The Structure and Bonding of Bis-(π-azulene)iron

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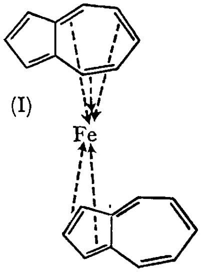
THE preparation of bis-(π-azulene)iron was initially reported by Fischer and Müller in 1964.[1] The results of ^1H n.m.r. studies and of hydrogenation experiments (the complex takes up 5 mol. of H_2) led to the suggestion that the complex had the structure (I). However, recent crystallographic studies on a variety of azulene–metal carbonyl complexes[2–4] indicate that azulene has a strong tendency to bind to a transition metal by utilizing its five-membered ring as a π-cyclopentadienyl system. A re-investigation of bis-(π-azulene)iron therefore seemed desirable.

(I)

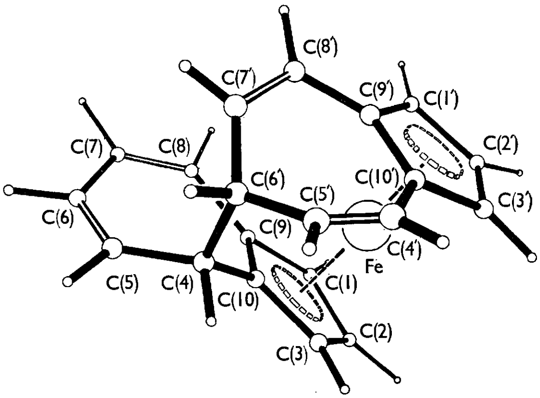


A mass-spectroscopic study of the complex shows well-defined peaks corresponding to the ions $(C_{10}H_8)_2Fe^+$, $C_{10}H_8Fe^+$, $C_{10}H_8^+$, and Fe^+, indicating that the stoicheiometry suggested[1] for the complex is correct. We have also undertaken a single-crystal X-ray structural analysis in order to ascertain unequivocally the molecular structure of the complex.

Bis-(π-azulene)iron crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5, No. 14) with $a = 7{\cdot}52$, $b = 12{\cdot}07$, $c = 15{\cdot}42$ Å, $\beta = 98{\cdot}26°$, $Z = 4$. Intensity data complete to $\sin\theta = 0{\cdot}38$ [Mo-K_α radiation] were collected with a Buerger automated diffractometer using the "stationary-background, ω-scan, stationary-background" counting sequence. The structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques, the present discrepancy index being 7·95% for the 1162 independent, non-zero reflections. All non-hydrogen atoms have been located accurately, present e.s.d.'s being ~0·012 for iron–carbon and ~0·016 Å for carbon–carbon bond lengths.

As may be seen from the Figure, the molecule is a substituted ferrocene in which two azulene systems have dimerized *via ortho–para* (*i.e.* 4-*endo*, 6′-*endo*) coupling. This is unique in azulene–transition-metal chemistry, although it has been shown previously that $[C_{10}H_8Mo(CO)_3CH_3]_2$[3] and $(C_{10}H_8)_2Fe_4(CO)_{10}$[4] dimerize *via ortho–ortho* (*i.e.* 4,4′) coupling. It seems probable that steric requirements preclude the attainment of the energetically more favourable[3] 4,4′-coupled geometry in the bis-(π-azulene)iron system.

Within experimental error each of the π-cyclopentadienyl systems has the expected D_{5h} symmetry. [The r.m.s. deviation from planarity is ~0·007 Å in each case, and carbon–carbon bond lengths range from 1·398 to 1·452 Å, averaging 1·431 Å.] The five-membered rings adopt a mutually staggered conformation, and are inclined to each other at an angle of 7° 33′. Individual iron–carbon distances range from 2·019 to 2·072 Å and average 2·045 Å.



FIGURE

The seven-membered rings are each grossly non-planar; in particular C(6′) lies 1·47 Å below the plane defined by C(1′)–C(2′)–C(3′)–C(9′)–C(10′). The bridging bond, C(4)–C(6′) is 1·584 ± 0·015 Å; all other carbon–carbon distances are close to the appropriate recognized values.

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