Tetrahedron Letters No. 14, pp. 468-472, 1961. Pergamon Press Ltd. Printed in Great Britain.

THE DETERMINATION OF π-ELECTRON DENSITIES IN AZULENE FROM C^{13} AND H^1 NUCLEAR RESONANCE SHIFTS*

H. Spiesecke and W.G. Schneider
Division of Pure Chemistry, National Research Council,
Ottawa, Canada

(Received 2 June 1961; in revised form 29 June 1961)

THERE is a considerable amount of evidence, derived mainly from measurements on substituted benzenes, to suggest that C^{13} and H^1 chemical shifts are related to the local π-electron density in aromatic molecules. In order to investigate the quantitative relationship between chemical shift and electron density we have measured the C^{13} resonance shifts of the series $C_5H_5^-$, C_6H_6, $C_7H_7^+$ and $C_8H_8^{2-}$, in each of which the local π-electron density is known. The H^1 resonances of the first three members of this series have been measured by Leto, Cotton and Waugh[1], and by Fraenkel, Carter, McLachlan and Richards.[2] Fig. 1 shows the relative C^{13} chemical shifts plotted against the π-electron density, ρ. The corresponding H^1 chemical shifts reported in ref. 2 above are also shown. In magnitude the C^{13} shifts are some fifteen times larger than the corresponding H^1 shifts. The striking parallelism of the resonance shifts of the two nuclei, which has also been observed in the resonance shifts of monosubstituted benzenes,[3] implies that the resonances of both

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* Issued as N.R.C. No. 6345.

[1] J.R. Leto, F.A. Cotton and J.S. Waugh, Nature,Lond. 180, 978 (1957).

[2] G. Fraenkel, R.E. Carter, A. McLachlan and J.H. Richards, J.Amer.Chem. Soc. 82, 5846 (1960).

[3] H. Spiesecke and W.G. Schneider, J.Chem.Phys. In press (1961).

nuclei respond in a parallel way to the local π-electron density on the carbon atom.

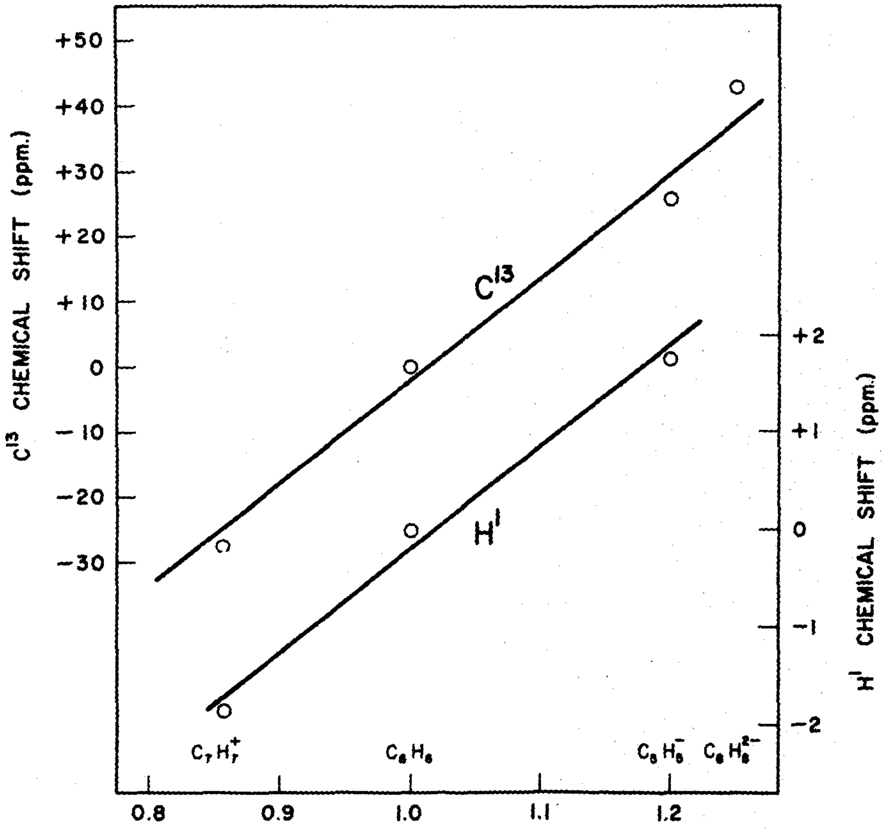

FIG. 1.

