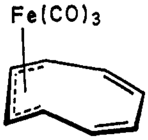
The Molecular Dynamics of Fluxional Molecules in the Solid State

By A. J. CAMPBELL, C. A. FYFE,* and E. MASLOWSKY, JUN.
(*Chemistry Department, University of Guelph, Guelph, Ontario, Canada*)

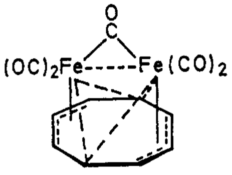
Summary 'Wide-line' n.m.r. measurements reveal that certain 'fluxional' organometallic molecules possess considerable motional freedom in the solid state which can be related to their bonding and reorientations in solution.

RECENTLY there has been considerable interest in the structure and bonding of 'fluxional' organometallic molecules.[1] The high resolution n.m.r. spectrum of cyclo-octatetraeneiron tricarbonyl (I) at room temperature shows a single ^1H resonance, while at 128 K it shows a multiplet structure.

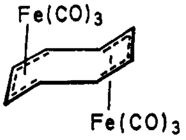
The 'wide-line' ^1H n.m r. spectrum of (I) in the solid state is very markedly temperature dependent. At room temperature it has a line width of 1·9 G and second moment of 1·0 G^2. On lowering the temperature the spectrum broadens in a transition centred at *ca.* 250 K to limiting low temperature values of 9·4 G and 7·9 G^2, respectively. Calculation of the theoretical second moment for a static system by the procedure of Van Vleck,[2] using the reported crystal structural data,[3] gives a second moment of 7·74 G^2, suggesting that at low temperatures the molecule is rigid in the lattice. Calculation of a theoretical second moment assuming reorientation of the cyclo-octatetraene ring gives a value of 0·75 G^2 in excellent agreement with the limiting high temperature value of 0·9 G^2 observed experimentally. Since *X*-ray diffraction results show no disorder in the ring carbon atoms,[3] this motion must involve simultaneous distortion and reorientation of the ring, so that as the molecule moves, the carbon atoms change positions and the ring takes up exactly the same position in the lattice as it had before rotation. It is only these positions of minimum energy that will be observed by *X*-rays. In the solid, the *X*-ray data reveal that the metal atom is fixed, and the total motion must therefore involve only rotation of the ring.



(I)



(II)



(III)

Similarly, solid state n.m.r. measurements, like those in solution,[4] show that the ring in $C_8H_8\cdot[Fe(CO)_3]_2$ (III) is rigidly fixed, suggesting that discrete bonding exists in this molecule. However in $C_8H_8\cdot Fe_2(CO)_5$ (II) the ring is mobile even at 77 K and it is unlikely that solution n.m.r. studies will yield a spectrum of the static form. Again, since *X*-ray studies show no disorder,[5] there must be simultaneous rotation and distortion of the ring.

Molecular reorientation is quite general in this type of organometallic molecules and occur in other cyclo-octatetraene–metal carbonyls and σ-bonded cyclopentadienyl complexes such as biscyclopentadienylmercury and cyclopentadienylmercury halides.

(*Received, June 2nd,* 1971; *Com.* 882.)

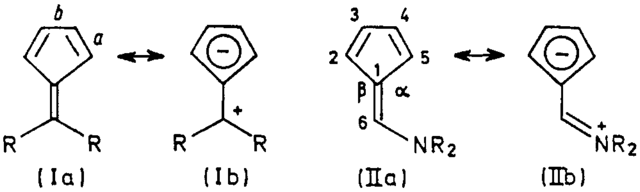
[1] F. A. Cotton, *Accounts. Chem. Res.*, 1968, **1**, 251.
[2] J. H. Van Vleck, *Phys. Rev.*, 1948, **74**, 1168.
[3] B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, 1962, **37**, 2084.
[4] C. E. Keller, G. F. Emerson, and R. Pettit, *J. Amer. Chem. Soc.*, 1965, **87**, 1388.
[5] E. B. Fleischer, A. L. Stone, R. B. K. Dewar, J. D. Wright, C. E. Keller, and R. Pettit, *J. Amer. Chem. Soc.*, 1966, **88**, 3158.

