

838. Transition-metal Complexes of Seven-membered Ring Systems. Part II.¹ Azulenemetal Carbonyls.²

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The reaction between azulene and various substituted azulenes with molybdenum, manganese, and iron carbonyls gives substituted metal carbonyl complexes such as (azulene)Fe₂(CO)₅.

Nuclear magnetic resonance spectra of, and other physical measurements on, the compounds are discussed and evidence for a novel type of isomerism in substituted azuleneiron carbonyls is presented.

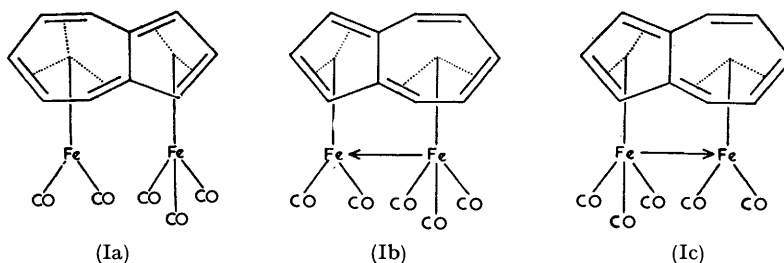
In a previous note¹ we described some metal carbonyl complexes derived from cycloheptatriene. We have now prepared compounds in which molybdenum, manganese, and iron carbonyl residues are bound to either or both of the seven- and five-membered rings in the hydrocarbon azulene and its derivatives.

High-resolution nuclear magnetic resonance studies on cycloheptatrienemolybdenum carbonyl^{3,4} and similar iron derivatives⁴ together with X-ray-diffraction studies of the molybdenum compound,⁵ indicate that the bonding of the hydrocarbon to the metal atom must be considered as involving essentially independent double bonds rather than a delocalised π -electron system. Present nuclear magnetic resonance studies of azulene complexes have shown that a similar view must be taken, as the spectra can be interpreted only if it is assumed that the bonding is olefin-like in nature. Since the iron complexes have been most suitable for detailed study, owing to their greater solubility in organic solvents, we consider them first.

The compounds prepared in this work together with some spectral data are listed in Table I. We note here that metal complexes of a different type have been prepared from metal halides and 4,6,8-trimethylazulene, *e.g.*, C₁₃H₁₄RhCl₃, C₁₃H₁₄PdCl₂; these compounds will be described separately.

A. AZULENE IRON COMPLEXES

Interaction of azulene and iron penta- or dodeca-carbonyl gives from each the same two products. The first, azulenedi-iron pentacarbonyl, is diamagnetic, dark-red,



crystalline, stable in air, moderately soluble in chloroform and polar solvents, but sparingly soluble in non-polar solvents. It sublimes *in vacuo* at 100°, but at higher temperatures regenerates azulene almost quantitatively. Possible structures for this compound are (Ia, b, and c), where both metal atoms have the formal inert-gas configuration; the iron

¹ Part I, Abel, Bennett, Burton, and Wilkinson, *J.*, 1958, 4559.

² Cf. (a) Burton and Wilkinson, *Chem. and Ind.*, 1958, 1205; (b) Burton, Green, Abel, and Wilkinson, *ibid.*, 1958, 1592.

³ Green, Pratt, and Wilkinson, *J.*, 1959, 3753.

⁴ Burton, Bennett, Pratt, and Wilkinson, unpublished work.

⁵ Dunitz, E. T. H., Zürich, personal communication.

carbonyl residues in (Ia) could be on the same side (*cis*) or on opposite sides (*trans*) of the azulene nucleus.

For the second product, because of its high molecular weight, it has proved difficult to obtain an empirical formula: analyses combined with related work on some polynuclear

TABLE I. *Azulenemetal carbonyls and their spectra.*

Compound	Colour	M. p.*	Infrared	Ultraviolet λ_{max} . (m μ)
			2100—1700 cm. ⁻¹ ^a	(log ϵ in parentheses)
Fe ₂ (CO) ₅ azulene	Dark red	d > 100°	2046s, 1996s, 1976s	280(4.02), 330(3.91) 405(3.57), 515(3.22)
Fe ₂ (CO) ₅ (1,3-dideuteroazulene)	"	d > 100	2046s, 1996s, 1976s	—
Fe ₂ (CO) ₅ (4,6,8-trimethylazulene)	"	122—125	2043s, 1990s, 1975s	
Fe ₂ (CO) ₅ (4-methylazulene)	"	oil	2043s, 1989s, 1971s	
Fe ₂ (CO) ₅ (guaiazulene A)	"	97—99	2041s, 1988s, 1966s ^c	243(4.42), 330 ^b (3.94), 410(3.41), 510(3.09)
Fe ₂ (CO) ₅ (guaiazulene B)	"	110—111	2039s, 1990s, 1965s ^c	243(4.42), 330 ^b (3.93), 410(3.37), 510(3.01)
Fe ₅ (CO) ₁₃ azulene	Pale brown	d > 170	2061s, 1999s, 1765m	
Mn ₂ (CO) ₆ azulene	Pale yellow	153—154d	2027s, 1938s	
Mn ₂ (CO) ₆ (4,6,8-trimethylazulene)	"		2028s, 1939s	
Mo ₂ (CO) ₆ azulene	Black	d > 150	2033s, 1960s, 1897w 1867w	275 ^b (4.33), 326(4.14) 403(3.95), 475(3.51)
Mo ₂ (CO) ₆ (4,6,8-trimethyl azulene)	"	d > 170	2028s, 1951s, 1886w, 1861w	
Mo ₂ (CO) ₆ guaiazulene	"	d > 170	2016s, 1949s, 1895w, 1866w	270 sh (4.33), 330(4.14), 403(4.00), 475(3.69)

^a In CHCl₃ solution with NaCl optics. ^b Fine structure present. ^c Spectra in 4000—600 cm.⁻¹ region given in Experimental section. * d = Decomposition.

cycloheptatriene iron complexes⁴ lead us to suggest (C₁₀H₈)₂Fe₅(CO)₁₃. It is a light brown solid, sparingly soluble in chloroform, ethanol, or benzene, and insoluble in light petroleum. The infrared spectrum shows a strong band at 1765 cm.⁻¹ suggesting the presence of bridging carbonyl group(s). The compound is paramagnetic. Although several conceivable structures can be drawn, there is at present no means of deciding between them.

(1) *Dipole Moments.*—The compound C₁₀H₈Fe₂(CO)₅ is sufficiently soluble to allow the dipole moment to be determined, and it was hoped that this would clearly indicate whether the iron carbonyl residues were in *cis*- or *trans*-positions.

Since the nuclear magnetic resonance measurements discussed below indicate that the metal-hydrocarbon bonding is similar to that in olefin-metal complexes, we assume that the major contribution to the dipole moment of the molecule arises from the metal-double bond dipole.* An approximate estimate of the dipole for the ring-iron bonds can be obtained from those of the cycloheptatriene-⁴ and cyclo-octatriene-iron carbonyl compounds,⁶ which are 2.3 and 2.37 D, respectively. The resultant moment for a *cis*-configuration in C₁₀H₈Fe₂(CO)₅ would then be *ca.* 2 × 2.3 D (any dipole contribution of the azulene nucleus, which would be relatively small, being neglected), which is to be compared with the observed moment of 3.97 D.

