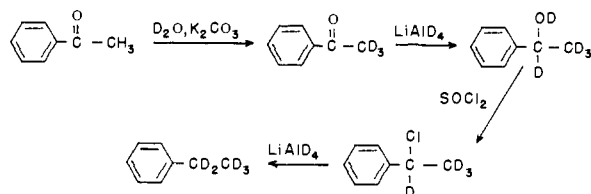


difference is combined with thermochemical data to give the required dissociation energy. If both measured appearance potentials contain the same excess energy term, it drops out when the difference is taken.

### Experimental

Ethylbenzene- $\alpha$ - $d$  and - $\beta$ - $d$  were prepared by reducing  $\alpha$ -chloro- and  $\beta$ -chloroethylbenzene with  $\text{LiAlD}_4$ .<sup>19</sup> Ethylbenzene- $\alpha$ - $d_2$  was made by the disproportionation of ethylbenzene- $\alpha$ - $d$  in the presence of potassium.<sup>19</sup> Ethylbenzene- $o$ - $d$ , - $m$ - $d$  and - $p$ - $d$  were made from the appropriate bromo-magnesium-ethylbenzenes by addition of  $\text{D}_2\text{O}$  of 99.8%



(19) H. Hart, *THIS JOURNAL*, **78**, 2619 (1956).

isotopic purity. Ethylbenzene- $\alpha,\beta$ - $d_5$  was prepared by the formula sequence shown.

The spectra were recorded on a Consolidated model 21-102 mass spectrometer. Isotopic species were determined from spectra obtained at an ionizing voltage sufficient to ionize molecules but insufficient to remove hydrogen atoms from the molecule-ions.<sup>20,21</sup> Spectra of the monodeuteroethylbenzenes and toluenes were corrected for contributions from undesired isotopic species.

**Acknowledgment.**—The ring-deuterated ethylbenzenes and ethylbenzene- $\alpha,\beta$ - $d_5$  were prepared by C. J. Norton. The ethylbenzene- $\alpha$ - $d$ , - $\beta$ - $d$  and  $\alpha$ - $d_2$  were prepared by Harold Hart of Michigan State College. Toluene- $\alpha$ - $d_3$  and - $p$ - $d$  were kindly supplied by H. C. Brown of Purdue University. Toluene- $\alpha$ - $d$ , - $o$ - $d$  and - $m$ - $d$  were kindly supplied by E. L. Eliel of the University of Notre Dame.

(20) R. E. Honig, *Anal. Chem.*, **22**, 1474 (1950).

(21) D. P. Stevenson and C. D. Wagner, *THIS JOURNAL*, **72**, 5612 (1950).

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## Nuclear Resonance Spectra of Hydrocarbons: The Free Electron Model

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The classical free electron model of Pople is used to predict the high resolution nuclear resonance spectra of some hydrocarbons. The modifications necessary to describe the spectra of simple substituted benzenes are discussed. Some previous measurements by other workers of the spectra of condensed aromatic substances are repeated somewhat more precisely, and agree only very crudely with the simple free electron theory. The spectra of two 1,4-polymethylenebenzenes are predicted and support the fundamental ideas of Pople. The spectrum of 2,2-paracyclophane is also reported.

Pople<sup>1</sup> has proposed recently a classical free electron model to account for the chemical shifts in nuclear resonance spectra of protons attached to aromatic rings. As in Pauling's<sup>2</sup> theory of the diamagnetic anisotropy of aromatic substances, the  $\pi$  electrons are considered to acquire a circulation about the ring as it is immersed in a magnetic field. The resulting supercurrent is responsible for a diamagnetic moment whose field is felt by nearby nuclei. Pople<sup>3</sup> has applied this model to an interpretation of the spectra of condensed hydrocarbons reported by Bernstein and Schneider.<sup>4</sup> Qualitative agreement was obtained despite the facts that: (1) the diamagnetic ring current, taken in the plane of the molecule, was replaced by an equivalent point dipole and (2) the available experimental data provided only *relative* chemical shifts, uncorrected for the effects of bulk diamagnetism.

In this paper we comment on the effects of refining the calculations somewhat (still preserving their classical basis) upon the quality of the agreement with an improved version of some of Bernstein and Schneider's results, and we also report on a test of the free electron hypothesis using molecules not all of whose protons are confined to the plane of an aromatic ring.

(1) J. A. Pople, *J. Chem. Phys.*, **24**, 1111 (1956).

(2) L. Pauling, *ibid.*, **4**, 673 (1936).

(3) J. A. Pople, private communication.

