

bromide<sup>4</sup> and for methyl benzenesulfonate and isopropyl benzenesulfonate. The differences as well as similarities in the slopes of these plots are consistent with our assumptions.

The slope for isopropyl bromide (1.21) indicates a larger temperature coefficient for  $k_{D_2O}/k_{H_2O}$  than for the relaxation process in bulk water. This result is consistent with a higher energy barrier to rotation in the initial state solvation shell about the halide compared to bulk water (4–5 kcal.) and the implication of equation 6. Similar enhanced stability is indicated for the initial state solvation shell about methyl bromide<sup>9</sup> and hence a similar temperature dependence for  $k_{D_2O}/k_{H_2O}$  would be expected and is found.

The slope for the benzenesulfonates is obviously less than unity. The difference between this value and that for the halides is consistent both with the absolute difference in the magnitude of the solvent isotope effect already noted<sup>3,4</sup> and with the explanation advanced above. If the sulfonic oxygens provide competing centers for hydrogen bonding and thus increase the rotational freedom of contiguous water molecules, or, alternately, if the adjacent water molecules are more strongly hydrogen bonded to these sulfonic oxygens in the initial state, the solvent isotope effect and the temperature dependence thereof will be reduced. The latter hypothesis is probably more likely since the ability of sulfonic groups to confer greater solubility on many organic molecules is well known. The close parallel between the differences in the temperature dependence of the solvent isotope effect for halides and sulfonates noted above and the corresponding differences in the heat capacity of activation for hydrolysis,  $\Delta C_p^*$ , may also be

traced to this common source—the difference in the initial state solvation shells.

**Derived Thermodynamic Parameters.**—If the usual assumptions are made concerning equilibrium between the initial and transition states and further we assume that  $dC_p^*/dT = 0$ ,<sup>12</sup> then from the empirical constants of equation 2, the derived parameters characterizing the activation process may be calculated. These are collected in Table III along with the corresponding terms from the hydrolysis of isopropyl bromide in  $H_2O$ .

TABLE III

A COMPARISON OF THERMODYNAMIC PARAMETERS FOR THE ACTIVATION PROCESS IN THE HYDROLYSIS OF ISOPROPYL BROMIDE IN  $H_2O$  AND  $D_2O$

Temp., °C.	In $H_2O$ <sup>a</sup>		In $D_2O$ <sup>b</sup>	
	$\Delta H^*$ , cal./mole	$\Delta S^*$ , cal./mole deg.	$\Delta H^*$ , cal./mole	$\Delta S^*$ , cal./mole deg.
0	27,180	8.05	27,920	9.94
50	24,360	-1.43	24,670	-1.03
100	21,540	-9.54	21,390	-10.43

<sup>a</sup>  $\Delta C_p^* = -56.4$  cal./mole deg. <sup>b</sup>  $\Delta C_p^* = -65.3$  cal./mole deg.

Since qualitative arguments lead to the conclusion that the major contribution to  $\Delta C_p^*$  is  $dF_s/dT$ , it is gratifying to discover that there is a significant difference between  $\Delta C_p^*(D_2O)$  and  $\Delta C_p^*(H_2O)$  and the values of both terms are more negative than that calculated by Conway<sup>30</sup> and ourselves<sup>32</sup> for the relaxation processes in bulk water. The differences between  $\Delta H^*$  and  $\Delta S^*$  for the two media may likewise be interpreted as reflecting the greater stability of the initial state solvation shell in  $D_2O$  than in  $H_2O$ .

[CONTRIBUTION FROM MELLON INSTITUTE, PITTSBURGH, PENNSYLVANIA]

## <sup>13</sup>C Nuclear Magnetic Resonance Spectroscopy. I. Aromatic Hydrocarbons

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The <sup>13</sup>C nuclear magnetic resonance spectra of benzene, toluene, the three xylenes, mesitylene, durene and hexamethylbenzene, and of biphenyl, naphthalene, phenanthrene, pyrene, acenaphthylene and fluoranthene have been obtained and partially analyzed. Tentative assignments for the spectra of azulene and 4,6,8-trimethylazulene are also presented. The ranges of <sup>13</sup>C chemical shifts in non-alternate hydrocarbons are much larger than those observed in alternates, suggesting that variations in  $\pi$ -electron densities are primarily responsible for such shifts in aromatic rings.

### Introduction

The <sup>13</sup>C nuclear magnetic resonance (n.m.r.) spectra of several series of substituted benzenes and heterocyclic aromatics have been obtained and analyzed. The analyses of the complex spectra were usually accomplished by comparisons among the spectra of the methyl derivatives, a procedure made possible by the relatively small effects of methyl substitution on <sup>13</sup>C shifts and carbon-hydrogen spin-spin couplings in aromatic ring systems. The interpretation of the measured <sup>13</sup>C shifts and carbon-hydrogen spin-spin couplings depends initially upon the establish-

ment of empirical correlations with more familiar chemical and physical parameters. This paper, the first of a series on the <sup>13</sup>C n.m.r. spectra of aromatic rings, therefore presents measurements and analyses of the spectra of benzene and seven methylbenzenes, and of biphenyl, three alternate and four non-alternate hydrocarbons. Deuteration of two of the latter, azulene and 4,6,8-trimethylazulene, in the 1,3 positions has made possible a tentative analysis of their spectra, from which it appears that the <sup>13</sup>C shifts may be determined largely by the  $\pi$ -electron density distribution in such molecules.

The spectrum of ferrocene has also been obtained. The <sup>13</sup>C resonance occurs at much higher

(1) Multiple Fellowship on Silicones sustained by the Dow-Corning Corporation and Corning Glass Works.

field than do those in other aromatic rings, and the spin-spin coupling is greater. The increase in the coupling may result from the increased s-character of the C-H bond expected for a carbon in a five-membered ring, but its magnitude is rather less than might have been predicted.

### Experimental

**N.m.r. Spectra.**—All spectra were measured at 8.50 Mc./s. in a magnetic field of about 7940 gauss, using a Varian 4300B High Resolution N.M.R. Spectrometer and a Varian 12-inch electromagnet with flux stabilizer. The dispersion mode was employed with radio-frequency fields ( $H_1$ ) of three to fifteen milligauss and sweep rates of about 0.4 gauss/min. The field inhomogeneity over the large samples was generally about 12 c./s. (11 milligauss). Under these conditions, spectra were usually of the "rapid passage" type<sup>2-4</sup> or intermediate between rapid and slow passage. Because of the asymmetry of such intermediate passage peaks, reliable measurements can only be made by measuring equivalent points in spectra taken with increasing and decreasing sweep fields and averaging the results. The inversion of rapid passage spectra with reversal of sweep direction and the often strong dependence of the appearance of a spectrum upon the sweep direction has made it desirable to deviate somewhat from the usual conventions followed in the presentation of n.m.r. spectra. All  $C^{13}$  spectra in this and following papers will be presented in pairs; one with the peaks pointing up and high applied field to the right and the other with peaks pointing down, as they are drawn by the recorder and high applied field to the left. For both types, the direction of the sweep is from left to right, increasing in the first case and decreasing in the second.

Another source of asymmetry and differences between spectra swept in the two directions is magnetization transfer,<sup>5</sup> which causes the second doublet peak traversed to be decreased in intensity by an amount dependent upon the rate of sweep and the relaxation times of both  $C^{13}$  and  $H^1$ . Reversal of the sweep reverses the inequality, and the averaged heights are equal. Higher multiplets behave similarly. Meaningful intensity estimates thus require measurements on spectra swept in both directions.

