

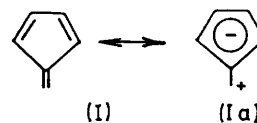
Nuclear Magnetic Resonance Study of Dipolar Contribution to the Ground State in a Series of Fulvenes

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A series of fulvenes derived from isodicyclopentadiene has been prepared and their n.m.r. spectra studied. The simple low-field spectrum enabled immediate assignment of H_α and both $H_{\gamma\text{-cis}}$ and $H_{\gamma\text{-trans}}$. The shifts are correlated with π -electron densities calculated for a model compound and the transmission of charge from the α -carbon to the five-membered ring was found to be between that for styrenes and *trans*-cinnamic acids.

SEVERAL theoretical and experimental approaches have been made to the problem to what extent dipolar forms, e.g., (Ia), which might show a higher degree of 'aromaticity,' contribute to the ground state of the fulvene system.¹ Amongst the methods employed was n.m.r. spectroscopy.²⁻⁷ However, it is known that the use of chemical shifts must be viewed with caution as especially Berson and co-workers^{8,9} have convincingly pointed out. The chemical shifts are influenced by such factors as substituent and group magnetic anisotropies and electric fields, which depend strongly on structural differences. We believed, however, that in a series of 6-substituted fulvenes, in which the contribution of the dipolar form

would become more pronounced with increasing electron-donating character of the *para*-substituent, the application of n.m.r. techniques would be unequivocal.



The increase in π -electron density on the ring carbon atoms due to such a contribution should cause an upfield shift of the corresponding proton chemical shifts.^{10,11} We have been encouraged in our approach by the observation that in a series of *para*- and *meta*-substituted

¹ (a) For a comprehensive survey of the chemistry of fulvenes see E. D. Bergmann, *Chem. Rev.*, 1968, **68**, 41; (b) for a comprehensive study of molecular geometry, bond energy, and reactivity, see D. H. Lo and M. A. Whitehead, *Tetrahedron*, 1969, **25**, 2615.

² (a) A. P. Downing, W. D. Ollis, and I. O. Sutherland, *J. Chem. Soc. (B)*, 1969, 111, and references therein; (b) A. Mannschreck and U. Koelle, *Tetrahedron Letters*, 1967, 863; (c) W. B. Smith and B. A. Shoulders, *J. Amer. Chem. Soc.*, 1964, **86**, 3118; (d) Y. Kitahara, *Bull. Chem. Soc. Japan*, 1965, **38**, 780.

³ H. L. Heffernan and A. L. Jones, *Austral. J. Chem.*, 1966, **19**, 1813.

⁴ W. B. Smith, W. H. Warson, and S. Chiranjeevi, *J. Amer. Chem. Soc.*, 1967, **89**, 1438.

⁵ A. P. Downing, W. D. Ollis, and I. O. Sutherland, *Chem. Comm.*, 1967, 143.

⁶ A. Kende, P. T. Izzo, and W. Fulmor, *Tetrahedron Letters*, 1966, 3697.

⁷ J. H. Crabtree and D. J. Bertelli, *J. Amer. Chem. Soc.*, 1967, **89**, 5384.

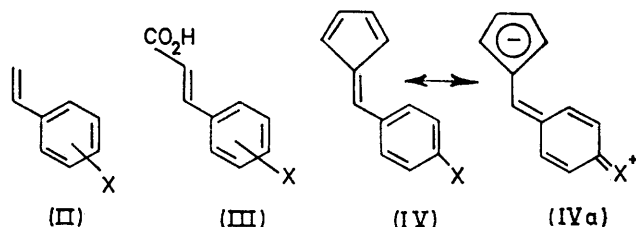
⁸ E. M. Evleth, jun., J. A. Berson, and S. L. Manatt, *Tetrahedron Letters*, 1964, 3087.

⁹ J. A. Berson, E. M. Evleth, jun., and S. L. Manatt, *J. Amer. Chem. Soc.*, 1965, **87**, 2901.

¹⁰ G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Amer. Chem. Soc.*, 1960, **82**, 5846.