Nuclear Magnetic Resonance Coupling Constant–Bond Length Relationships for Fulvenes†

By HERMAN L. AMMON* and GEORGE L. WHEELER
(*Department of Chemistry, University of Maryland, College Park, Maryland* 20742)

Summary *X*-Ray crystal structure data for three fulvenes are reported, with several C–C bond distance–n.m.r. vicinal coupling constant relationships which should provide a reliable estimate of 5-membered ring bond lengths from n.m.r. data.

A NUMBER of recent investigations of the fulvenes (I) and 6-aminofulvenes (II) have attempted to evaluate the importance of dipolar canonical forms such as (Ib) and (IIb) from n.m.r. determinations of the 5-membered ring vicinal proton coupling constants and energy barriers to rotation about the exocyclic C=C and C–N bonds.[1] Evidence for π-delocalization and dipolar character in the



† Taken in part from a Ph.D. dissertation to be submitted by G. L. Wheeler to the Graduate School of the University of Maryland.

aminofulvenes has been obtained from comparisons of these data with appropriate aromatic and olefinic models, as well as from dipole moment measurements. Here we report crystal structure data for three fulvenes and several C–C bond length–coupling constant relationships which should prove useful for providing a rapid and reliable estimate of single–double bond alternation from n.m.r. measurements.

X-Ray data were obtained using either a Picker FACS-I (HOG monochromatized Mo-radiation) or a Siemens AED (Ni-filtered Cu-radiation) diffractometer and the 2θ–θ scan technique. Reflections with intensities greater than 3σ above background were considered observed. Structures were solved by direct methods and all were refined by full-matrix least-squares with anisotropic temperature factors for the C, N, and O atoms and isotropic terms for the H atoms.‡ Preliminary crystal data have been reported for 6-dimethylamino-2-formylfulvene (III).[2]

6-Dimethylaminofulvene (IV). Crystals (by sublimation) were monoclinic, space-group $P2_1$; $Z = 4$; $a = 5{\cdot}871(3)$, $b = 17{\cdot}294(9)$, $c = 9{\cdot}356(3)$ Å, $\beta = 128{\cdot}97(3)°$. Picker: 2θ maximum = 50°; 1453 reflections, 1125 observed. $R = 0{\cdot}049$.

N-(6-Anilinofulven-2-ylmethylene)aniline (V). Crystals (supplied by Dr. U. Müller-Westerhoff[3]) were orthorhombic, space-group $P2_12_12_1$; $Z = 4$; $a = 5{\cdot}468(1)$, $b = 20{\cdot}442(6)$, $c = 13{\cdot}088(3)$ Å. Siemens: $2\theta = 120°$; 1293 reflections, 760 observed. $R = 0{\cdot}023$.

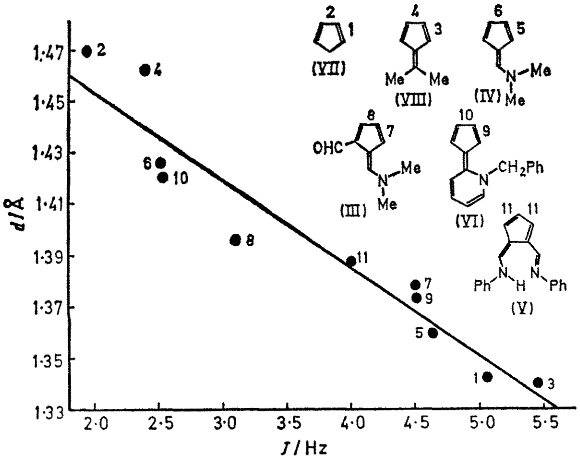


FIGURE 1. *Carbon–carbon distance* d (d_a *and* d_b) vs. *vicinal coupling constant* J (J_a *and* J_b) *for compounds* (III)—(VIII). *Arabic numerals are used to identify the fulvene bonds. The structural* (*first reference*) *and n.m.r.* (*second reference*) *data used in this plot were obtained from the following sources:* (III)[2,8]; (IV)[9,10], (V)[9,3]; (VI)[9,10]; (VII)[11,12]; (VIII)[13,14].