Peak widths are usually greater than the field inhomogeneity mentioned above. From the equations for pure rapid passage,<sup>2,3</sup> the signal has the form

$$+M \left[ 1 + \left( \frac{\gamma H_1}{2\pi \Delta\nu} \right)^2 \right]^{1/2}$$

where  $M$  is nearly constant during resonance and  $\Delta\nu$  is the distance, in c./s., from the center of the resonance. The sign depends, as mentioned above, upon the direction of approach to resonance, and the width of the peak is proportional to  $H_1$ . In practice,  $H_1$  is adjusted empirically to obtain the best compromise between signal strength and resolution in a given spectrum.

Another source of broadening is unresolved spin-spin couplings with distant hydrogens. These have been resolved in a few  $C^{13}$  spectra<sup>6</sup> and have been measured in proton spectra.<sup>7</sup> They can be propagated through at least three bonds and can be as large as 45 c./s. The peak widths in the absorption mode  $C^{13}$  spectrum of benzene<sup>6</sup> are less than 20 c./s., requiring *ortho*- and *meta*-hydrogen couplings of less than 10 c./s. Variation of the distant couplings with structure will result in changes in the widths and heights of peaks and will affect intensity estimates, since the latter are based almost solely on peak heights. Because of this and the low and variable signal-to-noise ratios, it is impossible to give any good estimate of the reliability of the relative intensities reported, even when peaks are well separated.

(2) F. Bloch, *Phys. Rev.*, **70**, 460 (1946).

(3) E. R. Andrew, "Nuclear Magnetic Resonance," Cambridge University Press, London, 1955, pp. 130-132, 222-223.

(4) J. G. Powles, *Proc. Phys. Soc.*, **71**, 497 (1958).

(5) Magnetization transfer by chemical reaction has been discussed by H. M. McConnell and D. D. Thompson, *J. Chem. Phys.*, **26**, 958 (1957), **31**, 85 (1959), and by A. Patterson, Jr., and R. Ettinger, *Z. Electrochem.*, **64**, 98 (1960). Transfer by relaxation of spin-coupled nuclei appears to be quite similar, although a quantitative treatment of the rapid passage case has not been carried out.

(6) P. C. Lauterbur, unpublished work.

(7) G. J. Karabatsos, *J. Org. Chem.*, **25**, 315 (1960).

The accuracy of the shift and coupling measurements is also difficult to assess. The variable asymmetries, signal-to-noise ratios and overlaps all affect the measurements. Errors are likely to be especially serious for peaks which are just barely resolved. Experiments at other frequencies, at which the pattern of interferences in spectra containing spin-spin multiplets will be completely different, will eventually provide more accurate data.

The methyl quadruplets of the methylbenzenes provide a suitable set of resonances, free from the complications of incomplete resolution, from which to estimate the precision of the measurements. As the multiplets are quite weak in several of the spectra, the precision estimate obtained will be conservative. The average difference between the methyl  $C^{13}$  shifts measured in two separately calibrated spectra of each of seven methylbenzenes was 0.4 p.p.m. For only two of the group, one of them the weak hexamethylbenzene spectrum, was the difference between two runs greater than 0.4 p.p.m. The average difference between the  $C^{13}H_3$  spin couplings, measured in the same pairs of spectra, was 2 c./s. If it is assumed that the couplings are the same in all of the methylbenzenes, the probable error or a single measurement is  $\pm 2$  c./s. More information on the precision of measurement is given below in connection with the referencing of the spectra.

The methylbenzene spectra and those of the polynuclear hydrocarbons were measured at different times, and two different techniques were used. For the former compounds, a 3 mm. o.d. glass tube was centered in the 15 mm. o.d. sample cell. The reference tube contained a saturated aqueous solution of  $K_2CO_3$ , enriched to about 58%  $C^{13}$ . The field inhomogeneity produced by the central tube<sup>8</sup> did not seriously affect the spectra under the conditions used. The shift of the  $K_2C^{13}O_3$  reference relative to the standard used in earlier measurements,<sup>9,10</sup> the carboxyl carbon in glacial acetic acid, was measured by the substitution technique<sup>10</sup> as +7.6 p.p.m. A new standard will be used in this and subsequent papers, however. The carboxyl  $C^{13}$  shift in acetic acid is concentration dependent, and the presence of small amounts of water can cause a measurable shift. The presence of the methyl resonance would also be undesirable if the acid was to be used as an internal reference. All measurements reported previously<sup>9,10</sup> have been ultimately referred to the same sample of acetic acid, sealed under vacuum, and should be internally consistent. A much better choice for general use seems to be carbon disulfide. It has a single strong sharp resonance at even lower field than acetic acid and appears to be almost immune to solvent shifts, thus fulfilling the most important requirement for an internal reference. For example, solutions of  $1/3$   $CS_2$  by volume in the solvents nitrobenzene, acetone, aniline, cyclohexane and bromoform gave shifts, after correction for bulk susceptibility differences,<sup>11</sup> of +0.5, 0, +0.2, +0.1 and -0.4 p.p.m., respectively, relative to pure  $CS_2$ . Each shift was based upon two measurements (each an average between the two sweep directions) which had a maximum difference of 0.4 p.p.m. The average difference was less than 0.2 p.p.m. Various other experiments have also failed to show any solvent effects definitely larger than experimental error.<sup>12</sup> Carbon disulfide has, therefore, been adopted as the new primary reference standard for  $C^{13}$  spectra in this Laboratory.

The symbol  $\delta_c$ , defined as

$$\delta_c = \frac{H_{\text{sample}} - H_{CS_2}}{H_{CS_2}} \times 10^6$$

will be used to distinguish shifts on the  $CS_2$  scale from those referred to other standards. Shifts on the acetic acid scale will be called  $\delta_a$  and are related to the new scale by

$$\delta_c = \delta_a + 15.6 \text{ p.p.m.}$$

for external referencing. For the time being, it will be assumed that internal and external referencing with  $CS_2$  are equivalent, since the experimental uncertainties are