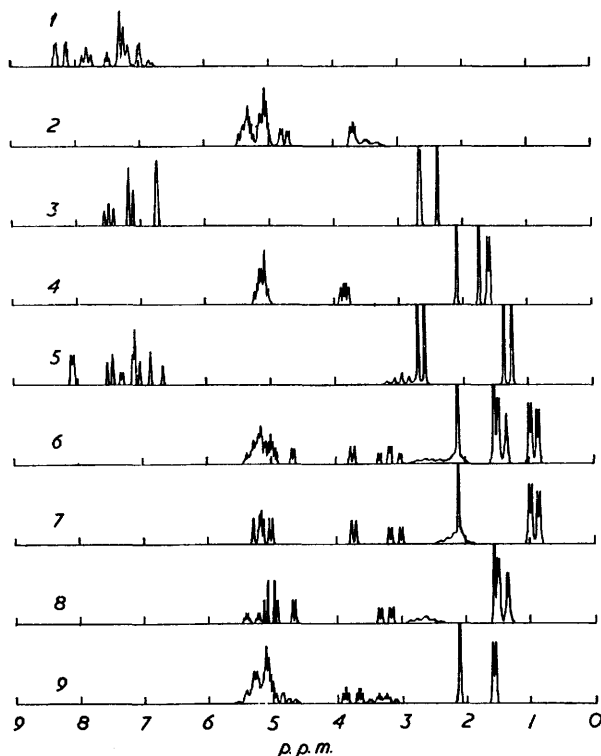
Although for structures of the type (Ib and c) the iron-carbonyl groups must be in *cis*-relation, a *trans*-configuration for (Ia) would almost certainly have a dipole moment much smaller than that observed. In the case of the azulenemolybdenum carbonyl discussed below (which unfortunately is too insoluble to allow dipole-moment measurements) it is very difficult to explain the observed stoichiometry except with a *cis*-form.

* The metal-carbon monoxide bond dipole is alleged to be small, *ca.* 0.4 D (Weiss, *Z. anorg. Chem.*, 1956, 287, 223) or 0.26 D (Fischer, Internat. Conf. Co-ordination Chem., Chem. Soc. Special Publ. No. 13, 1959, p. 87), so that the difference between -Fe(CO)₃ and -Fe(CO)₂ contributions will be only of this order.

⁶ Fischer, Palm, and Fritz, *Ber.*, 1959, 92, 2645.

In view of the existence of isomers (discussed below) in the substituted azuleneiron carbonyls the question could be raised whether these are merely *cis*- and *trans*-carbonyl forms. If this were the case, there seems no reason why azulene and symmetrically substituted azulenes should not show both *cis*- and *trans*-forms of the complexes, which, owing to the large differences in dipole moment, should be readily separable by chromatography. Very careful chromatography of the azulene and 4,6,8-trimethylazulene

FIG. 1. Proton resonance spectra of di-iron pentacarbonyl complexes of azulenes at 56.45 mc./sec., relative to tetramethylsilane as internal reference. Field increasing left to right.



(1) Azulene; (2) azulenedi-iron pentacarbonyl; (3) 4,6,8-trimethylazulene; (4) 4,6,8-trimethylazulenedi-iron pentacarbonyl; (5) guaiazulene; (6) mixture of guaiazulenedi-iron pentacarbonyl isomers; (7) isomer A; (8) isomer B; (9) mixture of 4-methylazulenedi-iron pentacarbonyl isomers.

complexes has given no evidence of such separation. We therefore believe, on the available evidence, that only the *cis*-form occurs.

In a preliminary theoretical treatment of the bonding in these metal complexes⁷ it was assumed that the *trans*-configuration occurs and also in the iron compound that the $-\text{Fe}(\text{CO})_2$ group is attached to the five-membered ring. As discussed below, the additional assumption that the metal atoms are symmetrically placed with respect to the rings may well not be so for the seven-membered ring. In view of the facts now available we feel that a re-evaluation of the theoretical approach is necessary.

(2) *High-resolution Nuclear Magnetic Resonance Spectra.*—The nuclear magnetic resonance spectra of the various azulenedi-iron pentacarbonyl complexes, together with those of the parent hydrocarbons, are shown in Fig. 1; details of the spectra are given in Table 2 and the Experimental section.

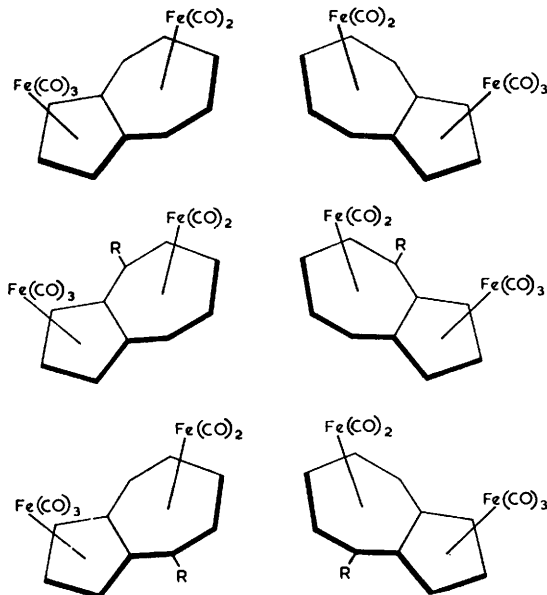
The spectra of the substituted parent azulenes agree with the assignments for azulene

⁷ Brown, *Chem. and Ind.*, 1959, 126.

itself first given by Pople, Bernstein, and Schneider.⁸ The spectra accord with the facts that in azulene, 1,3-dideuteroazulene, and 4,6,8-trimethylazulene, the ring protons in symmetrical positions relative to the $C_{(2)}-C_{(6)}$ axis are in equivalent environments and that in 4,6,8-trimethylazulene the 4- and the 8-methyl group are identical (this is not so in the complexes).

For the iron complexes, the resonances of all the ring protons occur at markedly higher fields than for the parent hydrocarbons, as has been observed for other unsaturated hydrocarbons bound to transition-metals.³ This shift probably arises partly because the π -electrons of the hydrocarbon which are involved in bonding to the metal atom do not have the same freedom to respond to the applied magnetic field as they have in the parent hydrocarbon with their paramagnetic contribution to the shift of the protons attached to the unsaturated group being decreased. In addition, there is probably a contribution from induced moments in the metal atom. As mentioned above, this up-field shift does

FIG. 2. *Isomers of di-iron pentacarbonyl complexes of azulenes.*



not necessarily mean that the hybridization of the carbon atoms of the co-ordinated double bonds has changed towards sp^3 with formation of σ -type metal-carbon bonds, and indeed infrared evidence contradicted this idea.³

Detailed assignments of the nuclear magnetic resonance spectra are given on p. 4300. Comparison of these spectra shows that two of the ring protons $H_{(1)}$ (or $H_{(3)}$) and $H_{(6)}$ are shifted to higher fields than are the others. Therefore in the five-membered ring in the complexes, $H_{(1)}$ and $H_{(3)}$ are in different environments. In the seven-membered ring, it is found that $H_{(4)}$ and $H_{(5)}$ are not equivalent to $H_{(8)}$ and $H_{(7)}$, respectively. Also in the 4,6,8-trimethylazulene complex, the 4- and the 8-methyl group are not equivalent, since three chemically shifted methyl peaks are observed and only one of the lines assigned to the 4- or 8-group shows a doublet structure due to coupling with a ring proton. Hence in the complexes the magnetic environment for protons or groups at positions 1, 8, and 7 is not equivalent to that at positions 3, 4, and 5, respectively. This lack of equivalence is discussed below and reasons for it are suggested. We now take it that there is a real asymmetry in the complexes about the $C_{(2)}-C_{(6)}$ axial plane. This implies that each compound derived from a symmetrically substituted azulene has enantiomeric forms,

⁸ Pople, Bernstein, and Schneider, *J. Amer. Chem. Soc.*, 1958, **80**, 3497.

and that a compound derived from an unsymmetrically substituted azulene has two geometrical isomers, each of these having two enantiomorphs.