N-Benzyl-2-cyclopentadienylidene-1,2-dihydropyridine (VI) was recrystallized from benzene. Crystals were monoclinic, space-group $A2/a$; $Z = 8$; $a = 16{\cdot}199$, $b = 7{\cdot}973(2)$, $c = 20{\cdot}472(5)$ Å, $\beta = 95{\cdot}92(2)°$. Picker: $2\theta = 55°$; 3042 reflections, 2330 observed. $R = 0{\cdot}053$.

(III), (IV), and the 6-amino-2-methyleneaminofulvene portion of (V) are planar within experimental error. The two benzene ring planes in (V) deviate by an average of 21° from the central fulvene plane. In (VI), the cyclopentadiene and dihydropyridine rings are twisted by 20° about the exocyclic double bond and the benzene ring is inclined at 84° to the pyridine moiety. Some bond length and angle data are given in the Table.

TABLE. α *and* β *Bond angles and* a *and* b *bond lengths for fulvenes* (III)—(VI)

Compound	α	β	*a*/Å	*b*/Å
(III)[6]	133·3[a]	120·3[a]	1·377[a]	1·396[a]
(IV)	134·6[a]	119·6[a]	1·360[a]	1·426[a]
(V)	131·9	121·5	1·387	
(VI	132·8	121·3	1·373	1·420

[a] Average value obtained from two molecules.

In the unsymmetrical fulvenes (III), (IV), and (VI), the C(1) exocyclic angles nearest to the C(6) amino-group [*e.g.* α in (II)] average 13° larger than the opposite β angles. These data show that steric factors involving the *N*-substituents and the 5-membered rings are responsible for the differences in α and β. An earlier statement by us[2] relating a vinylogous amide resonance form to this difference in 6-dimethylamino-2-formylfulvene (III)[4] must thus be corrected.

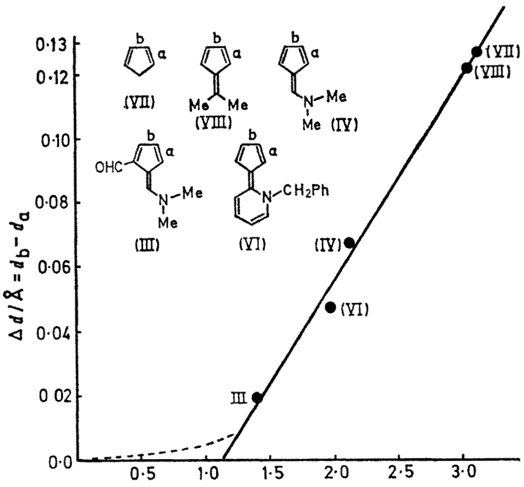


FIGURE 2. Δd(d_b − d_a) vs. ΔJ (J_a − J_b) *for compounds* (III), (IV), *and* (VI)—(VIII).

N.m.r. vicinal proton coupling constant data for planar, unsaturated systems provide a convenient and rapid method for estimating bond lengths and π-bond orders, which can in turn give a measure of ground state delocalization. Figures 1 and 2 present bond distance–coupling constant plots obtained from the available n.m.r. and structural data. A plot of single (bond *b*) and double (bond *a*) C–C distance *vs.* J_{vicinal} for cyclopentadiene and five fulvenes is shown in Figure 1. A least-squares fit for the 11 points gives d (Å) $= - 0{\cdot}035\ J$ (Hz) $+ 1{\cdot}523$ with a standard deviation of 0·013 Å. Figure 2 shows the relationship between Δd

---

‡ Calculations were done on the University of Maryland UNIVAC, 1108 computer with the 'Crystal Structure Program System,' ed. J. M. Stewart, Computer Science Center, University of Maryland.

and ΔJ, where $d = d_b - d_a$ and $\Delta J = J_a - J_b$, for (III), (IV), and (VI)—(VIII). A least-squares fit for the points gives Δd (Å) = 0·064 ΔJ (Hz) − 0·072 with a standard deviation of 0·004 Å. The linearity of the Δd *vs.* ΔJ plot is clearly better than that of the d *vs.* J plot.