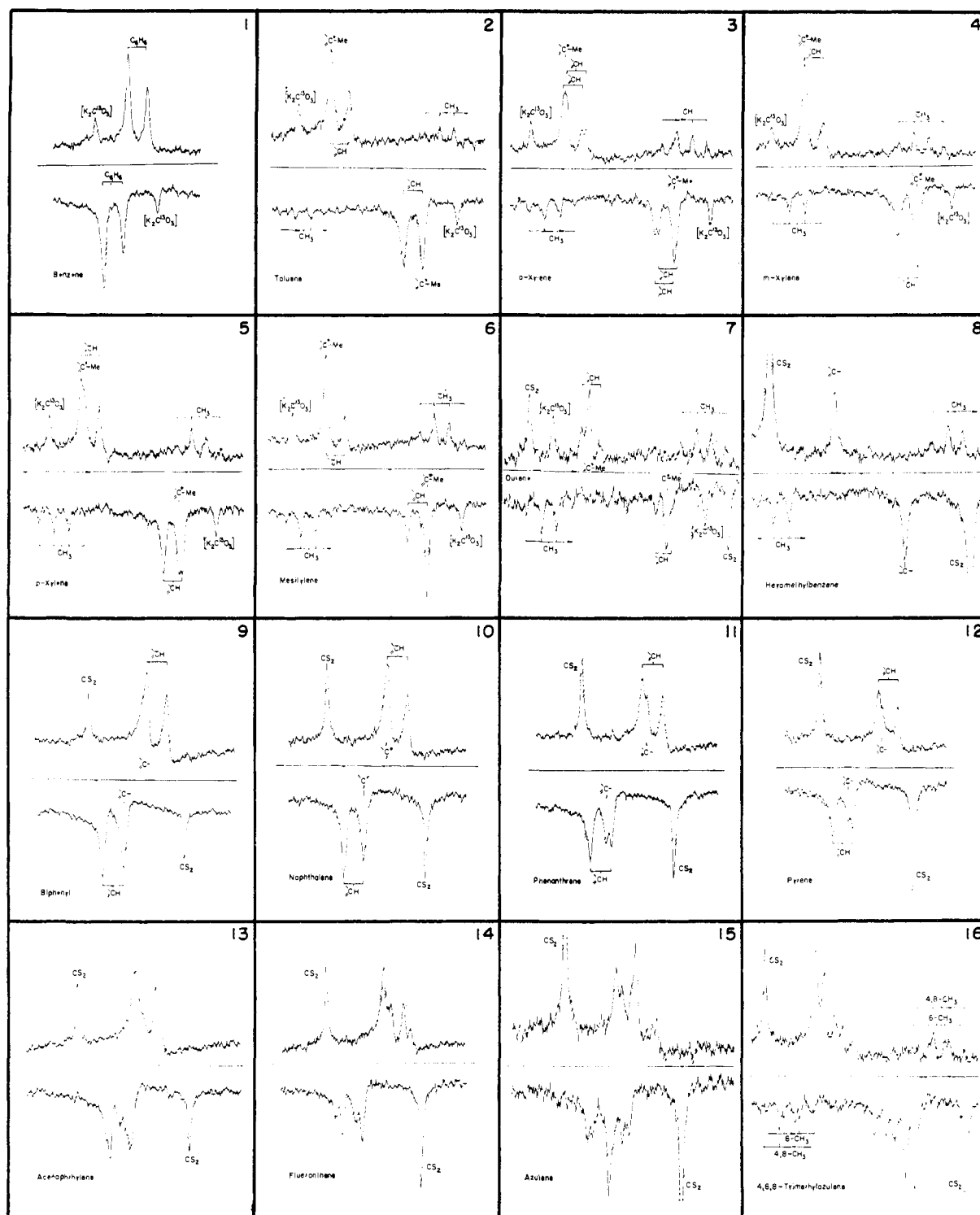
(8) J. R. Zimmerman and M. R. Foster, *J. Phys. Chem.*, **61**, 282 (1957).

(9) P. C. Lauterbur, *J. Chem. Phys.*, **26**, 217 (1957).

(10) P. C. Lauterbur, *Ann. N. Y. Acad. Sci.*, **70**, (4), 841 (1958).

(11) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, pp. 80-81 and Appendix C.

(12)  $CO_2$  has been found to be similarly inert in a wide variety of environments; R. Ettinger and P. C. Lauterbur, to be published.



Figs. 1-16.—8.50 Mc./s.  $C^{13}$  n.m.r. spectra of aromatic hydrocarbons.

usually larger than corrections for bulk susceptibility differences or solvent effects. The tube of aqueous  $K_2C^{18}O_3$  described above is used as a secondary reference with  $\delta(K_2C^{18}O_3) = 23.2$  p.p.m. Peak positions reported in frequency units (c./s.) will be symbolized by  $\nu_0$ .

Calibration was accomplished, usually both before and after each pair of sample spectra, by recording the spectrum of  $CS_2$  modulated at 720 c./s.<sup>13</sup> The oscillator frequency

(13) J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

was monitored by an electronic frequency counter. During the work on the methylbenzenes, the acetic acid spectrum was used as a secondary calibration standard, with a shift difference between the methyl and carboxyl carbons of 157.7 p.p.m.

The spectra of the deuterated azulenes were weak because only small quantities were available, and no one run gave a satisfactory picture of relative intensities. Tracings made from four or five superimposed spectra gave satisfactorily reproducible shifts and relative intensities, however.

**Samples.**—All samples were in 15 mm. o.d. glass tubes filled to depths of several cm. and contained  $C^{13}$  only in its natural abundance of 1.1%. The methylbenzenes and their solutions were deoxygenated by bubbling with  $N_2$  and were kept in tubes capped with standard taper ground glass joints. The ( $K_2C^{13}O_3$ ) reference tube was centered by a dimple in the flat bottom of the sample tube and a nipple on the cap. The other samples were sealed under vacuum in glass tubes, except for the deuterated azulenes, which were handled in the same way as the methylbenzenes, with the omission of the reference tube.

**Preparation of Deuterated Azulenes.**— $CF_3COOD$  was prepared by mixing the theoretical amount of  $D_2O$  with  $(CF_3CO)_2$  kept in a solid  $CO_2$ -trichloroethylene bath. Azulene or 4,6,8-trimethylazulene were added, at room temperature, in the approximate ratio of one mole of hydrocarbon to ten of acid. They dissolved at once to give yellow solutions whose proton spectra were immediately checked to confirm that exchange had taken place.<sup>14</sup> The solutions were neutralized with saturated  $K_2CO_3$  in  $D_2O$  and with anhydrous  $K_2CO_3$  and the precipitated deuterated azulenes were filtered off, washed, dried and dissolved in  $CS_2$ . Proton spectra<sup>14</sup> showed that at least 70% of the 1,3 protons had been replaced and that no exchange had taken place at other positions.

**Sources of Samples.**—Biphenyl, naphthalene, phenanthrene, benzene and the methylbenzenes were pure grades from standard commercial sources, except for durene, which was a gift from the Shell Development Company. Pyrene, acenaphthylene, fluoranthene and azulene were loaned by Drs. R. A. Friedel and G. Wood of the U. S. Bureau of Mines. 4,6,8-Trimethylazulene and an additional sample of azulene were purchased from the Columbia Organic Chemicals Company, Inc. Ferrocene was obtained from E. I. du Pont de Nemours & Company, Inc. A sample of *o*-xylene partially deuterated in the 4-position was furnished by Dr. G. H. Barnes of Mellon Institute.

### Results and Discussion

**Benzene and Methylbenzenes.**—Figures 1 through 8 are the spectra of benzene and seven methylbenzenes. The upper spectrum of each pair was produced by an increasing sweep field and the lower by a decreasing sweep. The peak positions and measured heights are given in Table I, along with the assignments and the corresponding calculated peak heights, normalized to the total number of carbon atoms in each molecule. The frequency is defined to have the same sign as  $\delta_c$ , so that resonances at higher field have larger  $\nu_c$  values.

Most of the assignments are obvious. The spectra consist of CH doublets, singlets for ring carbons carrying methyl groups and methyl quadruplets. The doublet splittings are about 150 c./s. and the single peak of the methyl-substituted carbons is usually almost coincident with the low-field components of the doublets at an operating frequency of 8.50 Mc./s. In the assignments, multiplet components are indicated by numbers in parentheses, counting from the lowest peak. The only ambiguity in the assignments for resolved peaks occurs in the *o*-xylene spectrum. Peaks 2 and 3 are obviously the high-field components of two CH doublets. The assignment shown is based upon

(14) Proton resonance spectra of azulene and of the azulene cation in  $CF_3COOH$  have been reported by S. S. Danyluk and W. G. Schneider, *J. Am. Chem. Soc.*, **82**, 997 (1960). The proton spectrum of 4,6,8-trimethylazulene has been reported by E. G. Hoffmann, *Z. Anal. Chem.*, **170**, 177 (1959), *Ann.*, **624**, 47 (1959). A detailed description of the proton spectra of the deuterated hydrocarbons and cations will be presented elsewhere. It should be noted now, however, that an irreversible reaction takes place if azulene is left in trifluoroacetic acid solution for several hours at room temperature. The blue-violet product dissolves in the acid without change in color and is much less soluble in organic solvents than is azulene.

the shift to high field characteristic of carbons *para* to a methyl group and upon the spectrum of *o*-xylene partially deuterated in the 4-position.