¹¹ H. Spiessicke and W. G. Schneider, *Tetrahedron Letters*, 1961, 468.

styrenes (II), *trans*-cinnamic acids (III), and similar compounds, the magnetic anisotropy and electric field changes at positions α and β were negligible (or possibly cancelled out)¹² and the X substituent is so far removed from the protons that the changes in the magnetic anisotropy of the phenyl ring resulting from mono-substitution are small. Linear correlations between proton chemical shifts and π -electron densities as calculated by the MO method were reported for these compounds.¹³



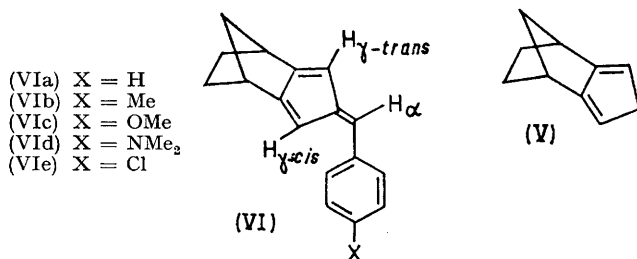
Such a series of compounds of structure (IV) has been studied previously by other physical methods¹⁴ with the result that in the sequence X = H, Me, OMe, or NMe₂ the contribution of (IVa) to the ground state increases.

TABLE I

Compound	Crystals	M.p./°C	Formula	Found/%			Required/%		
				C	H	N	C	H	N
(VIa)	Light yellow	61—73	C ₁₇ H ₁₆	90.1	7.0	—	92.7	7.3 ^a	—
(VIb)	Orange-red	70	C ₁₈ H ₁₈	91.5	7.5	—	92.3	7.7	—
(VIc)	Yellow needles	62	C ₁₈ H ₁₈ O	85.7	7.0	—	86.4	7.2	—
(VId)	Red-brown needles	128	C ₁₉ H ₂₁ N	86.5	7.9	5.2	86.7	8.0	5.3
(VIe)	Orange	50—51	C ₁₇ H ₁₅ Cl	80.6	6.6	—	80.3	6.7	—

^a Good analyses could not be obtained for (VIa) as it was unstable and decomposed rapidly. Its n.m.r. spectrum also changed with time.

We chose the readily available novel system (VI) prepared from isodicyclopentadiene (V)^{15,16} for our n.m.r. study in order to simplify the spectrum; thereby leaving for study only the data for positions α and γ in the fulvene nucleus.



Some molecular orbital calculations for comparison were carried out for structure (IV) thus assuming, reasonably, that the annelation on the five-membered ring acts as a constant perturbation [for (VI)] and does not affect any correlation, in particular for contributions of type (IVa).

¹² T. A. Wittstruck and E. N. Trachtenberg, *J. Amer. Chem. Soc.*, 1967, **89**, 3803.

¹³ F. W. Wehrli, E. Pretsch, and W. Simon, *Helv. Chim. Acta*, 1967, **50**, 2189, and references therein.

¹⁴ G. Kresze and H. Goetz, *Chem. Ber.*, 1957, **90**, 2161.

EXPERIMENTAL

The compounds were prepared by condensation of isodicyclopentadiene (V) with the corresponding *para*-substituted benzaldehydes in 20% alcoholic KOH [ethanol for (VIa) and (VIb) and methanol for (VIc)—(VIe)]. The parent isodicyclopentadiene (V) was formed according to a procedure in the literature,^{15,16} and had b.p. 80—90°/20 mm. (Found: C, 90.9; H, 8.8. Calc. for C₁₀H₁₂: C, 90.9; H, 9.1%). We thank Messrs. G. B. R. Giulini for a sample of their AGS alumina which was found ideal in this reaction.

The benzaldehyde was added to a cooled solution (0 °C) of (V) (2.6 g, 0.02 mol) in alcoholic KOH (5%), and the mixture kept in an ice-bath for 1 h and then for 24 h at room temperature. Then water was added and the aqueous layer extracted with dichloromethane, and dried (Na₂SO₄). After evaporation of the solvent (VIc)—(VIe) gave oily solids which were crystallized from ethanol. (VIa) and (VIb) yielded oils which were chromatographed on neutral alumina with *n*-hexane; the first yellow fractions were collected and evaporated giving *solids* which were recrystallized from 1 : 1 methanol-ethanol. All yields were 20—40%. For analyses *etc.* see Table I.

