The Molecular Structure of an Azulene Complex of Iron; $C_{10}H_8Fe_2(CO)_5$

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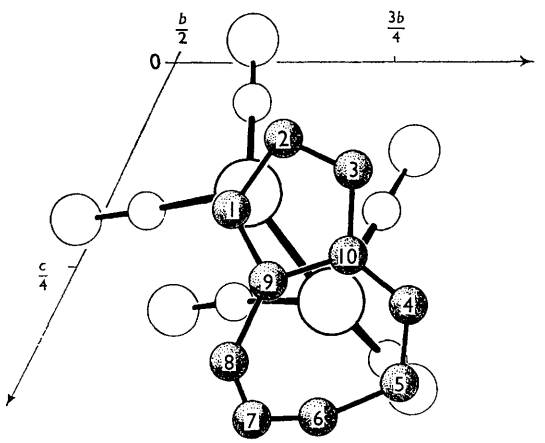
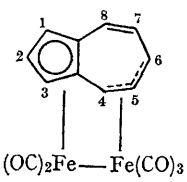
AZULENE complexes of transition metals have been known for some time,[1] but the exact nature of the azulene–metal bonding has not been ascertained. Azulenedi-iron pentacarbonyl, $C_{10}H_8Fe_2(CO)_5$, has been described and a number of possible structures (each involving metal–diene and metal–triene bonding) suggested. To obtain unambiguous information on azulene–metal bonding, a single-crystal *X*-ray-structural investigation of $C_{10}H_8Fe_2(CO)_5$ was undertaken.

The compound crystallizes in space-group $C\bar{1}$ (No. 2) with $a = 7{\cdot}32$, $b = 14{\cdot}48$, $c = 14{\cdot}76$ Å, $\alpha = 116{\cdot}2°$, $\beta = 92{\cdot}3°$, $\gamma = 93{\cdot}0°$, $Z = 4$. A three-dimensional analysis using Patterson, Fourier, and least-squares refinement techniques has led to the location of all atoms other than hydrogen. The present discrepancy index, R_1, is 10·75% for 2579 independent, non-zero reflections collected with a Buerger automated diffractometer. The present e.s.d.'s are ~0·015Å for metal–carbon and ~0·02Å for carbon–carbon bond lengths. The Figure shows the molecule viewed along *a*.



FIGURE

The iron atom of an $Fe(CO)_2$ group is symmetrically bonded to all carbon atoms in the five-membered ring of the azulene system. The observed carbon–carbon distances in this π-cyclopentadienyl system range from 1·414 to 1·452 Å (average 1·427 Å). The iron atom is 1·798 Å below this planar (r.m.s. deviation = 0·003 Å) ring; the iron–carbon distances range from 2·088 to 2·100 Å (average 2·093 Å). The other iron atom is bonded to three carbonyl groups and is associated with only three atoms of the seven-membered ring (Fe–C-4 = 2·142, Fe–C-5 = 2·050, Fe–C-6 = 2·200Å) The formation of this π-allyliron tricarbonyl system leaves one uncomplexed bond (C-7–C-8 = 1·325 Å) in the azulene ligand. The iron–iron distance of 2·782 Å indicates a metal–metal bond, giving each iron atom the eighteen-electron configuration consistent with the observed diamagnetism of the complex. The molecule may be formally written as in (I).



(I)

An interesting result of the joint requirements of metal–metal and metal–π-allyl bonding is that the azulene ligand, although formally conjugated, is no longer strictly planar. Referred to the least-squares plane of the π-cyclopentadienyl system, the remaining carbon atoms are displaced mainly towards the $Fe(CO)_3$ group, the maximum displacement being 0·91 Å for C-6.

The results of this analysis indicate that a reconsideration of the structures of azulene–metal complexes is necessary. For example, King[2] has noted that $[C_{10}H_8Fe(CO)_2]_2$ can also be obtained from azulene and iron pentacarbonyl. In the light of the present structural analysis, the probable relationship of this complex to $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ is greatly clarified.

I am grateful to Dr. P. Jolly for providing the sample of $C_{10}H_8Fe_2(CO)_5$.

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[1] R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1960, 4290.
[2] R. B. King, *J. Amer. Chem. Soc.*, 1966, **88**, 2075.