TABLE I  
THE 8.50 MC./S.  $C^{13}$  N.M.R. SPECTRA OF BENZENE AND SOME METHYLBENZENES

Compound	Peak	$\nu_c$ c./s.	—Height—		Assignments
			Obsd.	Calcd.	
Benzene	1	473	2.97	3.00	CH(1)
	2	632	3.03	3.00	CH(2)
Toluene	1	475	3.38	3.50	C-1 + CH(1)
	2	631	2.43	2.50	CH(2)
	3		0	0.12	CH <sub>3</sub> (1)
	4	1399	0.48	.38	CH <sub>3</sub> (2)
	5	1522	0.38	.38	CH <sub>3</sub> (3)
	6		0	.12	CH <sub>3</sub> (4)
<i>o</i> -Xylene	1	481	4.21 <sup>a</sup>	4.00	C-1, 2 + CH(1)
	2	618	1.00	1.00	CH-3, 6 (2)
	3	648	1.00	1.00	CH-4, 5 (2)
	4	1295	0.14	0.25	CH <sub>3</sub> (1)
<i>m</i> -Xylene	5	1411	.64	.75	CH <sub>3</sub> (2)
	6	1539	.64	.75	CH <sub>3</sub> (3)
	7	1667	.25	.25	CH <sub>3</sub> (4)
	1	479	3.98	4.00	C-1, 3 + CH(1)
	2	640	1.80	2.00	CH(2)
	3	1275	0.21	0.25	CH <sub>3</sub> (1)
	4	1404	.95	.75	CH <sub>3</sub> (2)
<i>p</i> -Xylene	5	1531	.85	.75	CH <sub>3</sub> (3)
	6	1652	.21	.25	CH <sub>3</sub> (4)
	1	473	2.12	2.00	CH(1)
	2	493	2.00	2.00	C-1, 4
	3	623	1.84	2.00	CH(2)
	4	1273	0.20	0.25	CH <sub>3</sub> (1)
	5	1400	.76	.75	CH <sub>3</sub> (2)
Mesitylene	6	1525	.72	.75	CH <sub>3</sub> (3)
	7	1649	.40	.25	CH <sub>3</sub> (4)
	1	479	4.32	4.50	C-1, 3, 5 + CH(1)
	2	639	1.58	1.50	CH(2)
	3	1273	0.32	0.38	CH <sub>3</sub> (1)
	4	1399	1.21	1.12	CH <sub>3</sub> (2)
Durene <sup>b</sup>	5	1527	1.16	1.12	CH <sub>3</sub> (3)
	6	1655	0.42	0.38	CH <sub>3</sub> (4)
	0	1		..	CS <sub>2</sub>
	1	455	1.07	1.00	CH(1)
	2	507	3.35	4.00	C-1, 2, 4, 5
	3	597	1.16	1.00	CH(2)
	4	1285	0.66	0.50	CH <sub>3</sub> (1)
Hexamethylbenzene <sup>b</sup>	5	1412	1.59	1.50	CH <sub>3</sub> (2)
	6	1539	1.67	1.50	CH <sub>3</sub> (3)
	7	1658	0.50	0.50	CH <sub>3</sub> (4)
	0	-1		..	CS <sub>2</sub>
	1	513	5.43		C-1, 2, 3, 4, 5, 6
2	1304	0.59		CH <sub>3</sub> (1)	
3	1424	2.63		CH <sub>3</sub> (2)	
4	1549	2.30		CH <sub>3</sub> (3)	
5	1679	0.85		CH <sub>3</sub> (4)	

<sup>a</sup> The actual measured height was doubled to take into account the obvious broadening of the peak. <sup>b</sup> Run as a saturated solution in  $CS_2$ .

Table II summarizes the parameters obtained by analysis of the data in Table I. The spin-spin coupling constants are in good agreement with those measured in the proton spectra,<sup>15</sup> except

(15) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959).

where overlapping peaks obscure one component, as in mesitylene. The CH shifts differ little from that in benzene, except for small shifts to low field caused by *o*-methyls and to high field caused by a *p*-methyl. The data in Table II are neither complete nor reliable enough to make a quantitative discussion of the methyl effects profitable, but the effects have been observed in the better-resolved spectra of methyl derivatives of a number of substituted benzenes and will be analyzed in detail in other papers of this series.

TABLE II

$C^{13}$  CHEMICAL SHIFTS AND SPIN-SPIN COUPLINGS IN BENZENE AND METHYLBENZENES

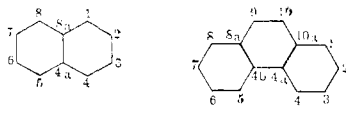
Compound	—CH—		C*—CH <sub>3</sub>	—CH <sub>3</sub> —	
	$\delta_c$ , p.p.m.	$J$ , c./s.		$\delta_c$ , p.p.m.	$J$ , c./s.
Benzene	65.0	159 <sup>a</sup>	...	...	...
Toluene	65.2 <sup>b</sup>	156 <sup>b</sup>	56.0 <sup>c</sup>	171.8	122 <sup>d</sup>
<i>o</i> -Xylene					
(CH — 3, 6)	63.6 <sup>e</sup>	(154) <sup>g</sup>	56.6 <sup>e</sup>	173.6	128
(CH — 4, 5)	67.2 <sup>f</sup>	(154) <sup>f</sup>			
<i>m</i> -Xylene	65.8 <sup>g</sup>	160 <sup>g</sup>	56.4 <sup>e</sup>	172.6	127
<i>p</i> -Xylene	64.5	150	58.0	172.1	124
Mesitylene	66.1 <sup>h</sup>	(154) <sup>h</sup>	56.4 <sup>e</sup>	172.2	128 <sup>d</sup>
Durene	62.0	142	59.6	173.6	127
Hexamethylbenzene	..	..	60.4	174.9	124

<sup>a</sup> Muller and Pritchard<sup>15</sup> report 159 c./s. from the H<sup>1</sup> spectrum. <sup>b</sup> Average for all CH; Muller and Pritchard<sup>15</sup> report an average coupling of 155 c./s. <sup>c</sup> Taken as the center of peak 1. <sup>d</sup> Muller and Pritchard<sup>15</sup> report 126 c./s. <sup>e</sup> The measured separation of peaks 1 and 2 is 136 c./s. The  $\delta_c$  given was calculated from the position of peak 2 by assuming a coupling of 154 c./s., about the same as those in mesitylene and toluene. <sup>f</sup> The measured separation of peaks 1 and 3 is 166 c./s.; A coupling of 154 was assumed in the calculation of  $\delta_c$ . <sup>g</sup> Average for all CH. <sup>h</sup> The measured separation of peaks 1 and 2 is 160 c./s., The coupling of 154 c./s. from the H<sup>1</sup> spectrum was used in calculating  $\delta_c$ .

Some of the methyl  $C^{13}$  shifts were measured in an earlier investigation.<sup>10</sup> After conversion of the data to the  $\delta_c$  scale and a slight adjustment of the calibration factor,<sup>16</sup> the two independent sets of data are in agreement within the stated experimental uncertainties, except for durene, for which the difference is 1.1 p.p.m.