(4) H. J. Bernstein and W. G. Schneider, *J. Chem. Phys.*, **24**, 468 (1956).

### Experimental

The sources of our samples and information bearing on their purities are shown in Table I.

Spectra were obtained with a Varian Associates V-4300-B high resolution spectrometer at a frequency of 40 Mc. Chemical shifts were measured with reference to a sealed Pyrex capillary filled with water and placed inside the 5 mm. Pyrex tube containing the sample. Where convenient, measurements were made by the method of superposing audio-frequency sidebands from a calibrated Hewlett Packard 200-I oscillator,<sup>5</sup> giving a precision for sharp lines of about  $\pm 1$  c.p.s. In other cases the shifts were read from recordings of the spectrum, corrected for sweep non-linearity. For substances very soluble in  $\text{CCl}_4$ , the shifts were determined at volume fractions of solute of approximately 1, 0.25, 0.06 and 0.015, and extrapolated to zero. In other cases, e.g., 2,2-paracyclophane, a single measurement was made at a very low concentration.

#### Calculations: The Chemical Shift in Benzene.—

As Pople<sup>1</sup> points out, a superconducting circular loop in a field  $\mathbf{H}_0$  carries a current  $I = e^2 \mathbf{H}_0 \cdot \mathbf{n} / 4 \pi m c$  for each free electron, where  $\mathbf{n}$  is a unit vector normal to the plane of the loop. In cylindrical coordinates  $(\rho, \phi, z)$ , referred to the loop and measured in units of its radius  $a$ , the  $z$ -component of this field is

$$H_z' = \frac{Ik}{4\pi ca\rho^{1/2}} \left[ K(k) + \frac{1 - \rho^2 - z^2}{(1 - \rho)^2 + z^2} E(k) \right]$$

$$k^2 = \frac{4\rho}{(1 + \rho)^2 + z^2}$$

(5) J. T. Arnold and M. E. Packard, *ibid.*, **19**, 1608 (1951).

TABLE I  
PROTON CHEMICAL SHIFTS  $\delta = (H_{H_2O} - H_{res})/H_{H_2O}$  IN PARTS PER MILLION

All values are  $\pm 0.05$ . In the case of molecules containing more than one group of equivalent protons of a given type, the tabulated value refers to the absorption maximum with the largest  $|\delta|$ . Where J-multiplets are resolved, the center of the multiplet is taken. All values are extrapolated to infinite dilution in  $CCl_4$ .

	Ar	CH <sub>2</sub>	=C <sup>H</sup>	Source and purity
Cyclohexane	..	-3.27	..	Eastman Yellow Label
Benzene	2.50	....	..	Fisher Reagent
Ethylbenzene	2.35	-2.15	..	Eastman White Label
Dibenzyl	2.35	-1.96	..	Matheson pure
<i>p</i> -Xylene	2.19	....	..	Eastman White Label
Cyclohexadiene-1,3	..	-2.60	1.02	Upjohn; b.p. 78-81°; $n_{D}^{25}$ 1.4720
Cyclooctatriene-1,3,5	..	-2.45	0.98	P. T. Moore prep.; $n_{D}^{25}$ 1.5243
Cyclooctatetraene	..	....	0.98	A. C. Cope; redistilled
1,2-Benzocyclooctene-1	..	-3.30	..	I. Goldman; b.p. 96-96.6° (6 mm.); $n_{D}^{22.5}$ 1.5388
1,4-Decamethylenebenzene	2.21	-4.0	..	D. Knutson prep.; <i>Anal.</i> 88.64% C, 11.18% H; $n_{D}^{25}$ 1.5240; infrared spectrum appears normal <sup>8</sup>
1,4-Dodecamethylenebenzene	2.2	-3.8	..	D. J. Cram; b.p. 163.5-164.5°; $n_{D}^{25}$ 1.5206
2,2-Paracyclophane	1.62	-1.71	..	M.p. 286-288°