The Δd *vs.* ΔJ line indicates that ΔJ values of *ca.* 1 Hz correspond to essentially equal *a* and *b* C–C distances and represent a lower limit for cyclopentadienes having sufficiently different proton chemical shifts to permit a clear measurement of J_a and J_b. The dashed portion of Figure 2, which presently has no experimental verification, has been added to account for cases like (V) and the 1,2-dimethoxycarbonylcyclopentadienide anion, each of which has equal *a* and *b* lengths and a single 5-membered J_{vicinal} value. Although structural data for the trimethylphosphonium and trimethylammonium cyclopentadienides are not now available, the ΔJ values of 1·04 and 0·88 Hz[6] place these materials on the dashed section of Figure 2 indicating a $d_b - d_a$ difference of 0·01 Å or less. The known chemical stability of triphenylphosphonium cyclopentadienide[7] is in accord with this prediction.

A third *d–J* equation, which should prove capable of predicting the 5-membered ring *a* and *b* distances within 0·01 Å or less, has been derived using the average *a* and *b* distance from (III)—(VIII) along with the Δd *vs.* ΔJ line of Figure 2: $d\ (\text{Å}) = 1{\cdot}395 + 0{\cdot}0636\,(J - \bar{J})\ (\text{Hz}) - 0{\cdot}0359\,(J - \bar{J})/|J - \bar{J}|$, where $\bar{J}$ is the average of J_a and J_b. This equation reproduces the *a* and *b* bond length data in (III)—(VIII) with a maximum deviation of 0·011 Å and an average deviation of 0·006 Å, whereas the Figure 1 line gives maximum and average differences of 0·022 and 0·011 Å

We are grateful to the National Science Foundation for support of this work. Computer time was made available, in part, through the facilities of the Computer Science Center, University of Maryland.

(*Received, June 7th,* 1971; *Com.* 917.)

[1] For a current review see P. Yates, *Adv. Alicyclic Chem.*, 1968, **2**, 59.

[2] H. L. Ammon and L. A. Plastas, *Chem. Comm.*, 1971, 356.

[3] U. Müller-Westerhoff, *J. Amer. Chem. Soc.*, 1970, **92**, 4849.

[4] Structure (IIIb), ref. 2.

[5] A. S. Kende, P. T. Izzo, and P. T. MacGregor, *J. Amer. Chem. Soc.*, 1966, **88**, 3359.

[6] W. B. Smith, W. H. Watson, and S. Chiranjeevi, *J. Amer. Chem. Soc.*, 1967, **89**, 1438.

[7] F. Ramirez and S. Levy, *J. Amer. Chem. Soc.*, 1957, **79**, 67.

[8] A. Mannschreck and V. Kölle, *Chem. Ber.*, 1969, **102**, 243.

[9] Unpublished work.

[10] J. H. Crabtree and D. H. Bertelli, *J. Amer. Chem. Soc.*, 1967, **89**, 5384.

[11] L. H. Scharpen and V. W. Laurie, *J. Chem. Phys.*, 1965, **43**, 2765.

[12] J. B. Lambert, L. J. Durham, P. Lepoutere, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1H65, **87**, 3896.

[13] J. F. Chiang and S. H. Bauer, *J. Amer. Chem. Soc.*, 1970, **92**, 261.

[14] W. B. Smith and B. A. Shoulders, *J. Amer. Chem. Soc.*, 1964, **86**, 3118.