Nuclear Magnetic Resonance Studies of Fulvenes[*1]

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Fulvene, a cross-conjugated non-alternant hydrocarbon, is of particular interest because of the relation of its properties to those of its isomer, benzene. Since 1900, when Thiele[1] reported the first synthesis of some simple fulvene derivatives, fulvene has been the subject of much research in both theoretical and experimental organic chemistry.[2,3] Some studies of the nuclear magnetic resonance spectra of fulvene derivatives described in the literature have dealt with 6-ethylfulvene,[4] 6-vinylfulvene,[5] 6-hydroxy-6-methyl-1-phenylazofulvene,[6] methylvinylfulvenes,[7] and fulvene itself.[8] A very recent paper on the nuclear magnetic resonance studies of some fulvene derivatives by Smith and Shoulders[9] has prompted us to report our own independent studies on the same subject.

In this paper, we will describe the proton magnetic resonance spectra of some fulvene derivatives, and we will discuss the magnetic constants, electron density, and especially the theoretical calculation of the ring current effect of the fulvene ring.

Experimental

The proton magnetic resonance spectra were taken with a Varian A-60 spectrometer on 10% (w./v.) solutions of the samples in carbon disulfide, containing tetramethylsilane as an internal standard at 60 Mc. p. s., and at room temperature. The chemical shifts are expressed as p. p. m. from tetramethylsilane.

All samples were synthesized according to the known procedures[2] and purified by vacuum distillation under a nitrogen atmosphere (6,6-dimethylfulvene, 6-ethyl-6-methylfulvene, 6,6-pentamethylenefulvene) or by recrystallization (6,6-diphenylfulvene, 1,2,3,4-tetraphenylfulvene).

Results and Discussion

The Analysis of the NMR Spectrum of 6,6-Diphenylfulvene.—The protons in the five-membered ring of 6,6-diphenylfulvene appear as a perfectly symmetrical twenty-line AA'BB' type[10-13] spectrum with chemical shifts of $\delta_A=\delta_{A'}=6.390$ and $\delta_B=\delta_{B'}=6.105$ p. p. m. The spectrum calculated from the magnetic parameters $\delta_A-\delta_B=0.285$ p. p. m., $J_{AB}=5.3_7$, $J_{AB'}=1.5_2$, $J_{AA'}=2.0_0$ and $J_{BB'}=2.2_8$ c. p. s., is in quite good agreement with the observed spectrum, as can be seen from Table I and Fig. 1.

TABLE I. A COMPARISON OF THE CALCULATED AND OBSERVED SPECTRA OF 6,6-DIPHENYLFULVENE

Line	Energy,[a] c. p. s.		Intensity[b]	
	Calcd.	Obs.	Calcd.	Obs.
8	4.3_1	4.4_5	0.2_3	0.2_9
4	5.4_1	5.7_9	1.4_9	2.5_7
3	5.7_9		1.3_7	
11	6.7_1	6.7_0	0.5_6	1.2_2
12	6.9_9	6.9_9	0.6_5	
7	8.6_7	8.7_3	0.8_1	0.8_6
6	9.8_0	9.9_2	0.7_3	0.7_9
9	10.5_7	10.8_5	0.4_3	0.7_9
10	10.8_5		0.3_5	
2	12.2_1	12.2_8	0.6_7	1.3_7
1	12.6_8	12.6_8	0.6_3	
5	14.1_7	14.2_1	0.0_8	0.0_9

a) Relative to the band center.
b) Normalized to the same total intensity as the calculated values.

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[9] W. B. Smith and B. A. Shoulders (*J. Am. Chem. Soc.*, **86**, 3118 (1964)) reported the analysis of the NMR spectra of 6,6-dimethylfulvene, 6,6-dibenzylfulvene and 6,6-diphenylfulvene; the charge density of the fulvene ring was also discussed briefly. Their results agree essentially with ours described in this paper.

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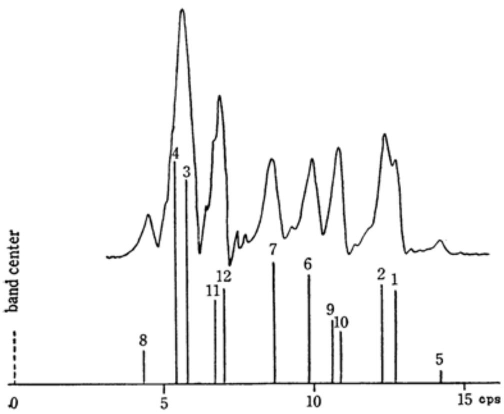
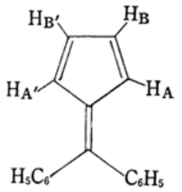


Fig. 1. The observed and calculated spectra of the ring proton of 6,6-diphenylfulvene (up-field portion).