TABLE II  
 $B_0(\rho, z)$

z	$\rho$													
	0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.5	3.0	4.0
0	1.000	1.031	1.141	1.410	2.255	$\pm\infty$	-1.066	-0.402	-0.212	-0.129	-0.086	-0.039	-0.021	-0.008
.2	0.942	0.965	1.038	1.177	1.299	0.425	-0.387	-.284	-.177	-.115	-.079	-.037	-.020	-.008
.4	.800	.806	0.818	0.806	0.672	.308	-.019	-.113	-.105	-.083	-.063	-.035	-.019	-.008
.7	.550	.542	.515	.456	.345	.214	.088	.011	-.023	-.034	-.034	-.024	-.016	-.007
1.0	.356	.345	.321	.278	.220	.153	.092	.045	.015	-.002	-.010	-.014	-.011	-.005
1.5	.171	.167	.156	.138	.116	.091	.068	.047	.030	.018	.009	-.006	-.004	-.002
2.0	.089	.088	.083	.076	.067	.057	.046	.036	.028	.020	.014	.004	.000	.000
3.0	.032	.031	.030	.029	.027	.024	.022	.018	.016	.014	.012	.007	.000	.000

where  $K$  and  $E$  are complete elliptic integrals. We wish the expectation value, over the motions of the molecule, in the direction  $H_0$

$$H'_{eff} = \frac{1}{H_0} \int \mathbf{H}_0 \cdot \mathbf{H}' d\Omega$$

We see that  $H_{\rho}'$  is eliminated, and the result is

$$H'_{eff} = \frac{ne^2 H_0}{24\pi mc^2 a} B_0$$

$$B_0 = \frac{1}{2\pi\rho^{1/2}} [K(k) + \frac{1-\rho^2-z^2}{(1-\rho)^2+z^2} E(k)]$$

in which  $n$  is the number of free  $\pi$  electrons. The function  $B_0$  plays the same role as that of  $2\pi r^{-3} P_2(\cos\theta)$  in the dipole approximation.  $B_0(\rho, z)$  is tabulated in Table II.

Using this result to find the chemical shift  $\delta = H'_{eff}/H_0$  for protons attached to an aromatic ring, we have  $\delta_{arom} = +2.2 \times 10^{-6}$ , assuming  $a = 1.4$  Å. and  $d_{CH} = 1.1$  Å. This is to be contrasted with a result of  $+1.75 \times 10^{-6}$  from the dipole approximation. In order to compare this result with experiment, we must have some idea of the "chemical" part of the total shift, *i.e.*, the absolute chemical shift these protons would have if their surroundings were in every respect like those in benzene except for the free circulation of  $\pi$  electrons. We have chosen cyclohexadiene-1,3, cyclooctatriene-1,3,5 and cyclooctatetraene as representative of the type of C-H bond hybridization found in benzene. The chemical shifts are given in Table I. Combining these results with the aromatic shift calculated above, we expect a total shift, relative to  $H_2O$ , of about  $+3.2$  p.p.m. for "aromatic" protons. The observed values fall

over a rather large range, with benzene having a representative shift of  $+2.50$  p.p.m.

These numbers can be brought into essential *ad hoc* agreement by remembering that the  $\pi$ -current is *not* confined to the plane of the aromatic ring, but has its maximum density in two regions on either side. Our predicted and measured values for  $\delta_{benzene}$  agree if we divide the  $\pi$ -current into two loops separated by about 0.9 Å. It is interesting to note that the separation of points of maximum electron density in the  $p_z$  orbital of carbon, according to a simple screening constant calculation<sup>6</sup> is about 0.7 Å.

The rather large spread of experimental aromatic shifts for substituted benzenes observed by many investigators may well be largely accounted for by differences in C-H bond structure, as it is in the case of substituted methylene groups, and not by differences in the free electron field. Many of the published values of such shifts exhibit in addition a spurious scatter due to neglect of solvent effects.<sup>7</sup>

**Condensed Aromatic Hydrocarbons.**—A somewhat more thoroughgoing test of the free electron model, but one which is not immune to the effect of differences in hybridization, is provided by the condensed hydrocarbons studied by Bernstein and Schneider.<sup>4</sup> In Fig. 1 are presented our experimental results for three of these substances at infinite dilution in  $CCl_4$ , together with the chemical shifts predicted by the classical free electron model including division of the  $\pi$ -current into two parts. It is evident that the agreement is rather qualitative. Only in anthracene is it possible to make

(6) J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

(7) A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.*, in press.