The methyl spin-spin couplings are all the same within experimental error, with an average value of 126 c./s., the same as those found by Muller and Pritchard<sup>15</sup> for toluene and mesitylene.

**Biphenyl and Alternate Polynuclear Hydrocarbons.**—The spectra of biphenyl, naphthalene, phenanthrene and pyrene are given in Figs. 9–12 and the peak positions, heights and assignments are listed in Table III. The numbering for the latter three is that of the Ring Index and is shown.



The spectrum of biphenyl is very similar to that of toluene, with no resolvable shifts between the

(16) In reference 10 a value of 158.0 p.p.m. was used for the secondary calibration by the acetic acid spectrum, compared to the 157.7 p.p.m. used in this work.

*o*-, *m*- and *p*-carbons. The assignment of the substituted carbon resonance to a position nearly coincident with that of the low-field component of the CH doublet is based upon relative intensities.

TABLE III

THE 8.50 Mc./s.  $C^{13}$  N.M.R. SPECTRA OF BIPHENYL AND THREE ALTERNATE HYDROCARBONS

Compound	Peak	$\nu_c$ , c./s.	Height,		Assignments
			Obsd.	Calcd.	
Biphenyl	1	468	6.24	7.00	C-1, 1' + CH(1)
	2	630	5.76	5.00	CH(2)
Naphthalene	1	481	5.16	6.00	C-4a, 8a + CH(1)
	2	638	4.84	4.00	CH(2)
Phenanthrene	1	479	5.10	5.00	CH(1)
	2	512	4.00	4.00	C-4a, 4b, 8a, 10a
	3	637	4.90	5.00	CH(2)
Pyrene	1	484	6.40	7.00	CH(1) + C-10b, 10c
	2	515	3.84	4.00	C-3a, 5a, 8a, 10a
	3	638	5.76	5.00	CH(2)

<sup>a</sup> Run as saturated solutions in CS<sub>2</sub>.

The naphthalene spectrum was analyzed in the same way. The shift between the  $\alpha$ - and  $\beta$ -carbons must be quite small. In the phenanthrene spectrum, the peaks of the junction carbons have moved slightly toward high applied field, but there is still no resolvable difference between the doublets, except for a possible shoulder on the high field side. The spectrum of pyrene is slightly different, in that the relative peak heights suggest that two of the junction carbons give a peak at lower field than the other four, combined with the low-field peaks of the doublets. A small high-field shoulder may also be present in this spectrum.

The chemical shifts and spin-spin couplings are listed in Table IV. There appears to be some

TABLE IV

$C^{13}$  CHEMICAL SHIFTS AND SPIN-SPIN COUPLINGS IN BIPHENYL AND THREE ALTERNATE HYDROCARBONS

Compound	—CH—		C-C $\delta_c$ , p.p.m.
	$\delta_c$ , p.p.m.	$J$ , c./s.	
Biphenyl	64.6	162	55.0 <sup>a</sup>
Naphthalene	65.9	158	56.6 <sup>a</sup>
Phenanthrene	65.6	158	60.2
Pyrene	66.0	154	56.9 <sup>a,b</sup> 60.6 <sup>b</sup>

<sup>a</sup> Taken as the center of peak 1. <sup>b</sup> Based upon the tentative assignment in Table III, the smaller shift would be that of C-10b, 10c and the larger that of C-3a, 5a, 8a, 10a. The existence of the resonance at lower field is not certain, however.

tendency for shifts to higher field than benzene in the spectra of the condensed polynuclear hydrocarbons, but the effect is small. The average spin couplings are all about the same as in benzene. Thus, whatever factors may be responsible for variations in the magnetic shieldings of carbon nuclei in aromatic rings do not vary much in the alternate hydrocarbons that have been studied. The other property that best fits this description is the  $\pi$ -electron density,  $q_r$ , at each carbon atom.<sup>17</sup> In fact, the most significant feature of the classi-

(17) C. A. Coulson and G. S. Rushbrooke, *Proc. Cambridge Phil. Soc.*, **36**, 193 (1940).

fication into alternates and non-alternates is that in the former all  $g_r$  are almost exactly unity, but that large migrations of charge may occur in non-alternate molecules.

**Non-alternate Hydrocarbons.**—The spectra of several non-alternate hydrocarbons have been obtained to test the hypothesis that the carbon shieldings are largely determined by the  $\pi$ -electron densities. Spectra of acenaphthylene and fluoranthrene are shown in Figs. 13 and 14, and the peak positions and heights are given in Table V. The numbering of the rings is shown.

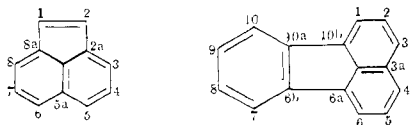


TABLE V

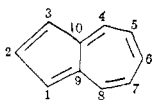
THE 8.50 Mc./s.  $C^{13}$  SPECTRA OF ACENAPHTHYLENE AND FLUORANTHRENE

Compound <sup>a</sup>	Peak	$\nu_c$ , c./s.	Height		Assignments	
			Obsd.	Calcd.		
Acenaphthylene	1	454	2.42	8.09	CH(1) + C-2a,5a,8a,8b	
	2	466	2.60			
	3	494	1.40			
	4	518	0.93			
	5	544	0.74			
	6	627	2.42			
Fluoranthene	7	650	1.49	3.91	CH(2)	
	1	470	6.56	9.78		CH <sub>k</sub> (1) + C <sub>1</sub> CH <sub>m</sub> (1) + C <sub>n</sub>
	2	524	3.22			
	3	628	4.00			
4	684	2.22	5.00			

<sup>a</sup> Run as saturated solutions in CS<sub>2</sub>.

There is a little more structure in the acenaphthylene spectra than in those of the alternates, but a complete assignment is not possible. The spectrum is centered at about the same point as is that of benzene. The fluoranthrene spectra show considerably more structure, with a small doublet shifted to high field. Without more data it is impossible to say which set of carbons gives rise to which peaks, but a tentative analysis into unidentified groups has been given in Table V on the bases of couplings and relative peak heights.

**Azulenes.**—The best evidence for a relationship between  $\pi$ -electron densities and shifts is found in the spectra of azulene and its derivatives. The structure and numbering of azulene are shown.



Its spectrum (Fig. 15 and Table VI) is complex and cannot be immediately interpreted. There appear to be at least three and possibly four sets of doublets, with a number of peaks overlapping in the center. A partial interpretation was made possible by a comparison with the spectra of 4,6,8-trimethylazulene, shown in Fig. 16. If it is assumed that the direct effect of methyl substitution is about the same as in the benzene series, the intensification of the low field part of the spectrum implies that one or both of peaks 1 and 2 of azulene contain contributions from CH-4,8(1) and CH-6-

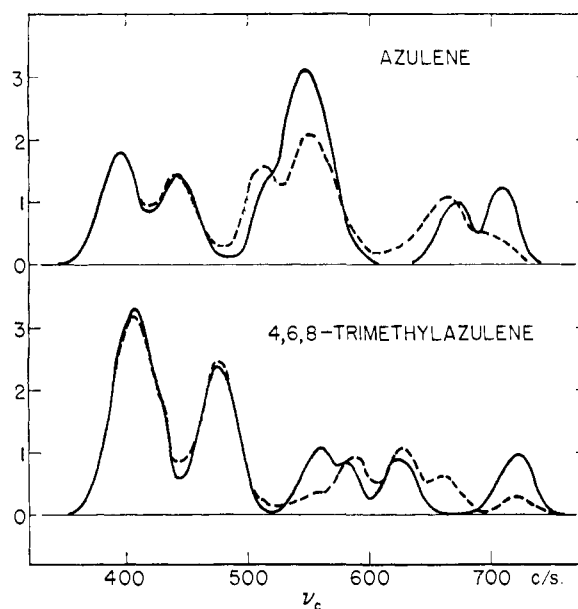


Fig. 17.—Effects of deuteration on the 8.50 Mc./s.  $C^{13}$  n.m.r. spectra of azulene and 4,6,8-trimethylazulene.