N.m.r. Spectra.—These were run on Varian A56/60 and HA-100 spectrometers; they all showed separate signals for the protons H $_{\alpha}$, H $_{\gamma-cis}$, and H $_{\gamma-trans}$, that for H $_{\alpha}$ being sharp

singlets and those for H $_{\gamma}$ broadened singlets. Figure 1 shows an example for (VIb) of the exceedingly simple low-field spectra obtained for these compounds. Spectra for series

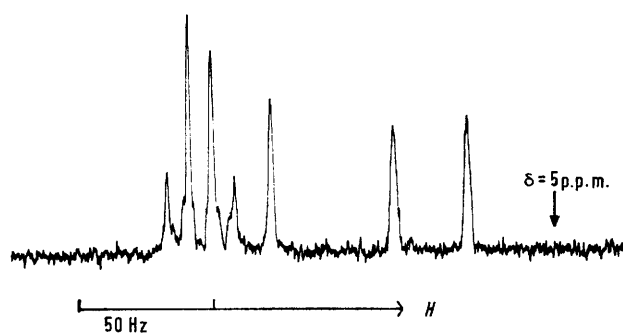


FIGURE 1 N.m.r. spectrum of compound (VIb). (Lowfield, 60 MHz)

(IV) are quite complex. The assignments were made by analogy with the styrenes. H $_{\alpha}$ indeed absorbs at *ca.* 6.7 p.p.m., the same as for H $_{\alpha}$ of the styrenes (II). Between the two remaining signals, we should expect H $_{\gamma-cis}$ to absorb at lower field than H $_{\gamma-trans}$ owing to the magnetic anisotropy

¹⁵ K. Alder, F. H. Flock, and P. Janssen, *Chem. Ber.*, 1956, **89**, 2689.

¹⁶ R. Riemschneider and K. Heymons, *Monatsh.*, 1961, **92**, 1080.

of the phenyl ring (even if the ring is not entirely coplanar with the fulvenic double-bond); this assumption is strengthened by the observed values of $\delta H_{\gamma\text{-cis}}$ and $\delta H_{\gamma\text{-trans}}$ in the series (see below), and by the fact that $\delta H_{\gamma\text{-trans}}$ is closer to the value for the olefinic ring proton of (V).

The shifts were found to be solvent-dependent; therefore, all compounds were examined in very dilute solutions in carbon tetrachloride. We thank Dr Yoel Kashman for the use of the Varian HA-100 instrument at Tel Aviv University for this work.

DISCUSSION

Table 2 shows the proton shifts for compounds (VIa)–(VIe) in carbon tetrachloride as well as q_i , the

TABLE 2

Chemical shifts* (p.p.m.) from internal tetramethylsilane and π -electron densities for fulvenes

	$\delta H_{\gamma\text{-trans}}$	$\delta H_{\gamma\text{-cis}}$	δH_α	q_γ	q_α
(VIa)	5.535	5.970	6.770	1.0610	1.8734
(VIb)	5.530	5.981	6.754	1.0620	0.8747
(VIc)	5.521	5.975	6.725	1.0637	0.8766
(VI d)	5.501	6.028	6.672	1.0668	0.8810
(VIe)	5.535	5.923	6.729	1.0606	0.8733

* ± 0.003 .

π -electron densities calculated for (IV) (see below) by a modified ω -technique assuming a planar structure for the 6-phenylfulvene entity. The method employed was an ω -technique taking $\beta_{ij} = k_{ij}\beta_0$ shown to be useful for predicting charge densities in these compounds by Berson *et al.*;⁹ k was taken as in their paper, 0.90, for formal single bonds and 1.06 for double bonds. k_{ij} and h_i for heteroatoms appear in Table 4 where $\alpha_i = \alpha_0 + h_i\beta_0$. These values were compiled from various sources and found to be good for correlative purposes in several cases in our laboratory. All charge densities converged to 0.001 consistency in less than two iterations. The proton chemical shifts for H_α and $H_{\gamma\text{-trans}}$ progress consistently to higher field with increasing π -electron density on the adjacent carbon atoms, so that they do give an indication of increasing contribution of dipolar structures (see below). For $\delta H_{\gamma\text{-cis}}$ a poor correlation is found, showing that $\delta H_{\gamma\text{-cis}}$ changes in the opposite sense to $\delta H_{\gamma\text{-trans}}$ and δH_α , in accordance with the increasing coplanarity of the rings as the σ_p^+ value of the substituent decreases and conjugation increases. We thank a Referee for pointing out that, for compounds (VIa)–(VI d), the values in Table 2 correlate excellently with σ_p^+ constants.