The slope of the averaged lines in Fig. 1 yields the proportionality factors, $\delta_{C}13 = 160\rho$ and $\delta_{H}1 = 10.6\rho$.[*] In both cases, however, the deviation of the individual points from the linear correlation line exceeds

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[*] A value of 160 p.p.m. per electron has also been deduced from C^{13} shifts by Lauterbur (private communication) by an indirect pror

the experimental error of the δ-measurements. A satisfactory explanation of these deviations is not immediately apparent. The bond angle varies slightly in the different ring systems and the consequent changes in bond hybridization of the carbon orbitals may be expected to contribute to the resonance shifts. However, examination of the C^{13} shifts of the corresponding cyclic olefins (Table 1) reveals no discernable trend with ring size, nor is there any consistent pattern in the magnitudes of the C-H spin-coupling constants. The latter have been shown to reflect changes in bond hybridization in other compounds.[4,5]

Table 1

Relative C^{13} Chemical Shifts of CH Groups in Olefinic and Aromatic Compounds

Compound	$\delta_{C^{13}}$ (p.p.m. relative to benzene)	J_{CH} (C/S)
Cyclooctatetraene	-4.1	155
Cycloheptatriene	-2.9,1.3,7.6	156,154,161
1,3-Cyclohexadiene[a]	2.4	163
Cyclopentadiene[b]	-4.2	170
Butadiene[c]	-9.5	158
Cyclooctatetraene dianion	42.5	145
Tropylium ion	-27.6	171
Cyclopentadienyl anion	25.7	157

[a] Two broad doublets unresolved

[b] No resolved shift between position 2 and 3

[c] Terminal CH_2 (1,4 positions), +11.5 p.p.m.

Subject to these limitations the calibration plots of Fig. 1 may be employed to evaluate the local π-electron densities of other aromatic systems.

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[4] J.N. Shoolery, J.Chem.Phys. 31, 1427 (1959).

[5] N. Muller and D.E. Pritchard, J.Chem.Phys. 31, 768 (1959).

Table 2

C^{13} and H^1 Chemical Shifts and π-Electron Densities of Azulene

(Chemical shifts in p.p.m. relative to benzene)

Posit-ion	$\delta_{C^{13}}$		J_{CH} (C/S)	δ_{H^1}		ρ derived from		ρ calculated		
	Meas.	Corr.[a]		Meas.	Corr.[a]	δ_{H^1}	$\delta_{C^{13}}$	Pariser[b]	Julg[c]	Brown[d] Heffernan
2	-6.7	-5.9	183	-0.583	-0.23	0.978	0.977	0.979	0.997	0.988
3,1	8.8	7.5	165	-0.067	+0.58	1.055	1.061	1.096	1.049	1.059
4,8	-8.9	-7.7	158	-0.945	-0.34	0.968	0.967	0.879	0.908	0.954
5,7	4.6	4.2	161	+0.280	+0.48	1.045	1.041	1.049	1.034	1.011
6	-8.9	-8.6	158	-0.170	-0.03	0.997	0.962	0.948	0.938	0.969
9.10								1.013	1.042	0.998

[a] Corrected for shift due to ring current of neighbour ring.

[b] R. Pariser, J.Chem.Phys. 25, 1112 (1956).

[c] A. Julg, J.Chim.Phys. 52, 377 (1955).

[d] R.D. Brown and M.L. Heffernan, Aust.J.Chem. 13, 38 (1960).

Table 2 shows the results obtained in this manner for the non-alternant hydrocarbon, azulene.[6] For comparison the calculated density values reported by several authors are shown in the last three columns. The relative C^{13} and H^1 shifts, as measured, are influenced by ring current circulation of the neighbor ring in the azulene molecule, and must be corrected. The corrected values, shown in Table 2, were obtained by employing a simple dipole approximation.[7] The overall accuracy of the final values is roughly estimated to be about 15%. There is a very close correspondence between the values derived independently from the H^1 and C^{13} resonances. The largest deviation (~4%) occurs at the 6-position, for which the C^{13} signal was not independently resolved and was overlapped by other signals. So far no satisfactory resonance signals have been obtained for the 9,10 positions, which may be due to unfavorable relaxation times for these particular nuclei. This point is being investigated.

The C^{13} resonance shift measurements of the aromatic ring systems were carried out on 2-3 molar solutions in tetrahydrofuran, except tropylium cation, which was measured as tropylium fluoroborate in aqueous solution containing some HBF_4 to prevent hydrolysis. Dimethylcarbonate enriched in C^{13} in the carbonyl group was used as an external reference. The azulene C^{13} resonance shifts were measured in a saturated solution of azulene in CS_2. The H^1 resonance shifts were measured in a 5 mole % solution of azulene in cyclohexane, the solvent signal serving as an internal reference. Measurement of a 5 mole % solution of benzene in cyclohexane in a similar manner permitted all shifts to be converted relative to benzene.

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[6] The C^{13} resonance shifts of azulene have recently been reported by Lauterbur [J.Amer.Chem.Soc. 83, 1838 (1961)] and correlated with the theoretically calculated charge densities in azulene.

[7] J.A. Pople, W.G. Schneider and H.J. Bernstein, High Resolution Nuclear Magnetic Resonance p. 254. McGraw-Hill, New York (1959).