Tetrahedron Letters No.41, pp. 3079-3082, 1964. Pergamon Press Ltd.
Printed in Great Britain.

THE CRYSTAL STRUCTURE OF TRICARBONYL-π-TETRACYCLO$[6.0^{1.8}{}_0{}^{9.16}{}_0{}^{10.15}{}_4]$ HEXADECA-2,4,6,11,13-PENTAENE IRON

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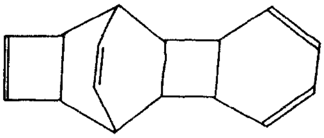
(Received 27 August 1964)

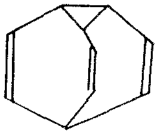
Jones[1] found that under mild conditions cyclooctatetraene dimerised to give two isomers, one (A) with m.p.76° and the other (B) with m.p. 52°. He formulated (A) as I, with four double bonds. Jones' experimental findings were confirmed by Schröder[2] who also observed that isomer (A) undergoes photolytic decomposition to benzene and an unidentified hydrocarbon, (C), $C_{10}H_{10}$. He obtained enough evidence to conclude that (C) was bullvalene, tricyclo $[3.3.2.0^{4.6}]$deca-2,7,9,-triene, II, and that the dimer (A) was related to it having formula III. Bullvalene itself had been a hypothetical compound postulated by Doering and Roth[3] in a review of transannular interactions in cyclopropane derivatives.

Schrauzer, Glockner and Merényi[4] found that the reaction of (A) with $Fe(CO)_5$ at 160-170° gave two isomers of $C_{16}H_{16}Fe\ (CO)_3$ and one binuclear and one trinuclear complex. The mononuclear isomers differ in melting point and in their infra-red and n.m.r. spectra. The isomer which melts at 118° has a temperature dependent n.m.r. spectrum as have compounds (A) and (C); the other isomer melts at 175-180° and its n.m.r. spectrum is not temperature dependent.



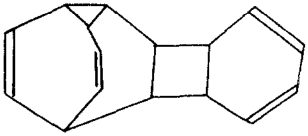
I

Dimer (A) (Jones)



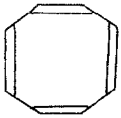
II

Bullvalene

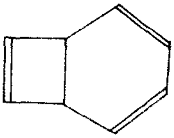


III

Dimer (A) (Schröder)



IV



V

We have investigated the compound $C_{16}H_{16}Fe(CO)_3$ with m.p.118° by X-ray diffraction. Photographs taken at room temperature (20-25°C) and at 115°K showed only small changes in unit cell dimensions and in the relative intensities of the reflections, indicating that the molecular structure in the solid is the same at both temperatures. A three-dimensional crystal structure analysis has been carried out with observations collected at 115 ± 5°K. In a unit cell having a = 20.86, b = 6.78, c = 10.99 Å, β = 94.5° and space group $P2_1/a$, there are four molecules. The iron atoms have been located from Patterson projections and the carbon atoms by three-dimensional Fourier difference syntheses. No assumptions were made about the molecular structure which was found to be as in Fig.1. The hydrogen atoms have also been located; there is one to each carbon atom completing a planar arrangement for atoms 2-7 and 11-14, and a distorted tetrahedral arrangement for the others. Anisotropic thermal vibration

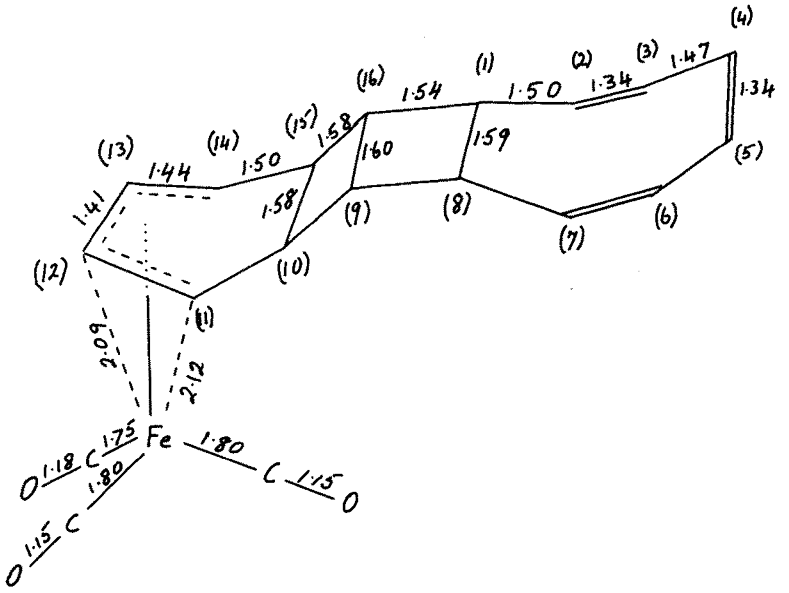


FIG. 1

Diagram of one Molecule Showing the Numbering of the Atoms and the Average Bond Lengths.

parameters have been determined for the iron atom and for the eight carbon atoms in the cyclooctatriene ring and individual temperature factors for the other atoms. The value of R is 0.081 for 878 observations.

The standard deviations in the bond lengths are 0.012 Å for C-Fe, 0.015 Å for C-O and 0.017 Å for C-C. Within the limits of experimental error, the molecule shows a non-crystallographic plane of symmetry passing through the centres of the bonds between C(4) and C(5), between C(12) and C(13), and the three bridges. The bond lengths shown in Fig.1 are the average values.

The iron atom is co-ordinated to the π-bond system of the six-membered ring, as predicted[4] but the remainder of the molecule does not resemble bullvalene. Further the anisotropic vibration parameters give no evidence for trans-annular interactions in the cyclooctatriene ring. The hydrocarbon ligand shown in Fig.1 has not yet been identified as a free molecule. Its formation by addition of one molecule of cyclooctatetraene IV to one molecule of the tautomeric[5,6] bicyclo form, V, seems highly plausible. It is possible that the strain in the adjacent four-membered rings is relieved by further re-arrangements in the free molecule and that such re-arrangements are inhibited when part of the six-membered ring is co-ordinated.

The crystal structures of the other isomers[4] of $C_{16}H_{16}Fe(CO)_3$ are being investigated.

We are grateful to Dr. G.N. Schrauzer for providing a sample of the compound.

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