This situation is shown diagrammatically in Fig. 2, where the asymmetry about the axial plane is indicated by the heavier line on one side; we use structure (Ia) as an example but the situation would be similar for (Ib and c).

(3) *Guaiazulene- and 4-Methylazulene-iron Compounds.*—The nuclear magnetic resonance spectrum of the guaiazulenedi-iron pentacarbonyl, as first isolated, appeared to be particularly complicated and the band intensities could not be interpreted by comparison with the spectra previously obtained. Interpretation was possible on the basis of an isomeric mixture; very careful chromatography enabled us to separate two isomers A and B occurring in a 1:1 ratio.

Partial resolution of isomer A was attempted on a 90-cm. column of (+)-lactose by the procedure⁹ used for chromium and cobalt trisacetylacetonate complexes. No rotation was, however, detected in the first or final fraction, which was not surprising in view of the neutral character of the compounds.

The isomers A and B have virtually the same infrared spectrum throughout the 4000—600 cm^{-1} range (see p. 4299) though a few weak peaks appear to shift but in no case by more than 30 cm^{-1} . The band positions in the visible and ultraviolet spectra are the same with only slight differences in intensity. Thermal decomposition of the complex in both cases regenerated guaiazulene, as demonstrated by nuclear magnetic resonance measurement. The chemical properties of the isomers appear to be the same, but there is a notable difference in melting point (Table 1).

The nuclear magnetic resonance spectra of the isomers show considerable differences (Fig. 1). Superposition of the individual spectra (with intensities corresponding to equimolar quantities) gives a resultant spectrum identical in all details with that originally obtained for the mixture.

We have been unable to separate the isomers of 4-methylazulenedi-iron pentacarbonyl chromatographically but the nuclear magnetic resonance spectrum (Fig. 1) can again be interpreted in terms of an equimolar isomeric mixture.

(4) *Discussion.*—The proton resonance lines can be satisfactorily assigned by inter-comparison of the various spectra, without specification of the configuration of the isomers. In addition, however, it is possible on the nuclear magnetic resonance evidence to assign configurations to the guaiazulene isomers and, by analogy, to those of 4-methylazulene. Before doing so, we consider some of the reasons for the asymmetry about the $\text{C}_{(2)}\text{-C}_{(6)}$ axial plane in the complexes.

It is possible that carbon monoxide groups adopt some preferred orientation which is not symmetrical about this axial plane or that the π -electron distribution in the coordinated azulene is asymmetric. Both of these effects could arise with any of the structures (Ia, b, c).

Considering, first, (Ia), if we assume that the trigonal bipyramidal configuration of iron pentacarbonyl is approximately retained in the azulene complexes, then since the two apical positions are different from the equatorial ones, it becomes impossible to form three equivalent iron-olefin bonds from the $\text{Fe}(\text{CO})_2$ group to the seven-membered triene ring. Thus we can expect that the $\text{Fe}(\text{CO})_2$ group would be bound unsymmetrically with respect to the axial plane, and that one of the metal-ring (apical) bonds would confer properties on the π -electron density localised in this bonding position of the hydrocarbon ring differing (*e.g.*, in the coupling constants across the double bond) from those in the other two positions. Further, the two Fe-CO distances in the $\text{Fe}(\text{CO})_2$ group should be different, and finally there is also the possibility that the carbon skeleton of the azulene nucleus is not planar.*

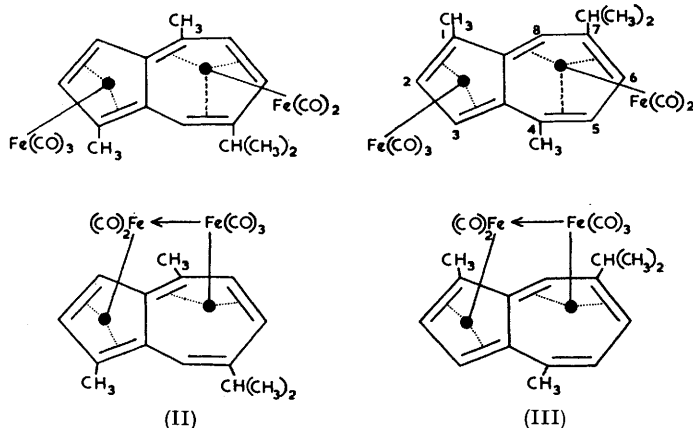
* For an $\text{Mo}(\text{CO})_3$ group bound to the seven-membered ring, three equivalent bonds to the metal (octahedral) would be expected but distortions of the azulene skeleton could again be present.

⁹ Moeller and Gulyas, *J. Inorg. Nuclear Chem.*, 1958, **5**, 245.

In structures (Ib and c), the iron carbonyl group [$\text{Fe}(\text{CO})_3$ and $\text{Fe}(\text{CO})_2$, respectively] is bound to only two of the conjugated double bonds in the seven-membered ring, leaving the third double bond free. Thus, if we consider the hydrocarbon rings only, the principal difference between structures of type (I) is the degree to which the "lone" double bond of the seven-membered ring is involved in bonding to the iron atom. On the basis of either infrared or nuclear magnetic resonance spectra it is not possible to distinguish between these types. The fact that all of the ring protons in the azulene and other complexes are shifted to high fields relative to the normal olefinic resonances does not rule out the possibility of a lone, non-co-ordinated double bond since an up-field shift of the protons on the latter could be produced entirely by fields from the induced moments in the metal atom. Attempts to hydrogenate the azulene and 4,6,8-trimethylazulene complexes over Adams catalyst failed, but further studies on the chemical properties of the complexes are now in progress.

Irrespective of the details of the bonding, however, any of the structures (Ia, b, c) can account for the nuclear magnetic resonance spectra and the existence of isomers derived from asymmetrically substituted azulenes.

Thus, using the guaiazulene compound as an example, we have (II) and (III) [for structural types (Ia and b)] as geometrical isomers, which we designate respectively 3,8-dimethyl-5- and 1,4-dimethyl-7-isopropylazulenedi-iron pentacarbonyl.



On this basis we can make an approximate interpretation of the nuclear magnetic resonance spectra, partly by analogy with our previous experience with other conjugated olefin-metal complexes where it was found that when a conjugated diene³ or similar system such as cyclopentadienone¹⁰ is bound to a transitional metal the resonances of the protons on the terminal carbon atoms of the conjugated diene are shifted to higher magnetic fields than those of the protons on the central carbon atoms.

In structures (II) and (III), if the five-membered ring can be considered as a diene group, it should have a spectrum similar to that of co-ordinated cyclopentadiene or butadiene,³ so that only the proton $\text{H}_{(1)}$ in (II) (corresponding to the "terminal" position) would appear at the higher fields. Only one of the guaiazulene isomers, A, has a single high-field proton resonance associated with the five-membered ring. In structure (III), there is a methyl group at position 1 and no high-field line for the five-membered ring can be expected; in fact guaiazulene isomer B has no such line. Hence considering the five-membered ring we can make the assignment: isomer A = (II); isomer B = (III).

