The Structure and Bonding of Acenaphthylenepentacarbonyldi-iron

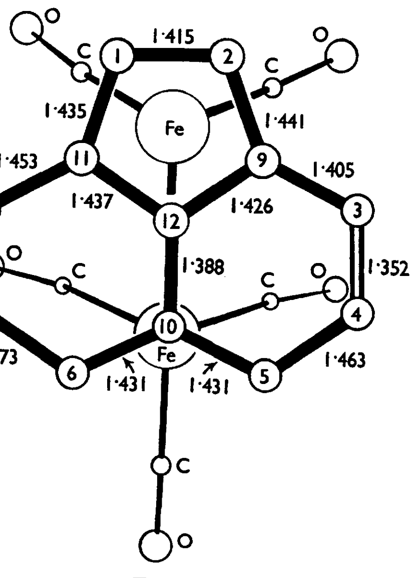
By MELVYN R. CHURCHILL* and JOHN WORMALD

(*Department of Chemistry, Harvard University, Cambridge Massachusetts* 02138)

THE reaction of acenaphthylene with $Fe_3(CO)_{12}$ was first reported as yielding $C_{12}H_8[Fe(CO)_3]_2$,[1] but a subsequent mass-spectral investigation[2] makes it more probable that the correct formulation is $C_{12}H_8Fe_2(CO)_5$. We have treated acenaphthylene with $Fe(CO)_5$ and obtained the same product [carbonyl stretching frequencies at 1984 and 2036 cm.$^{-1}$; mass spectrum showing peaks corresponding to $C_{12}H_8Fe_2(CO)_{5-n}{}^+$ (n = 0—5), $C_{12}H_8{}^+$, Fe^+], and have undertaken a single-crystal *X*-ray diffraction study of this complex with a view to determining unequivocally its molecular structure.

Acenaphthylenepentacarbonyldi-iron crystallizes in the centrosymmetric monoclinic space group, $P2_1/n$ (C_{2h}; No. 14) with a = 10·056, b = 16·089, c = 9·376 Å, β = 91·53°, and Z = 4. Intensity data complete tosin θ = 0·40 (Mo-K_α radiation) were collected with a Buerger automated diffractometer using a "stationary-background, ω-scan, stationary-background" counting sequence. The use of conventional Patterson, Fourier, and least-squares refinement techniques has led to the location of all atoms including hydrogens. The present discrepancy index, R equals 6·73% for the 1792 independent non-zero reflections. Estimated standard deviations are *ca.* 0·008 Å for iron–carbon and *ca* 0·012 Å for carbon–carbon bond lengths.

As shown in the Figure, the iron atom of an $Fe(CO)_2$ group is bonded symmetrically to all carbon atoms in the five-membered ring. Carbon–carbon bond lengths within this substituted π-cyclopentadienyl system have an average value of 1·431 Å. The iron atom lies 1·725 Å beneath this planar (r.m.s. deviation 0·005 Å) ring, while iron–carbon distances range from 2·078 to 2·140 Å

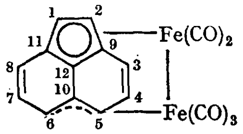


FIGURE

(average, 2·112 Å). The second iron atom is associated with three carbonyl groups and bonds to three atoms of the acenaphthylene system *via* a π-allyl linkage in which individual iron–carbon distances are: Fe–C(5) = 2·241, Fe–C(10) = 2·051, Fe–C(6) = 2·242 Å. [It may be noted that the Fe–C(12) distance of 2·652 Å is essentially non-bonding.] The iron–iron distance of 2·768 Å is indicative of a metal–metal bond; each iron atom thus obtains the appropriate rare-gas configuration in keeping with the observed[1] diamagnetism of the complex. The molecule may formally be represented by (I).

As may be seen from carbon–carbon bond lengths in the Figure, the co-ordination of acenaphthylene to an $Fe_2(CO)_5$ moiety virtually destroys the aromaticity of the free hydrocarbon.

(I)



All carbon–carbon bond lengths are in the expected ranges, except that C(10)–C(12) is rather shorter than might be expected for a simple $C(sp)^2$–$C(sp^2)$ single bond.

As is the case with azulenepentacarbonyldi-iron,[3] the organic ligand is no longer strictly planar. Referred to the least-squares plane through the five-membered ring, the remaining carbon atoms of the acenaphthylene ligand are displaced towards the iron atoms by the following extents: 0·017 for C(3), 0·011 for C(8); 0·224 for C(4), 0·215 for C(7); 0·440 for C(5), 0·411 for C(6); and 0·158° Å for C(10). The dihedral angle between the π-cyclopentadienyl and π-allyl systems is *ca.* 155°, and the molecule as a whole has approximate C_s symmetry.

This work has been supported by the National Science Foundation and the Advanced Research Projects Agency. J.W. acknowledges the receipt of a Graduate National Fellowship from Harvard University.

(*Received, October 14th*, 1968; *Com.* 1398.)

---

[1] R. B. King and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 4557.
[2] R. B. King, *J. Amer. Chem. Soc.*, 1966, **88**, 2075.
[3] M. R. Churchill, *Inorg. Chem.*, 1967, **6**, 190.