(1). Peaks 5 and 6, nearly equal in height, must then be assigned as CH-1,3(2) and CH-5,7(2), although it cannot be determined at this point which is which. Fig. 17 compares the average spectra of azulene, azulene-1,3- $d_2$ , 4,6,8-trimethylazulene and 4,6,8-trimethylazulene-1,3- $d_2$ . It is immediately apparent that peak 6 in each spectrum must be assigned as CH-1,3(2) and that peak 3 in the trimethylazulene spectrum is CH-1,3(1). Peak 5 of azulene should therefore be assigned as CH-5,7(2), as should peak 5 of trimethylazulene. The latter, if the assignment is correct, has been shifted considerably to low field by the flanking methyl groups. By elimination, peak 4 of trimethylazulene must be CH-2(2), an assignment supported by its relatively small height, even though it appears as a shoulder on peak 3. The assignments in the lower portion of the azulene spectrum present some difficulties. It seems unlikely that peak 2 could be the low-field component of a doublet because the second component would be expected at about  $\nu_c = 600$  c./s. Only if  $J$  were less than about 120 c./s. could the peak be concealed in peak 3. Consequently, peak 2 has been assigned as C-9,10. This leaves peak 1 to be attributed to CH-4,8(1) and CH-6(1). CH-2(1) probably falls between peaks 1 and 2, probably closer to 1, in which it has been included in Table VI. The peak heights would be in better agreement with those observed if peak 1 were CH-6(1) + CH-2(1) + C-9,10 and peak 2 were CH-4,8(1), but this seems less likely on the other grounds cited above.

The shifts and couplings in all four compounds, assuming the assignments to be those of Table VI, are given in Table VII.

By making use of the best resolved peaks in the four sets of spectra, along with the assumptions that  $J(\text{CH-1,3})$ ,  $J(\text{CH-2})$  and  $\delta_c(\text{CH-2})$  are not changed by the methyl substitution, a set of best

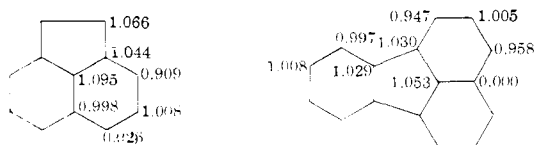
TABLE VI  
THE 8.50 Mc./s. C<sup>13</sup> N.M.R. SPECTRA OF AZULENE AND OF  
METHYL- AND DEUTERIOAZULENES

Compound <sup>a</sup>	Peak	$\nu_c$ , c./s.	Height, <sup>c</sup>		Assignments <sup>b</sup>
			obsd.	calcd.	
Azulene	1	396	1.81	2.00	CH-2(1) + CH-4,8-(1) + CH-6(1)
	2	443	1.45	2.00	C-9,10
	3	517	1.37	1.00	CH-5,7(1)
	4	547	3.13	3.00	CH-2(2) + CH-4,8-(2) + CH-6(2) + CH-1,3(1)
	5	673	1.00	1.00	CH-5,7(2)
	6	709	1.24	1.00	CH-1,3(2)
4,6,8-Trimethylazulene	1	407	3.28	3.50	CH-2(1) + C-4,8 + C-6
	2	476	2.38	3.00	CH-5,7(1) + C-9,10
	3	560	1.07	1.00	CH-1,3(1)
	4	581	0.82	0.50	CH-2(2)
	5	624	.90	1.00	CH-5,7(2)
	6	723	.98	1.00	CH-1,3(2)
	7	1210	.12	0.12	6-CH <sub>3</sub> (1)
	8	1232	.33	.25	4,8-CH <sub>3</sub> (1)
	9	1328	.41	.38	6-CH <sub>3</sub> (2)
	10	1358	.82	.75	4,8-CH <sub>3</sub> (2)
	11	1452	.41	.38	6-CH <sub>3</sub> (3)
	12	1480	.82	.75	4,8-CH <sub>3</sub> (3)
	13	1576	.12	.12	6-CH <sub>3</sub> (4)
	14	1608	.53	.25	4,8-CH <sub>3</sub> (4)
Azulene-1,3-d <sub>2</sub>	1	396	1.79	2.00	CH-2(1) + CH-4,8-(1) + CH-6(1)
	2	439	1.44	2.00	C-9,10
	3	512	1.57	1.00	CH-5,7(1)
	4	550	2.10	2.00	CH-2(2) + CH-4,8-(2) + CH-6(2) + [CH-1,3(1)]
	5	664	1.09	1.00	CH-5,7(2)
	6	691	[.52]	(0)	[CH-1,3(2)]
4,6,8-Trimethylazulene-1,3-d <sub>2</sub> <sup>d</sup>	1	405	3.34	3.50	CH-2(1) + C-4,8 + C-6
	2	477	2.55	3.00	CH-5,7(1) + C-9,10
	3	558	[0.38]	(0)	[CH-1,3(1)]
	4	589	0.98	0.50	CH-2(2)
	5	627	1.13	1.00	CH-5,7(2)
	6	660	[0.63]	(0)	[CD-1,3]
	7	721	[0.30]	(0)	[CH-1,3(2)]

<sup>a</sup> Run in CS<sub>2</sub> solution. <sup>b</sup> All assignments, except for CH-1,3, are tentative. <sup>c</sup> Numbers enclosed in brackets were not included in height normalization. <sup>d</sup> The methyl quartets were not measured.

values for the azulene parameters has been calculated and is presented in Table VIII.

**Charge Distributions in Non-alternate Hydrocarbons.**—The  $\pi$ -electron charge densities in acenaphthylene and fluoranthene have been calculated by the simple Hückel i.c.a.o.-m.o. method<sup>18-20</sup> and are shown below on the molecular diagrams.<sup>20</sup>



These values of  $q_r$ , however, correspond to dipole moments of 2.86  $D$  and 1.97  $D$  for acenaphthylene and fluoranthene, respectively, and the observed moments are about 0.3  $D$  and 0.0  $D$ .<sup>18</sup> Because of this exaggeration of the charge

(18) A. Pullman, B. Pullman, E. D. Bergmann, G. Berthier, E. Fischer, Y. Hirshberg and J. Pontis, *J. chim. phys.*, **48**, 359 (1951).

(19) C. Sandorfy, *Compt. rend.*, **227**, 198 (1948).

(20) B. Pullman and A. Pullman, "Les Theories Electroniques de la Chimie Organique," Masson et Cie, Paris, 1952, p. 409.