In the seven-membered ring, the spectra can be interpreted by regarding the four carbon atoms constituting one side (about the $\text{C}_{(2)}$ - $\text{C}_{(6)}$ axial plane) as a conjugated diene system, with a separate or metal-co-ordinated double bond on the opposite side of this

¹⁰ Green, Pratt, and Wilkinson, *J.*, 1960, 989.

axial plane. For structure (Ia), this arrangement corresponds approximately to the bonding of two "equatorial" positions of the penta-co-ordinated iron atom to the diene group and the axial position to the lone double bond. Again only one proton, $H_{(6)}$, is a "terminal" one and its resonance would appear at high fields for both forms (II) and (III). In both guaiazulene isomers, the line assigned to $H_{(6)}$ lies at high fields. In isomer B, the magnitude of the splitting of one of the methyl groups is about the same as that observed across a single double bond in simple olefins containing this *cis*-CMe:CH group.¹¹ Thus it seems reasonable to assign the split methyl peak to a methyl group attached to the "lone" double bond, *i.e.*, to the 4-methyl group in structure (III). Now the single proton adjacent to this methyl group in isomer B ($H_{(5)}$) shows a quartet splitting, while in isomer A, a similar proton ($H_{(7)}$) adjacent to the 8-methyl group shows only a doublet. This difference is consistent with the weaker coupling across the 7,8-bond in A than across the 4,5-bond in B. Hence again we can equate isomer A = (II), isomer B = (III), and we can now proceed to assign all of the lines observed for the guaiazulene isomers in terms of structures (II) and (III). The assignments are listed in Table 2. The isomeric mixture of the 4-methylazulene complex can be treated similarly.

TABLE 2. Proton magnetic resonance spectra of guaiazulenedi-iron pentacarbonyl isomers.

Position of line centre *	Rel. int.	Components and splitting (c./sec.)	Assignment
A, 5-Isopropyl-3,8-dimethylazulenedi-iron pentacarbonyl (II)			
5.21	1	Doublet, ~ 8.5	$H_{(7)}$ (split by $H_{(6)}$)
5.19	1	?Doublet, ~ 1.2	$H_{(4)}$
5.02	1	Doublet, 2.8 ± 0.1	$H_{(2)}$ (split by $H_{(1)}$)
3.74	1	Doublet, 2.9 ± 0.1	$H_{(1)}$ (split by $H_{(2)}$)
3.08	1	Doublet, 8.5 ± 0.1 ; doublets, 1.6 ± 0.1	$H_{(6)}$ (split by $H_{(7)}$ and by $H_{(4)}$ or tertiary isopropyl-H?)
~ 2.17	1	5 of expected septuplet, ~ 6.5	Tertiary isopropyl-H
2.10	6	Single	3-CH ₃ and 8-CH ₃
0.942 } 0.911 }	6	Doublets, each 6.7 ± 0.1	$2 \times$ CH ₃ of isopropyl group
B, 7-Isopropyl-1,4-dimethylazulenedi-iron pentacarbonyl (III)			
5.30	1	Doublet, $\sim 8.9 \pm 0.2$; quartets, ~ 1.4	$H_{(5)}$ (split by $H_{(6)}$ and 4-CH ₃)
5.10	1	Doublet, 2.9 ± 0.1	} $H_{(2)}$ + $H_{(3)}$ (split each other)
4.96	1	Doublet, 2.9 ± 0.1	
4.67	1	Doublet, 1.8 ± 0.1	$H_{(6)}$ (split by $H_{(5)}$ or tertiary isopropyl-H)
3.24	1	Doublet, 8.9 ± 0.1 ; doublets, 2.0 ± 0.1	$H_{(6)}$ (split by $H_{(5)}$ and by $H_{(3)}$ or tertiary isopropyl-H?)
2.63	1	5 of expected septuplet, $\sim 6.7 \pm 0.3$	Tertiary isopropyl H
1.53	3	Singlet	1-CH ₃
1.49	3	Doublet, 1.3 ± 0.2	4-CH ₃ (split by $H_{(5)}$)
1.41 _s	6	Doublet, 6.7 ± 0.2	$2 \times$ CH ₃ of isopropyl group

* In p.p.m. on the low-field side of SiMe₄ as reference zero.

The resonances of the protons in the isopropyl groups of the two guaiazulene isomers occur at different positions. This shift may be due to the induced magnetic moments associated with the metal atom and carbonyl groups. The small (0.03 p.p.m.) shift in the isopropyl-methyl lines in isomer A may arise from some restriction of rotation of the isopropyl group due to steric interaction with the iron carbonyl group, leading to slightly different environments for the methyl groups. This small shift is not observed in isomer B, but the component lines of the main isopropyl doublet appear significantly broader than the other lines in the spectrum; the broadening could result from incomplete averaging out of a small shift, owing to a partially restricted rotation of the isopropyl group.

B. AZULENE-MANGANESE AND -MOLYBDENUM CARBONYLS

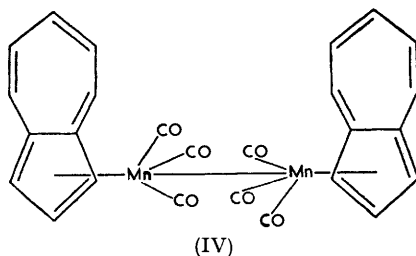
(1) *Manganese*.—Prolonged reaction of azulenes with manganese carbonyl gives compounds of stoichiometry $[A]_2Mn_2(CO)_6$, which are very hard to purify. The azulene

¹¹ Jackman, personal communication.

compound is diamagnetic and air-stable; it is soluble in most organic solvents but its solutions slowly decompose, even in the dark, regenerating azulene. The most reasonable structure is (IV). As with other complex carbonyls containing metal-metal bonds, treatment of the compounds with halogens and with sodium amalgam in tetrahydrofuran causes cleavage, giving the tricarbonyl halides and the sodium salt of the azulenemanganese tricarbonyl, respectively.

We have been unable to obtain well-resolved nuclear magnetic resonance spectra of the manganese compounds, presumably owing to their instability in solution, which quickly produces traces of paramagnetic material. The spectra are consistent with structure (IV).

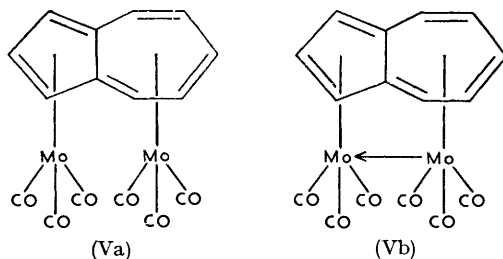
(2) *Molybdenum*.—Reaction of molybdenum hexacarbonyl with azulene, guaiazulene, and 4,6,8-trimethylazulene has produced crystalline compounds of the unexpected stoichiometry $[A]Mo_2(CO)_6$. These complexes are all very dark red, almost black,



insoluble in non-polar solvents, and only sparingly soluble in chloroform ($\sim 0.3\%$ for the azulene compound), tetrahydrofuran, and acetic acid, and give dark red solutions. The compounds may be stored indefinitely, but their solutions decomposed slowly in air and light and gave almost quantitative yields of the azulene. The hydrocarbon was also regenerated above *ca.* 150° ; it has been impossible to obtain infrared spectra for these compounds except in the region $2100\text{--}1700\text{ cm}^{-1}$ (Table 1) because of their low solubility and opacity when in the form of mulls or potassium halide discs.

The azulene compound was first thought to be paramagnetic^{2a} on the basis of solid-state bulk susceptibility measurement. However, determination of the susceptibility in solution by the very sensitive nuclear magnetic resonance method,¹² and bulk susceptibility measurement of the guaiazulene compound, indicated diamagnetism in both cases. After very careful purification, the azulene complex was therefore re-measured and found to be diamagnetic in the solid state; the previous result was undoubtedly due to magnetic contaminant in the compound, which is very difficult to purify by crystallisation because of its low solubility.

Two types of structure, (Va and b), are again possible for these compounds, and their



low solubility makes it impossible to decide by dipole-moment measurements whether the $Mo(CO)_3$ groups are *cis* or *trans*.