The Electron Density of Fulvene.—The signals of the ring protons in 6,6-dimethylfulvene (6.27 p. p. m.), 6-ethyl-6-methylfulvene (6.28 p. p. m.), and 6,6-pentamethylenefulvene (6.31 p. p. m.) are different from those of 6,6-diphenylfulvene, and they are shifted to higher fields where they appear as singlets at almost the same position in each case. The proton at the 6-position of 1,2,3,4-tetraphenylfulvene appears as a singlet at 5.90 p. p. m. The signals arising from the fulvene ring protons show a shift from the olefinic protons of cyclopentadiene, (6.35 p. p. m.), while the 6-proton shows a shift from the olefinic protons of the methylenecycloalkanes [4.68±0.15 p. p. m.[14)]; these shifts are regarded as being due to the increased charge density on the fulvene nucleus and were calculated according to Schneider's equation.[15,16)] In the case of the phenyl derivatives, Pople's simple dipole approximation[17)] was used to calculate the effect of the diamagnetic shift caused by the ring current of the phenyl group. These diamagnetic shifts of the protons at the 1- or 4-position and at the 2- or 3-position in the 6,6-diphenylfulvene are 0.91 p. p.m. and 0.21 p. p.m. respectively. The shift of the proton at the 6-position of the 1,2,3,4-tetraphenylfulvene is 0.93 p. p. m. However, in the above calculations, the entire molecule was assumed to be coplanar, and the ring current of the fulvene ring was assumed to be small and was neglected. The validity of this assumption about the ring current effect of the fulvene ring was revealed by the theoretical calculations of the LCAO MO method (vide infra). The charge densities obtained were compared with the theoretical values calculated by the MO method and are shown in Table II.

It is clear from Table II that the charge densities obtained from the chemical shifts are in good agreement with those calculated by the MO method. In the case of the diphenylfulvene, however, the observed charge densities are rather high. If the non-planarity of the phenyl groups is allowed for, better results would be obtained. Charge migration from the phenyl group is thought to be responsible for the larger charge density at $C_{(1)}$ than at $C_{(2)}$.

TABLE II. ELECTRON DENSITIES (ρ) OF FULVENE

	ρ Derived from δ_H					ρ Calcd.	
	a)	b)	c)	d)	e)	Berthier[f)]	Nakajima Katagiri[g)]
$C_{(1)}$	1.009	1.008	1.005	1.083		1.017	1.019
$C_{(2)}$	1.009	1.008	1.005	1.043		1.016	1.018
$C_{(5)}$						1.038	1.016
$C_{(6)}$					0.974	0.897	0.916

a) 6,6-Dimethylfulvene
b) 6-Ethyl-6-methylfulvene
c) 6,6-Pentamethylenefulvene
d) 6,6-Diphenylfulvene
e) 1,2,3,4-Tetraphenylfulvene
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TABLE III. RING CURRENT SHIELDING IN FULVENE

k	Relative to benzene[a]			Calculated shielding constants (p. p. m.)[b]		
	$\bar{\sigma}_{F(1)}/\bar{\sigma}_B$	$\bar{\sigma}_{F(2)}/\bar{\sigma}_B$	$\bar{\sigma}_{F(6)}/\bar{\sigma}_B$	$\bar{\sigma}_{F(1)}$	$\bar{\sigma}_{F(2)}$	$\bar{\sigma}_{F(6)}$
1.0	0.118	0.116	0.041	0.206	0.202	0.072
0.8	0.047	0.046	0.016	0.082	0.081	0.028
0.6	0.011	0.010	0.004	0.020	0.019	0.007

a) $\bar{\sigma}_B$ and $\bar{\sigma}_F$ are the shielding constants for benzene and fulvene respectively. The position of each proton in fulvene is shown in parentheses.

b) Based on an experimental estimate of 1.75 p. p. m. for the ring current shift in benzene.[20]

The Ring Current Effect in Fulvene. — The ring current effect of the fulvene ring was not considered in the previous calculations of the charge density. It is important, however, to decide whether the ring current effect, which depends on the aromaticity of fulvene, can, in fact, be neglected. The chemical shift of each proton in fulvene was calculated by the use of the LCAO MO theory of McWeeny.[18] In this case, electron diffraction data[19] for dimethylfulvene were used to obtain the following dimensions for the fulvene nucleus; $C_{(1)}-C_{(2)}=C_{(3)}-C_{(4)}=C_{(5)}-C_{(6)}=1.382\,\text{Å}$, $C_{(1)}-C_{(5)}=C_{(4)}-C_{(5)}=C_{(2)}-C_{(3)}=1.496\,\text{Å}$, $\angle C_{(1)}C_{(2)}C_{(3)}=109°$, $\angle C_{(5)}C_{(1)}C_{(2)}=107°46'$, and $\angle C_{(1)}C_{(5)}C_{(4)}=106°20'$. The fulvene nucleus in diphenylfulvene is non-benzenoid; therefore, one needs to allow for bond alternation by using the bond-alternation parameters $k=\beta_{\text{single}}/\beta_{\text{double}}$ (no magnetic field) of 1.0, 0.8 and 0.6 respectively. The results are shown in Table III.

The theoretical ratio, $\bar{\sigma}_F/\bar{\sigma}_B$, when $k=1$, is about 0.1; when $k=0.6$, it decreases to a very small value. The chemical shift of each proton in fulvene was calculated by using the estimated ring current shift of benzene. Nakajima and Katagiri[21] have proposed $k=0.57$ as a reasonable value for fulvene. Therefore, as can be seen from Table III, the chemical shift induced by the π-electron ring current in fulvene is very small and can be neglected. Although the difference is small, the chemical shift of the $C_{(1)}$ proton is larger than that of the $C_{(2)}$ proton. However, the opposite might be expected from a consideration of the charge densities. The fact that the ring protons in 6,6-dialkylfulvene appear as a singlet may be ascribed to the above opposing effects.

The calculations were made on a NEAC-2230 computer at the Tohoku University Computing Center. Some of the NMR spectra were measured at the Research Institute of the Shionogi Pharmaceutical Company, to which company we express our gratitude.

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