TABLE VII  
C<sup>13</sup> CHEMICAL SHIFTS AND SPIN-SPIN COUPLINGS IN  
AZULENES<sup>a</sup>

Compound	Group	$\delta_c$ , p.p.m.	$J$ , c./s.
	CH-2	55.4	152
	CH-4,8	55.4	152
	CH-5,7	70.0	156
	CH-6	55.4	152
	C-9,10	52.1	..
Azulene-1,3-d <sub>2</sub>	CH-1,3 <sup>b</sup>	73.0	141
	CH-2	55.6	154
	CH-4,8	55.6	154
	CH-5,7	69.2	152
	CH-6	55.6	154
	C-9,10	51.6	..
4,6,8-Trimethylazulene	CH-1,3	75.4	164
	CH-2	58.1	174
	C-4,8	47.9	..
	CH-5,7	64.7	148
	C-6	47.9	..
	C-9,10	56.0	..
	4,8-CH <sub>3</sub>	167.0	122
	6-CH <sub>3</sub>	163.6	123
4,6,8-Trimethylazulene-1,3-d <sub>2</sub>	CH-1,3	75.3	162
	CD-1,3 <sup>c</sup>	77.6	<sup>d</sup>
	CH-2	58.5	184
	C-4,8	47.6	..
	CH-5,7	65.0	150
	C-6	47.6	..
	C-9,10	56.1	..

<sup>a</sup> Based upon the tentative assignments of Table VI. <sup>b</sup> The peaks were weak and the calculated shift and coupling are not accurate; the CD-1,3 resonance was not detected. <sup>c</sup> The peak is broad, weak and difficult to measure. The shift may not be very accurate. <sup>d</sup> The expected 1:1:1 triplet splitting was not resolved.

TABLE VIII  
ESTIMATED BEST VALUES FOR C<sup>13</sup> CHEMICAL SHIFTS AND  
SPIN-SPIN COUPLINGS IN AZULENE

Group	Source	$\delta_c$ , p.p.m.	$J$ , c./s.
CH-1,3	Calculated from $\nu_c$ [CH-1,3(2)] of azulene and $J$ [CH-1,3] from 4,6,8-trimethylazulene	73.8	164
CH-2	Average values from 4,6,8-trimethylazulene and 4,6,8-trimethylazulene-1,3-d <sub>2</sub>	58.3	179
CH-4,8	Azulene-1,3-d <sub>2</sub> . (Azulene gives almost the same $\delta_c$ and $J$ )	55.6	154
CH-5,7	Average values from azulene and azulene-1,3-d <sub>2</sub>	69.6	154
CH-6	Same as for CH-4,8	55.6	154
C-9,10	Azulene	52.1	..

displacements typical of simple Hückel m.o. calculations, the  $q_r$  shown above have only qualitative significance. More complete calculations have been carried out for azulene.<sup>21-23</sup> The Hückel m.o. model predicts a dipole moment of 6.9  $D$ , but by the inclusion of configuration interaction Pariser<sup>21</sup> was able to reduce the calculated moment to 1.88  $D$ , and a moment of 1.33  $D$  was obtained by the v.e.s.c.f. method,<sup>22</sup> in good agree-

(21) R. Pariser, *J. Chem. Phys.*, **25**, 1112 (1956).

(22) R. D. Brown and M. L. Heffernan, *Austral. J. Chem.*, **13**, 38 (1960).

(23) For a general review and discussion of earlier work, see E. Heilbronner in D. Ginsburg, "Non-benzenoid Aromatic Compounds," Interscience Publishing Co., New York, N. Y., 1959, pp. 177-205.

ment with the experimental value of 1.0  $D$ .<sup>24</sup> In Table IX, the values of  $q_r-1$  obtained from the simple Hückel m.o.,<sup>21</sup> m.o. with configuration interaction<sup>21</sup> and v.e.s.c.f.<sup>22</sup> calculations are compared with the differences between the azulene shifts, taken from Table VIII, and that of benzene. The general correlation between the two parameters is fairly good. Except for the apparent equality of the shifts of CH-4,8 and CH-6, the v.e.s.c.f.  $\Delta q_r$  and  $\Delta\delta_c$  values occur in the same order and have the same signs. The shift of C-9,10 is difficult to compare with the calculated electron density. As a first approximation, the shift relative to C-4a,8a in naphthalene has been given in the table. The 9,10 bond in azulene is apparently unusually long,<sup>25,26</sup> and there might be a contribution to the shift from the change in the  $\sigma$ -bond.

The uncertainties in the experimental data and in the theoretical calculations are so large that a detailed discussion of the correlation displayed in Table IX would be of little use. Even if all molecular properties other than the  $\pi$ -electron densities make only negligible contributions to the shifts, better agreement than that shown in Table IX could hardly be hoped for. Comparison of the results obtained by Pariser<sup>21</sup> from a Hückel m.o. calculation including configuration interaction with those obtained by Brown and Hefferman<sup>22</sup> from a variable electronegativity s.c.f. treatment will show that, although the calculated dipole moments are not very different, the  $\Delta q_r$  found by Pariser are much larger. Similar charge distributions are found by both methods, but the charges are so distributed that the dipole moment is relatively insensitive to their magnitudes. The simple Hückel m.o. charge distributions in acenaphthylene and fluoranthene show less variation than do those calculated for azulene by the same method, and the smaller extensions of their spectra therefore support the proposed correlation. Calculations with improved wave functions would presumably give qualitatively similar but less exaggerated charge separations.

TABLE IX

A COMPARISON OF CALCULATED  $\pi$ -ELECTRON DENSITY DIFFERENCES WITH  $C^{13}$  CHEMICAL SHIFTS IN AZULENE

Group	$\Delta q_r^a$			$\Delta\delta_c, b$ p.p.m.
	h.m.o. <sup>c</sup>	h.m.o. + c.i. <sup>c</sup>	v.e.s.c.f. <sup>d</sup>	
CH-1,3	0.173	0.096	0.059	8.8
CH-2	.047	— .021	— .012	— 6.7
CH-4,8	— .141	— .122	— .046	— 9.4
CH-5,7	— .014	.049	.011	4.6
CH-6	— .130	— .052	— .031	— 9.4
C-9,10	.027	.013	— .002	(— 4.5) <sup>e</sup>

<sup>a</sup> Equal to  $q_r-1$ . <sup>b</sup> Relative to benzene. <sup>c</sup> Ref. 21. <sup>d</sup> Method (ii) of ref. 22. <sup>e</sup> Relative to C-4a, 8a of naphthalene.

If the v.e.s.c.f.  $\Delta q_r$  for azulene are plotted against the experimental  $\Delta\delta_c$ , the best straight line through the points passes near the origin and has a slope  $\Delta\delta_c/\Delta q_r$  of about 200 p.p.m./electron. Detailed

(24) G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949).

(25) J. M. Robertson, H. M. M. Shearer, G. A. Sim and B. G. Watson, *Nature*, **182**, 177 (1958).