Since azulene has only ten π -electrons, it is impossible for both metal atoms in form (Va)

¹² Evans, *J.*, 1959, 2003.

to possess a formal inert-gas structure. Thus the metal atom bound to the five-membered ring, which can be considered to be a four- π -electron donor, has only sixteen electrons in the valency shell. However, if the bonds at this molybdenum atom are trigonal bipyramidal (or approximately so) using ds^3 hybrid bonds, then there could well be sufficient separation between the remaining d -orbitals for a lower group of three to be occupied by the six valency electrons, and this would lead to diamagnetism. There does not appear to be any other known example where molybdenum(0) gives trigonal bipyramidal molecules with strong field ligands. The present case can be conceived to arise because of steric factors due to *cis*-bonding of the metal carbonyl groups (by analogy with the iron compounds). If the molybdenum carbonyl groups are in the *trans*-position, it is not apparent why an $\text{Mo}(\text{CO})_4$ group could not be bound to the five-membered ring. Inspection of a model shows that with *cis*-bonding attachment of an $\text{Mo}(\text{CO})_4$ group to the five-membered ring would be very difficult to achieve.

In form (Vb), involving a metal-metal dative bond, both molybdenum atoms attain an inert-gas configuration, and the metal atom bound to the seven-membered ring would have a formal co-ordination number of seven.

EXPERIMENTAL

Microanalyses and molecular weights (ebullioscopic in benzene) are by the Microanalytical Laboratory, Imperial College.

Interaction of Iron Carbonyl and Azulenes.—For products see Table 3. Azulene (0.45 g.)

TABLE 3. *Analyses and molecular weights.*

Compound	Found (%)					Required (%)				
	C	H	O	Metal	M	C	H	O	Metal	M
$\text{Fe}_2(\text{CO})_5$ azulene	47.9	2.8	21.2	29.8	395	47.5	2.1	21.1	29.3	379
$\text{Fe}_2(\text{CO})_5$ 4,6,8-trimethylazulene	51.5	3.7	19.1		400	51.2	3.3	19.0		422
$\text{Fe}_2(\text{CO})_5$ 4-methylazulene	49.2	3.5		28.2		48.7	2.5		28.4	
$\text{Fe}_2(\text{CO})_5$ guaiazulene	53.3	4.5	18.2	24.6	440	53.3	4.0	17.8	24.9	450
$\text{Fe}_2(\text{CO})_{13}$ diazulene	44.0	2.4	23.7		1050	44.0	1.8	23.1		900
$\text{Mn}_2(\text{CO})_6$ diazulene	58.6	3.7	18.5		500	58.4	3.0	18.0		534
$\text{Mn}_2(\text{CO})_6$ di-(4,6,8-trimethylazulene)	60.2	4.6	15.8		630	62.2	4.5	15.5		618
$\text{Mo}_2(\text{CO})_6$ azulene	38.8	1.9	20.2	39.2	510	39.3	1.6	19.7	39.3	488
$\text{Mo}_2(\text{CO})_6$ 4,6,8-trimethylazulene	42.9	2.6	18.5	36.1	545	43.0	2.6	18.1	36.2	530
$\text{Mo}_2(\text{CO})_6$ guaiazulene	45.3	3.4	17.3	34.4	550	45.1	3.2	17.2	34.4	558

and an excess of iron pentacarbonyl (10 ml.) were heated at 100° for 5 days in light petroleum (b. p. 100 – 120°) (50 ml.). After removal of the solvent and excess of carbonyl at $20^\circ/0.2$ mm., the residue was extracted with boiling light petroleum (b. p. 40 – 60°) (100 ml.). Successive removal of quantities of solvent from the filtered petroleum extract and slow cooling to -20° gave crops of *azulenedi-iron pentacarbonyl* (0.21 g.). The residue remaining after extraction of this compound was washed with light petroleum and extracted with chloroform (2×50 ml.); addition of light petroleum to the extract precipitated light brown crystals of the compound, $(\text{C}_{10}\text{H}_8)_2\text{Fe}_5(\text{CO})_{13}$.

The 1,3-dideuteroazulene compound, $\text{C}_{10}\text{H}_6\text{D}_2\text{Fe}_5(\text{CO})_5$, was prepared in a similar way from 1,3-dideuteroazulene;¹³ similarly were prepared the 4,6,8-trimethylazulene, 4-methylazulene, and guaiazulene compounds, which were purified by crystallisation and chromatography on a 20-cm. alumina column.

The compounds were also prepared from iron dodecacarbonyl, the reaction times necessary being shorter (*ca.* 2 days).

Separation of the Guaiazuleneiron Carbonyl Isomers.—The mixture (300 mg.) was placed on a 90×3 cm. column of alumina (Brockmann grade 2) and eluted with 1 : 4 chloroform–light petroleum for 4 hr. Clean separation was obtained and the two isomers appeared to be present in approximately equal quantities in agreement with the estimate from nuclear magnetic resonance spectra. The first fraction is referred to as isomer A; the later isomer is called B.

¹³ Bauder and Gunthard, *Helv. Chim. Acta*, 1958, **41**, 889.

Under the same conditions little, if any, separation of the 4-methylazuleneiron carbonyl complex was obtained.

Interaction of Manganese Carbonyl and Azulenes.—Azulene (0.3 g.) and the carbonyl (1.0 g.) were heated for 36 hr. under reflux in light petroleum (b. p. 100–120°) (30 c.c.). After removal of solvent at 60°/0.1 mm. and unchanged carbonyl and azulene, extraction of the residue with light petroleum (b. p. 60–80°) followed by chromatography in nitrogen on alumina and crystallisation afforded *diazulenedimanganese hexacarbonyl* (0.04 g.) (see Table 3). In a similar manner *di-(4,6,8-trimethylazulene)dimanganese hexacarbonyl* was prepared.

Interaction of Molybdenum Carbonyl and Azulenes.—Azulene (0.4 g.) and excess of carbonyl were refluxed for 15 hr. in light petroleum (b. p. 100–120°) (50 c.c.). Removal of solvent at 20°/0.5 mm. and unchanged carbonyl at 60°/0.2 mm. gave a black solid, which was washed with light petroleum (4 × 20 c.c.) and extracted with chloroform (2 × 50 c.c.). At –20°, the filtered chloroform extracts gave *azulenedimolybdenum hexacarbonyl* (see Table 3) (0.17 g.) as fine black crystals.

Similar preparations gave *guaiazulene-* and *4,6,8-trimethylazulene-dimolybdenum hexacarbonyl*.

Decomposition of Azulenedimolybdenum Hexacarbonyl.—The complex (0.03 g.) was dissolved in chloroform (15 ml.) and left in the presence of air for 6 days. Solvent was removed at 20°/20 mm. and the residue extracted with light petroleum. Concentration of the extracts followed by chromatography on alumina yielded azulene (0.0054 g., 68%, estimated spectrophotometrically).

The guaiazuleneiron pentacarbonyl complex was decomposed and guaiazulene recovered similarly.

Magnetic Susceptibilities.—These were measured by the Gouy method, with finely powdered solids, at 298–100° K and with two field strengths.

Absorption Spectra.—Measurements were made with 1-cm. silica cells in a Perkin–Elmer model 4000 spectrophotometer.

Infrared Spectra.—Measurements were taken on a Perkin–Elmer model 21 instrument with calcium fluoride and sodium chloride optics. Details of the spectra of the guaiazuleneiron isomers are (4000–1350 cm.⁻¹ in CCl₄ with CaF₂; 1350–620 cm.⁻¹ in CS₂ with NaCl):

Isomer A: 2961s, 2920s, 2866s, 2033vs, 1985vs, 1967vs, 1664vs, 1626w, 1464s, 1455s, 1437m, 1387s, 1368s, 1327w, 1318w, 1292m, 1286m, 1258m, 1214w, 1179m, 1161w, 1095m, 1083m, 1051m, 1042m, 1032m, 995m, 944m, 920w, 886m, 827s, 805m, 782w, 703m, 684m, 628m cm.⁻¹.

