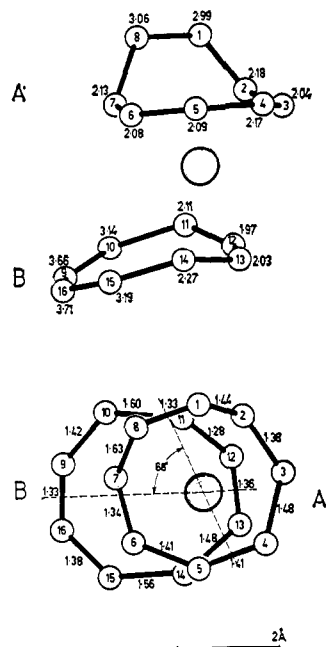


Figure 1. Two views of molecule I (not affected by structural disorder). Each view is obtained from the other by rotating the molecule around a horizontal axis. In the bottom view the planes of pseudo-symmetry of both rings are normal to the plane of the paper; their dihedral angle is shown. The Fe-C distances (top view) and the C-C bond lengths (bottom view) are also reported ( $\sigma_{\text{Fe-C}} \approx 0.02 \text{ \AA}$ ;  $\sigma_{\text{C-C}} = 0.03 \div 0.04 \text{ \AA}$ ).

atom. This atom is  $\pi$  bonded with six carbon atoms of one ring and four of the other (rings A and B, respectively, in Figures 1 and 2), so that the Kr electron configuration is attained. The main structural features of molecule I may be summarized from its comparatively accurate data as follows (see Figure 1).

(i) The conformation of the A ring and its coordination to the metal are similar to those found in the case of  $\text{C}_8\text{H}_8\text{Mo}(\text{CO})_3$ .<sup>7</sup> In fact, the values of the dihedral angles around C-C bonds and the Fe-C distances suggest an idealized mirror symmetry, in spite of some inconsistencies existing in the ring bond lengths and angles. Furthermore, the 2-3-4-5-6-7 group shows very much the same distortion from the planar arrangement as that reported for the Mo complex. Finally, in this case too, the distance between the two noncoordinated C atoms (8 and 1) seems to be close to the normal double bond length.

(ii) Also the over-all shape and coordination of the B ring resemble those found for  $\text{C}_8\text{H}_8\text{Fe}(\text{CO})_3$ .<sup>8</sup> A pseudo-mirror symmetry may be observed, and the two quasi-planar groups (14-15-16-9-10-11 and 11-12-13-14) form a dihedral angle of  $33^\circ$  (cf. with  $41^\circ$  for the  $\text{Fe}(\text{CO})_3$  complex).

(iii) The molecule as a whole has neither crystallographic nor idealized symmetry, since the planes of pseudo-symmetry for the separate rings are not coincident.

On the basis of the X-ray data presently available, we cannot decide whether the structural disorder of molecule II, representing one-third of the molecules in the crystal, is of a static type (*i.e.*, a random distribution of molecules having two alternative, fixed orienta-

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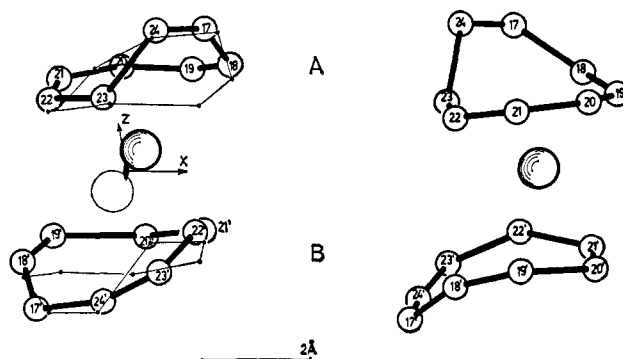


Figure 2. Two views of the disordered molecule II. On the left, it is seen along the crystallographic twofold axis ( $x = 1/2a$ ;  $z = 1/4c$ ); only the skeleton of one of the two symmetry related molecules is shown in heavy lines. On the right, a molecular projection similar to that in the top side of Figure 1 is reported.

tions) or of a dynamic type, involving a rapid interchange from the A to the B mode of coordination for each ring, and *vice versa* (internuclear tautomerism). The second hypothesis seems to be indirectly favored by nmr evidence, which shows that the internuclear tautomerism is certainly present in solution until  $-20^\circ$ .<sup>6</sup>

Crystallographic investigations on bis(cyclooctatetraene)iron at different temperatures are presently in progress in our laboratory.

**Acknowledgment.** The authors thank Drs. A. Carbonaro, G. Dall'Asta, and A. Greco for kindly supplying the samples and for useful discussions.

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Received February 20, 1968

## Deuterium Isotope Effects in the Photochemistry of an Azetidine Ketone<sup>1</sup>

Sir:

Although the photochemistry of heterocyclic three-ring compounds has been extensively studied in recent years,<sup>2</sup> relatively little is known about the photochemistry of the homologous four-ring system. Recently, we reported on the photorearrangement of a *cis*-aroylazetidine, a photoreaction that involved expansion of the four-membered nitrogen ring.<sup>3</sup> The extensive structural reorganization observed prompted us to carry out a detailed investigation of the mechanism of this unprecedented photoreaction. At this time we wish to report the results of deuterium-labeling experiments which provide evidence for a 1,3-diradical intermediate.

Exposure of a dilute solution of *trans*-1-*t*-butyl-2-phenyl-3-benzoylazetidine (I) in 95% ethanol to a

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(2) For a review see A. Padwa in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p 92.

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