(26) Ref. 23, pp. 205-207.

calculations of the shifts would be difficult and possibly not worth attempting until better wave functions have been obtained. An approximate estimate of the effect of changes in  $\pi$ -electron densities on shifts can be made by extending the Saika and Slichter analysis of fluorine shifts.<sup>27</sup> They first assume that the differences in the diamagnetic shielding for the atom in question will be negligible. For carbon it has been calculated<sup>28</sup> that one  $p$ -electron contributes only about 15 p.p.m. to the diamagnetic shielding term, which may therefore be neglected. The second assumption is that contributions to the shielding from electrons on other atoms can be neglected, so that a fluorine atom in a purely covalent molecule can be approximated by an isolated fluorine atom with one  $2p$ -electron missing and a resulting paramagnetic shift term<sup>29</sup> given by

$$\Delta\delta = 2/3 (e\hbar/mc)^2 \langle (r^{-3})_{ave} \rangle_{2p} (1/\Delta E) \quad (1)$$

where  $\langle (r^{-3})_{ave} \rangle_{2p}$  is the average of  $r^{-3}$  for the  $2p$ -electrons and  $\Delta E$  is an average excitation energy. The shift given by eq. 1 will decrease as the bond becomes more ionic until it vanishes for the closed-shell fluoride ion. If we make the assumption that only changes in the  $\pi$ -electron distribution affect the ring  $C^{13}$  shifts, eq. 1 may be used to obtain a first approximation to the shift produced by a change in the electron density in the  $\pi$ -bonding  $2p$ -carbon orbital. Taking the Barnes and Smith<sup>30</sup> value of 1.23 a.u. for  $\langle (r^{-3})_{ave} \rangle_{2p}$  of carbon and assuming that  $\Delta E = 5$  ev.,  $\Delta\delta$  is found to be about 240 p.p.m. The very close agreement with the estimate made above from the azulene data is certainly fortuitous; the best value for  $\Delta E$  might well be considerably different from the 5 ev. assumed,<sup>31</sup> and the approximations in the theory are severe. Nevertheless, the reasonable magnitude of the result is encouraging and suggests that efforts to improve the calculations might be worthwhile.

**Methyl  $C^{13}$  Shifts in 4,6,8-Trimethylazulene.**—The two methyl quadruplets in the 4,6,8-trimethylazulene spectrum are well resolved and have been assigned as shown in Tables VI and VII on the basis of their intensities. Both appear at markedly lower fields than do methyl groups on a benzene ring,<sup>10</sup> and the difference between the shifts is surprisingly large, considering the absence of any measurable shift between the 6 and 4,8 ring atoms. The possible alternative assignment for azulene mentioned above, with CH-6 at lower field than CH-4,8, would be more compatible with the methyl shifts. Contributions to the shielding from ring currents<sup>32</sup> are too small to account for the methyl shifts and are of the wrong sign. Data on methyl-naphthalenes and on other methylazulenes are needed for comparison.

**Ferrocene.**—The spectrum of a  $CS_2$  solution of ferrocene is shown in Fig. 18. The doublet peaks

(27) A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1955).

(28) P. C. Lauterbur, to be published.

(29) N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950).

(30) R. G. Barnes and W. V. Smith, *ibid.*, **93**, 95 (1958).

(31) No satisfactory way of estimating these  $\Delta E$  values has been proposed. Judging by the known excited states, it is unlikely to be much less than 5 ev., but it is difficult to estimate a reasonable upper limit.

(32) Ref. 11, pp. 256-257.



are located at  $\nu_c = 964$  and  $1138$  c./s., and  $\delta_c = 123.6$  p.p.m. and  $J = 174$  c./s. For  $\Delta\delta_c/\Delta q_r = 200$ , the shift relative to benzene corresponds to a  $q_r$  of about 1.3, or a total of 1.5 electrons per ring. This is not significantly different from the 1.0 electrons per ring and  $q_r$  of 1.2 of the  $C_6H_6^-$  ion. The involvement of the  $\pi$ -orbitals of the ring with the iron may have an important effect on the shifts; measurements on the spectra of the  $C_5H_5^-$  ion itself (and on  $C_7H_7^+$ ) would be most interesting.

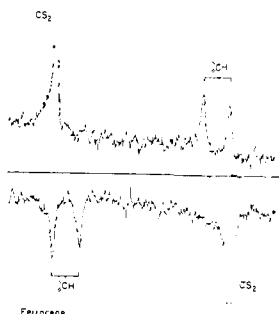


Fig. 18.—The 8.50 Mc./s.  $C^{13}$  n.m.r. spectrum of ferrocene.

**Carbon-Hydrogen Spin-Spin Coupling Constants.**—A relationship between the  $s$  characters of carbon-hydrogen bonds and the carbon-hydrogen spin-spin couplings has been proposed by several authors.<sup>15,33,34</sup> For non-equivalent hy-

brids, the  $s$  character can be calculated from the orthogonality conditions.<sup>35</sup> A set of plane trigonal hybrids with one angle of  $108^\circ$  requires about 53%  $s$  character in the opposite bond and a coupling constant of about 250 c./s. if the value for  $120^\circ$  and 33%  $s$  character is taken as 159 c./s. from benzene. The 174 c./s. coupling in ferrocene, in which the C-C-C angles are  $108^\circ$ , requires that the bonds be strongly bent, with only a slight disturbance of the  $sp^2$  hybridization of the carbons. It might be argued that ferrocene is unusual, but couplings of about 175 c./s. have also been found for the  $\beta$ -carbons in pyrrole, furan and thiophene.<sup>36</sup> The couplings in the five-membered ring of azulene also appear to be larger than those in benzene. Couplings of about 110 c./s. might be expected for seven-membered rings; although none of the experimental couplings for the large ring in azulene are believed to be very accurate, they are all slightly less than the benzene value and imply that there has been little change in the hybridization. Table II shows that methyl substitution changes the benzene couplings. Hybridization changes might be responsible, but there is no good independent way of estimating them.

(33) M. Karplus and D. M. Grant, *Proc. Natl. Acad. Sci. U. S. A.*, **45**, 1269 (1959).

(34) J. N. Shoolery, *J. Chem. Phys.*, **31**, 1427 (1959).

(35) C. A. Coulson, "Valence," Oxford University Press, London, 1953, pp. 193-195.

(36) P. C. Lauterbur, to be published in later papers of this series.

[CONTRIBUTION FROM MELLON INSTITUTE, PITTSBURGH, PENNSYLVANIA]

## $C^{13}$ Nuclear Magnetic Resonance Spectroscopy. II. Phenols, Anisole and Dimethoxybenzenes

BY PAUL C. LAUTERBUR<sup>1</sup>

RECEIVED AUGUST 5, 1960

The  $C^{13}$  n.m.r. spectra of phenol and five methylphenols and of anisole, the three dimethoxybenzenes and 3,4-dimethoxytoluene have been obtained and complete assignments have been made. The effects of methyl groups on the spectra of methylphenols have been analyzed in detail, and the ring  $C^{13}$  chemical shifts caused by OH,  $OCH_3$  and  $CH_3$  are compared with other n.m.r. data, calculated charge distributions and substituent constants. The effects of the methoxy groups in the dimethoxybenzenes are found to be nearly additive when they are *meta* or *para* to one another but not when they are *ortho*.

### Introduction

The  $F^{19}$  chemical shifts in substituted fluorobenzenes have been correlated with Hammett  $\sigma$  constants<sup>2</sup> and with separated inductive and resonance substituent constants.<sup>3-5</sup> Proton chemical shifts in substituted benzenes appear to be related to substituent constants in much the same way,<sup>3,4,6,7</sup> even to having about the same ratio of susceptibilities to inductive and resonance parameters.<sup>4</sup> Methyl  $C^{13}$  shifts in substituted toluenes have also

been studied,<sup>8</sup> but the shifts found for *meta* and *para* methyl groups were so small compared to the experimental uncertainties that no firm conclusions could be reached. The shifts of *ortho* methyl groups were found to be proportional to those of *ortho* fluorines after adjustment by an empirical factor meant to compensate for the different susceptibilities of methyl groups and fluorine atoms to resonance interactions. The chemical shifts of the ring carbon atoms themselves might be expected to reflect substituent effects more clearly than those of any substituent. The shifts are large<sup>8</sup> and the effects are not complicated by interactions with substituents other than that being studied. The proton shifts share the latter advantage but are small and subject to long range shielding and to solvent effects,<sup>9</sup> to which  $C^{13}$  shifts appear to be nearly inert.<sup>8</sup> There is also

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