Isomer B: 2961s, 2920s, 2866s, 2032vs, 1988vs, 1966vs, 1685w, 1620w, 1462s, 1455s, 1444m, 1386s, 1368s, 1343w, 1331w, 1302m, 1282w, 1258m, 1228m, 1179w, 1161w, 1095m, 1077m, 1059m, 1043m, 1032m, 989m, 975w, 938w, 922w, 876m, 858m, 842m, 822m, 805w, 778w, 710s, 679m, 650m, 628m cm.⁻¹.

Dipole Moments.—Benzene solutions were measured at 25° ± 0.1° with a heterodyne-beat capacitance meter similar to that described by Sutton and Hill¹⁴ with a modified Sayce–Briscoe cell.¹⁵ The dipole moments were calculated by Guggenheim's method.¹⁶ The equation used was

$$P_0 = \frac{3M_2}{d_1} \left[\left(\frac{\Delta\epsilon}{w} \right)_{w \rightarrow 0} / (\epsilon_1 + 2)^2 - \left(\frac{\Delta n^2}{w} \right)_{w \rightarrow 0} / (n_1^2 + 2)^2 \right]$$

where $\Delta\epsilon$ is the difference in dielectric constant of the solution, ϵ_{12} , and pure solvent, ϵ_1 ; Δn^2 is the difference in the squares of the refractive index of the solution, n_{12}^2 , and pure solvent, n_1^2 , and w is the weight fraction of the solute. Since the azulene–iron complex is highly coloured and refractive-index measurements could not be made, the Guggenheim method could not be applied directly. However it can be shown¹⁷ that

$$\left(\frac{\Delta n^2}{w} \right)_{w \rightarrow 0} = \frac{d_1(n_1^2 + 2)^2}{3M_1} \left[\frac{M_1 R_2}{M_2} - R_1(1 - k) \right]$$

where R_2 is the calculated molar refractivity of the solute, R_1 the molar refractivity of the

¹⁴ Sutton and Hill, *J.*, 1953, 1482.

¹⁵ Sayce and Briscoe, *J.*, 1925, 127, 315.

¹⁶ Guggenheim, *Trans. Faraday Soc.*, 1949, 45, 714; *Proc. Phys. Soc.*, 1955, 68, B, 186.

¹⁷ Cf. Harris, Le Fèvre, and Sullivan, *J.*, 1953, 1622.

solvent, M_2 and M_1 the molecular weights of the solute and the solvent, respectively, and d_1 the density of the solvent. The constant k is given by $k = 1 - d_1 V_2$ when V_2 (the specific volume of the solute) is derived from the relation $V_2 = \frac{1}{d_1} \left(1 - \frac{d_{12} - d_1}{d_{12} w} \right)$, d_{12} being the density of one solution in which the solute weight fraction is w .

The molar refractivity of the azulene complex was calculated from atomic refractivity values of azulene = 44.4,¹⁸ Fe = 18.55 [Fe(CO)₅ = 41.7,¹⁹ CO = 4.63²⁰]. The dipole moments calculated in this way involve the approximation for the atom polarisation, P_A , suggested by Guggenheim. Since the specific volume, V_2 , has been determined, any other approximation for P_A (such as $P_A = 0.05P_e$) can be used and the revised dipole moments calculated from the expression given by Smith.²¹ The dielectric constant of benzene at 25° was taken as 2.2727.

$$R_1 = 26.18;^{20} R_2 = 104.6; V_2 = 0.540 \text{ ml./g.}$$

w	0.002185	0.003333	0.003908	0.004559	0.005531	0.006204
$\epsilon_{12} - \epsilon_1$	0.01214	0.01787	0.02214	0.02124	0.03412	0.03555
$(\epsilon_{12} - \epsilon_1)/w$	5.557	5.361	5.665	4.659	6.169	5.730

$$\left(\frac{\Delta n^2}{w} \right)_{w \rightarrow 0} = 0.6143; \left(\frac{\Delta \epsilon}{w} \right)_{w \rightarrow 0} = 5.12; P_0 = 322.4 \text{ c.c. } \mu = 3.97 \pm 0.07 \text{ D.}$$

High-resolution Proton Magnetic Resonance Measurements.—The spectra were recorded at $22^\circ \pm 1^\circ \text{C}$ at frequencies of 56.4 and 40 mc./sec. with Varian spectrometers V-4311 and 4310C respectively, together with the associated 12" magnet system. The samples were contained in Pyrex spinning tubes of 5 mm. outside diameter; a little tetramethylsilane was usually added to the solution as an internal reference standard. Line positions were measured by the conventional side-band technique.

The parent azulenes were measured in solution in carbon tetrachloride; the iron complexes, which are not sufficiently soluble in this solvent, were measured in solution in chloroform, and some were also measured in solution in deuteriochloroform or methylene chloride, to ensure that no lines were obscured by the single resonance line of the chloroform.

In the following lists, the line positions in each spectrum are given in order of increasing field strength. The data for each line are presented in the following order: centre position of line, in p.p.m. and/or c./sec. on the low-field side relative to tetramethylsilane as zero; relative intensity; splitting in c./sec.; assignment, and source of observed splitting. The data at 40 and 56.4 mc. sec. are in full agreement, and the differences between them are quoted only when they are significant, *e.g.*, to demonstrate the occurrence of an AB pair. In all cases the values of the splittings, which are produced by the field-independent electron-coupled interaction, are the same at the two measuring frequencies.

*Azulene.*⁸ 8.20 p.p.m., two protons, each a doublet (~ 8.8 c./sec.) with additional structure, $H_{(4)}$ and $H_{(6)}$, split by $H_{(5)}$ and $H_{(7)}$ respectively, and by more distant protons; 7.81 p.p.m., one proton, triplet ($3.7_5 \pm 0.2$ c./sec.), $H_{(2)}$, split by $H_{(1)}$ and $H_{(3)}$; [7.49 p.p.m., part of $H_{(6)}$ triplet]; 7.28 p.p.m., two protons, each a doublet (3.9 ± 0.2 c./sec.), $H_{(1)}$ and $H_{(3)}$, each split by $H_{(2)}$; approx. 7.3₂ p.p.m., one proton, complex triplet (~ 9.5 c./sec.), $H_{(6)}$ split by $H_{(5)}$ and $H_{(7)}$; ~ 7.03 p.p.m., two protons, complex doublet (~ 8.8 c./sec.), doublet (~ 9.5 c./sec.), $H_{(5)}$ and $H_{(7)}$, each split by $H_{(6)}$ and by $H_{(4)}$ and $H_{(8)}$ respectively (the inner components of the lines at 7.3₂ and 7.0₃ overlap to give a line at 7.18 p.p.m.).

1,3-Dideuteroazulene. 8.20 p.p.m., as for azulene (although not identical), $H_{(4)} + H_{(8)}$; 7.78 p.p.m., one proton, singlet (width = 2 c./sec.), $H_{(2)}$; 7.49 p.p.m., part of $H_{(6)}$ triplet; remainder of spectrum ($H_{(5)}$, $H_{(6)}$, $H_{(7)}$) as for azulene.

4,6,8-Trimethylazulene. 7.50 p.p.m., triplet (3.9 ± 0.1 c./sec.), $H_{(2)}$, split by $H_{(1)}$ and $H_{(3)}$; 7.15 p.p.m., two protons, each a doublet (3.9 ± 0.1 c./sec.), $H_{(1)}$ and $H_{(3)}$, each split by $H_{(2)}$; 6.75 p.p.m., two protons, singlet (2.3 c./sec. width), $H_{(5)}$ and $H_{(7)}$; 2.68 p.p.m., six protons, singlet, 4- and 8-methyl groups; 2.39₅ p.p.m., three protons, singlet, 6-methyl group.