Figure 2 shows a plot of $\delta H_{\gamma\text{-trans}}$ against δH_α ; the slope of the line is 0.32 ± 0.06 [excluding (VIe)] so that site γ is less sensitive by this ratio to the substitution at position 6.¹² (The chloro-compound deviates from any correlation; this is evidently due to some exceptionally strong field effect.) This is markedly less than would be suggested by the charge densities in Table 2; a plot of q_γ against q_α gives a slope of *ca.* 0.8. Evidently, the ω -calculation employed here, although good for other systems,^{8,9} exaggerates the extent of π -electron de-

localization; it appears that the bond alternation introduced in the calculation is too small. Thus, the n.m.r. results show that transmission of electron effects from the *para*-substituent through the 6-phenylfulvene nucleus, although probably facilitated by the cyclopentadiene moiety, is nevertheless markedly dampened as compared with the fulvene nucleus itself.^{8,9} This is supported by observing the respective dipole moments which indicate much less 'zwitterionic-character' for (IV).^{9,14}

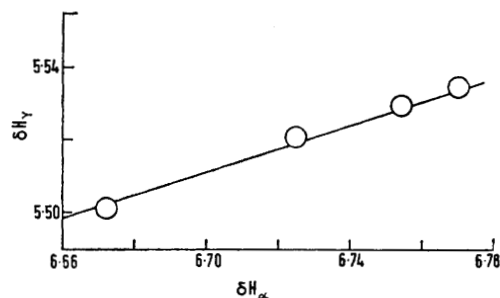


FIGURE 2 Chemical shifts of $H_{\gamma\text{-trans}}$ against those of H_α for fulvenes (VI)

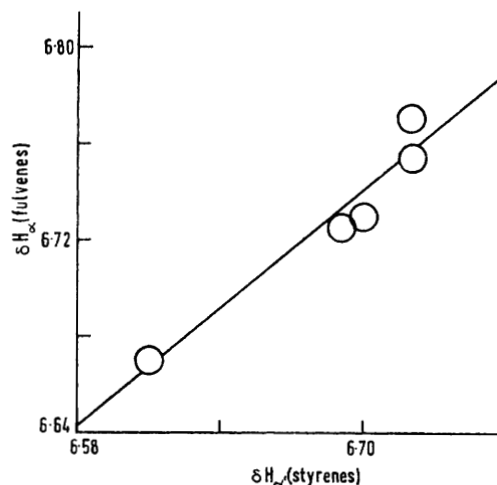


FIGURE 3 Chemical shifts of H_α of fulvenes (VI) against those of H_α of styrenes (II)

One can estimate the extra transmittance of charge from the α -carbon to the five-membered ring by comparison with reference series (II). Figure 3 shows that a plot of δH_α against δH_α has a slope of 0.82 (values of δH_α are taken from ref. 13 and of $d\delta H_\alpha/d\delta H_\alpha'$ from ref. 12). Thus (Table 3) transmission of charge from site α in our series of fulvenes is intermediate between those for styrenes and *trans*-cinnamic acids.

TABLE 3

Relative sensitivity of δH to *para*-substitution compared with styrene as standard

Compound	$d\delta H_\alpha/d\delta H_\alpha'$
II	1.00
VI	0.82
III	0.63

TABLE 4
Parameters for MO calculations

	<i>i</i>	<i>j</i>	<i>k_{ij}</i>	<i>h_i</i>	<i>h_j</i>
C≡H ₃	≡H ₃	C≡	2.0	-0.2	0
	C≡	C	0.7	0	-0.1
OMe	O	C	0.8	2.0	0
NMe ₂	N	C	1.0	1.5	0
Cl	Cl	C	0.4	2.2	0.2

The n.m.r. shifts in a series such as this can be used to compare the extent of dipolar contribution to the ground state between the related compounds. However, before a quantitative approach can be undertaken, more sophisticated methods of calculation are needed as well as more observations on compounds of similar structure.

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