Guaiazulene (7-isopropyl-1,4-dimethylazulene). 8.07 p.p.m., one proton, doublet (1.9 ± 0.2

¹⁸ Wheland and Mann, *J. Chem. Phys.*, 1949, **17**, 264.

¹⁹ Weiss, *Z. anorg. Chem.*, 1956, **287**, 223.

²⁰ Landolt-Börnstein, "Tabellen," 1923, Vol. II.

²¹ Smith, *Trans. Faraday Soc.*, 1950, **46**, 394.

c./sec.), $H_{(8)}$ split by $H_{(6)}$; 7.50 p.p.m., one proton, doublet (3.9 ± 0.2 c./sec.), $H_{(2)}$ split by $H_{(3)}$; 7.20 p.p.m., one proton, doublet (11.2 ± 0.3), doublet (1.8 ± 0.3 c./sec.), $H_{(6)}$ split by $H_{(5)}$ and by $H_{(8)}$; 7.06 p.p.m., one proton, doublet (~ 3.9 c./sec.), $H_{(3)}$ split by $H_{(2)}$; 6.79 p.p.m., one proton, doublet (11.2 ± 0.3 c./sec.), $H_{(6)}$ split by $H_{(6)}$; 2.97 p.p.m., one proton, five components of expected septuplet (6.8 ± 0.2 c./sec.), tertiary isopropyl proton, split by the six protons of isopropyl methyl groups; 2.71 p.p.m., three protons, singlet, (?) 4-methyl group; 2.63 p.p.m., three protons, singlet, (?) 1-methyl group; 1.31 p.p.m., six protons, each a doublet (6.8 ± 0.2 c./sec.), isopropyl methyl groups, split by tertiary proton.

4-Methylazulene. 8.10 p.p.m., one proton, doublet (9.0 ± 0.3 c./sec.) with additional structure, $H_{(8)}$ split by $H_{(7)}$ and by more distant protons; 7.70 p.p.m., one proton, triplet (3.9 ± 0.2 c./sec.), $H_{(2)}$ split by $H_{(1)}$ and $H_{(3)}$; 7.23 p.p.m., two protons, each a doublet (3.8 ± 0.2 c./sec.), $H_{(1)}$ and $H_{(3)}$, each split by $H_{(2)}$; remaining lines in this band (not assigned) at 7.10 p.p.m., (? doublet, 1.7 c./sec.), 6.96, 6.92, 6.82, 6.75 (? doublet, 1.5 c./sec.) and 6.64 p.p.m., from $H_{(5)}$, $H_{(6)}$, and $H_{(7)}$; 2.69 p.p.m., three protons, singlet, 4-methyl group.

Azulenedi-iron pentacarbonyl. Band centred at ~ 5.36 p.p.m., \sim two protons, structure complex, ? $H_{(6)}$ and $H_{(7)}$; band centred ~ 5.08 p.p.m., \sim three protons, structure complex, ? $H_{(2)}$, $H_{(3)}$, and $H_{(4)}$; 4.76 p.p.m., one proton, doublet (5.8 ± 0.3 c./sec.), doublet (1.4 ± 0.2 c./sec.), probably $H_{(8)}$ split by $H_{(7)}$ and by (?) $H_{(6)}$; 3.70 p.p.m., one proton, "triplet" (2.1 ± 0.3 c./sec.), $H_{(1)}$ split by $H_{(2)}$ and $H_{(3)}$; 3.48 p.p.m., one proton, "triplet" (~ 8.7 c./sec.), $H_{(6)}$, split by $H_{(5)}$ and $H_{(7)}$.

1,3-Dideuteroazulenedi-iron pentacarbonyl. Band centred at ~ 5.34 p.p.m., \sim two protons, complex, ? $H_{(5)}$ and $H_{(7)}$; band centred ~ 5.1 p.p.m., \sim two protons, ? $H_{(2)}$ (at ~ 5.06 p.p.m.) and $H_{(4)}$; 4.77 p.p.m., one proton, doublet (5.8 ± 0.3 c./sec.), doublet (1.4 ± 0.2 c./sec.), probably $H_{(8)}$ split by $H_{(7)}$ and by (?) $H_{(6)}$; 3.46 p.p.m., one proton, "triplet" (~ 8.5 c./sec.), $H_{(6)}$, split by $H_{(5)}$ and $H_{(7)}$.

4,6,8-Trimethylazulenedi-iron pentacarbonyl. Band at ~ 5.2 p.p.m., (line positions 5.23, 5.20, 5.18, 5.13, 5.06₅, 5.02₅), four protons, complex, represents $H_{(2)}$, $H_{(3)}$, $H_{(5)}$, and $H_{(7)}$; 3.85 p.p.m., one proton, doublet (2.9 ± 0.1 c./sec.), doublet (1.9 ± 0.1 c./sec.), $H_{(1)}$ split by $H_{(2)}$ and $H_{(3)}$; 2.09₈ p.p.m., three protons, singlet, 8-methyl group; 1.76 p.p.m., three protons, singlet, 6-methyl group; 1.61₂ p.p.m., three protons, each a doublet (1.4 ± 0.2 c./sec.), 4-methyl group split by $H_{(5)}$.

4-Methylazulenedi-iron pentacarbonyl. (The intensities are assigned for a mixture of two isomers in approximately equimolar amounts. The positions around the azulene rings in these isomers are specified by the numbering shown in III.) Low-field band (line positions 5.45, 5.30, 5.27, 5.12, 5.08, 5.02, 4.97, 4.85, 4.76₅, 4.63 p.p.m.), \sim ten protons at positions 2, 3, 5, 7, and 8 in the 4-methyl isomer, and 2, 3, 4, 5, and 7 in the 8-methyl isomer; 3.87 p.p.m., one proton, "triplet" (2.2 ± 0.2 c./sec.), $H_{(1)}$ in one isomer, split by $H_{(2)}$ and $H_{(3)}$; 3.66 p.p.m., one proton, doublet (2.8 ± 0.2 c./sec.), doublet (1.8 ± 0.2 c./sec.), $H_{(1)}$ in other isomer, split by $H_{(2)}$ and $H_{(3)}$; 3.38 p.p.m., one proton, "triplet" ($\sim 7.9 \pm 0.3$ c./sec.), doublet (1.4 ± 0.2 c./sec.), $H_{(6)}$ of one isomer, split by $H_{(5)}$ and $H_{(7)}$ and by another proton (? $H_{(4)}$ or $H_{(8)}$); 3.24 p.p.m., one proton, "triplet" ($\sim 7.2 \pm 0.3$ c./sec.), doublet (1.7 ± 0.2 c./sec.), $H_{(6)}$ of other isomer; 2.11 p.p.m., three protons, singlet, 8-methyl group in 8-methyl isomer; 1.58 p.p.m., three protons, each a doublet (1.3 ± 0.1 c./sec.), 4-methyl group in 4-methyl isomer, split by $H_{(5)}$.

Assignments of Nuclear Magnetic Resonance Spectra.—The arguments for the assignments are as follows:

The resonances of some of the ring protons in the azuleneiron complexes occur at higher fields than others, and measurements of the relative areas under the peaks show that the higher-field lines at *ca.* 3.5 p.p.m. represent two of the eight ring protons in $C_{10}H_8Fe_2(CO)_5$ and only one proton in $C_{10}H_6D_2Fe_2(CO)_5$ and in the 4,6,8-trimethyl derivative. Hence the two proton resonances at the higher field in $C_{10}H_8Fe_2(CO)_5$ are due to protons in different rings, one being either $H_{(1)}$ or $H_{(3)}$ and the other one of $H_{(4)}$, $H_{(6)}$, or $H_{(8)}$. In the 4,6,8-trimethyl compound, the line at 3.85 p.p.m. assigned to $H_{(1)}$ (or $H_{(3)}$) appears as a double doublet, presumably owing to electron-coupled spin-spin interaction in the five-membered ring, first, with $H_{(2)}$ and then with $H_{(3)}$ (or $H_{(1)}$) which is not equivalent to $H_{(1)}$ (or $H_{(3)}$). The "high-field" proton from the seven-membered ring is best assigned as $H_{(6)}$, the line being split into a triplet by coupling (not necessarily equally) with the protons $H_{(5)}$ and $H_{(7)}$. The higher-field band (*ca.* 3.5 p.p.m.) in $C_{10}H_8Fe_2(CO)_5$ appears to be a superposition of the double doublet and broader triplet lines.

The difference between the spectra of the compounds $C_{10}H_8Fe_2(CO)_5$ and $C_{10}H_6D_2Fe_2(CO)_5$

shows that $H_{(2)}$ is centred at *ca.* 5.04 p.p.m. The proton resonances of $H_{(5)}$ and $H_{(7)}$ must be split by $H_{(6)}$ and also by $H_{(4)}$ and $H_{(8)}$ respectively (as observed in the parent hydrocarbons), but the combination of several shifts and splittings makes the spectrum complicated. However, the double doublet observed at *ca.* 4.77 p.p.m., which represents a single proton, appears to be a chemically shifted proton; this probably implies that at least one of the protons of the 4,8- or 5,7-pair is not equivalent to the other proton of the pair.

Since the positions of the $H_{(5)}$ and $H_{(7)}$ resonances in the parent hydrocarbons are shifted on introduction of methyl substituents into the ring, we cannot assign $H_{(5)}$ and $H_{(7)}$ of $C_{10}H_8Fe_2(CO)_5$ by direct comparison with the spectrum of the 4,6,8-trimethylazuleneiron complex. The latter does show, however, that the 4- and the 8-methyl group are *not equivalent* since *three* chemically shifted methyl peaks are observed. In addition, only one of the three peaks shows a doublet structure, which may result from a coupling to a single ring proton, probably $H_{(5)}$ or $H_{(7)}$. Comparison of the 4,6,8-trimethyl- with the 4-methyl-azulene complex suggests that the doublet can be assigned to the 4- or the 8-methyl group. Thus the spectra of the above three azulene complexes confirm the non-equivalence of the 4,8- and 5,7-positions.

The lines in the spectra of the alkyl derivatives can be assigned as follows. In the spectrum of the 4-methylazulene compound there are two methyl peaks, a singlet at 2.11 p.p.m. and a doublet at 1.58 p.p.m.; these positions correspond to two of the three methyl-group resonances observed in the 4,6,8-trimethylazulene derivative. Guaiazulene isomer A has a singlet methyl resonance at 2.1 p.p.m., and isomer B appears to have a doublet methyl peak at 1.5 p.p.m. (partly obscured by the isopropyl-methyl resonances). Thus all the compounds show similar and distinguishable lines for methyl groups in the 4- or 8-position. Both of these lines occur with the 4,6,8-trimethyl derivative but only one of them occurs with guaiazulene isomer A, and only the *other* in isomer B. The presence of the same *two* lines in the 4-methylazulene compound indicates an isomeric mixture, and a similar duplication of other lines (see below) supports this interpretation.

The doublet structure on the methyl peak in all the methyl complexes at *ca.* 1.5—1.6 p.p.m. is field-independent and presumably therefore represents an electron-coupled spin-spin interaction with a single ring proton, probably that adjacent on the seven-membered ring. The 6-methyl group in the 4,6,8-trimethylazulene complex gives a singlet at 1.76 p.p.m. and the peak for the methyl group on the five-membered ring in the guaiazulene compounds occurs at 1.53 p.p.m. with isomer B and is coincident with the other methyl resonance at 2.10 p.p.m. for A.

The remaining high-field lines in the spectra of isomers A and B appear to have the features normally found in an isopropyl group although the lines are at different positions for the two isomers. For B, the doublet methyl resonance (intensity 6, splitting 6.7 c./sec.) is centred at 1.41₅ p.p.m., being partly obscured by the other methyl peaks, and the resonance of the tertiary isopropyl-proton is centred at 2.63 p.p.m. (only five of the expected seven components, splitting *ca.* 6.7 c./sec., could be clearly observed, probably since the outer components are too weak). The resonance for the tertiary proton in isomer A appears to be centred at *ca.* 2.17 p.p.m. where it is partially obscured. The doublet (splitting 6.7 c./sec.) methyl resonance is centred at 0.942 and 0.911 p.p.m., showing a smaller doublet structure which, in contrast to the main splitting, is field-dependent and must represent a small chemical shift. For the guaiazulene and 4-methylazulene compounds, the lines which can be assigned to the $H_{(6)}$ and $H_{(1)}$ or $H_{(3)}$ occur at markedly higher fields than those of the remaining ring protons. The double doublet at 3.24 p.p.m. for isomer B is assigned to $H_{(6)}$, the large splitting (8.9 c./sec.) being produced by the adjacent proton and the smaller splitting by a more distant proton. In the 4-methylazulene mixture, where there are adjacent protons on both sides, $H_{(6)}$ appears to show a main splitting into a triplet.*

Guaiazulene isomer A also shows a doublet line at 3.74 p.p.m. which is absent in isomer B. This line must represent the proton $H_{(1)}$ or $H_{(3)}$ (split into a doublet by $H_{(2)}$) which is moved up field (cf. ref. 3). For isomer B, this particular position on the five-membered ring must be blocked by the methyl group.

As mentioned above, the $H_{(1)}$ or $H_{(3)}$ resonance in the 4,6,8-trimethylazulene derivative occurs at 3.84₅ p.p.m. as a double doublet, and the two lines at 3.87 (triple) and 3.66 p.p.m. (double doublet) in the 4-methylazulene isomeric mixture can be assigned similarly, one to

* The observed quartet could result from partial overlapping of two such triplets, one from each isomer. In agreement, the separation between the two middle peaks of the quartet is a chemical shift.

$H_{(1)}$ or $H_{(3)}$ in one isomer, and one to the same position in the other isomer, the structure in each case arising from coupling with the other two protons on the five-membered ring.

The symmetrical group of four lines in guaiazulene isomer B, which is centred at 5.03 p.p.m., represents the other two protons on the five-membered ring. The proton adjacent to $C_{(6)}$ appears to be centred at 5.3 p.p.m. and shows a main doublet splitting by $H_{(6)}$ of *ca.* 9 c./sec.; in addition, each doublet component shows fine structure, apparently a quartet, which would arise from a splitting by the three equivalent protons of the adjacent methyl group. The remaining doublet at 4.67 p.p.m. is assigned to the remaining proton at the 4- or 8-position split by either $H_{(6)}$ or the tertiary proton of the isopropyl group.

For isomer A, the doublet at 5.02 p.p.m. represents $H_{(2)}$, the splitting (2.8 c./sec.) being the same as that of the doublet ($H_{(1)}$ or $H_{(3)}$) at 3.74 p.p.m. The proton adjacent to $C_{(6)}$ is a doublet (splitting *ca.* 8.5 c./sec.) centred at 5.21 p.p.m. and the remaining proton, on $C_{(4)}$ or $C_{(8)}$, at *ca.* 5.19 p.p.m.

For the other azulene iron complexes it is difficult to make unambiguous assignment of the remaining low-field lines since there is an intricate combination of overlapping shifts and splittings.

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