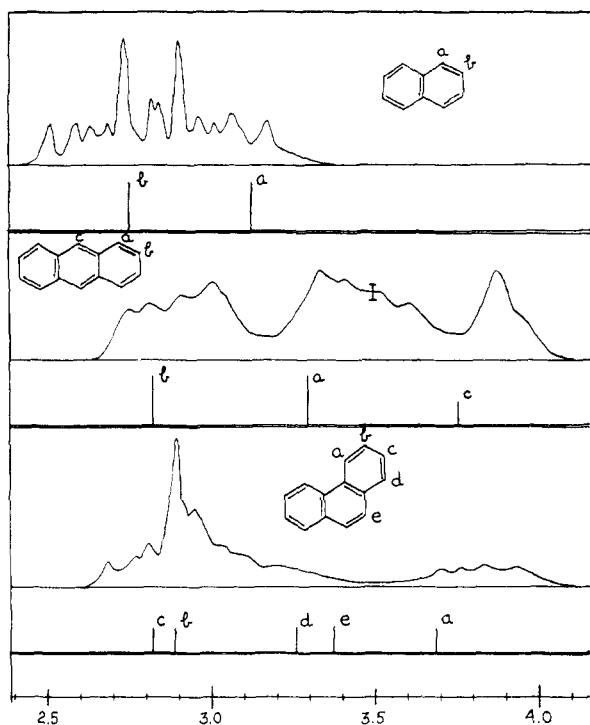
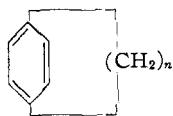


Fig. 1.—Experimental and predicted spectra of some condensed aromatic hydrocarbons. The horizontal scale is in parts per million at infinite dilution in  $\text{CCl}_4$ , measured from  $\text{H}_2\text{O}$ . The  $\pi$  currents are separated by  $1 \text{ \AA}$ . No prediction of J-multiplets has been made.

even a partial experimental assignment of absorption peaks to specific positions in the molecule. In this instance we corroborate the already convincing conclusion of Bernstein and Schneider. It is not altogether pleasant to ascribe the incomplete agreement to hybridization differences, as is clear when we compare the spectra of Fig. 1 with one another.

**Methylene Bridged Hydrocarbons.**—Another test of the theory, which lends strong qualitative support to its fundamental premise, is afforded by



the 1,4-polymethylenebenzenes.<sup>8</sup> In the lower members of this series ( $n \geq 8$ ), the central  $\text{CH}_2$ -groups are confined to a region near the center of the aromatic nucleus, and are expected therefore to experience a free electron field of appreciable magnitude and of sign opposite to that associated with "aromatic" protons. We have predicted the spectra for the cases  $n = 10$  and  $n = 12$  as follows:

(1) The "aromatic" protons are expected to give a single line at about the same position as in *p*-xylene (see Table I).

(2) The  $\text{CH}_2$ -protons directly adjacent to the ring (hereafter denoted by  $\alpha$ ) are expected to experience nearly the same combination of "chemical" effects and free electron field as the corre-

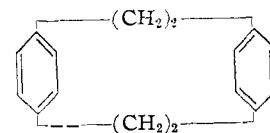
(8) D. J. Cram and H. U. Daeniker, *THIS JOURNAL*, **76**, 2743 (1954).

sponding protons in ethylbenzene. We thus predict a triplet (due to J-coupling with the  $\beta$  protons) with  $\delta = -2.2$  p.p.m.

(3) The remaining ( $\beta, \gamma, \dots$ ) protons should have chemical shifts characteristic of saturated, unstrained cyclic hydrocarbons ( $\delta = -3.27$  p.p.m. for cyclohexane) modified by the free electron field. To estimate this, we have constructed Fisher-Hirschfelder models of the molecules and measured the positions of the protons involved. This procedure was repeated several times in order that the positions obtained be representative of those actually taken on in the twisting motions of the methylene bridge. The function  $B_0$  was evaluated for each point (see Table II) and averaged separately for each of the non-equivalent types of protons. The resulting predicted chemical shifts are shown in Fig. 2, together with the experimentally obtained spectra. The agreement is reasonably good, especially for 1,4-decamethylenebenzene. Of course, each chemically shifted component is split by J-interaction with its neighbors into a generally complicated multiplet. In addition, most of the lines obtained, even at elevated temperatures and in  $\text{CCl}_4$  solution, are broadened considerably beyond the resolution of the spectrometer. The reasons for this behavior, which we have observed to be rather common, are not altogether clear to us at present.

The most significant qualitative feature of the spectra of Fig. 2 is the occurrence of absorption at significantly greater negative chemical shifts than are found for  $\text{CH}_2$ -groups in other compounds. In benzocyclooctene (1,2-hexamethylenebenzene), which we have also examined for comparison purposes, the last  $\text{CH}_2$  absorption maximum occurs at  $-3.3$  p.p.m., which is entirely characteristic of cyclic methylene groups. The spectrum of this compound, which also appears in Fig. 2, was calculated in the manner described above, except that no free electron effect was included.

**2,2-Paracyclophane.**—We have also obtained the spectrum of 2,2-paracyclophane<sup>9</sup>



Initially we had hoped that it would throw some further light on the free electron model; but calculations show that both varieties of protons lie in regions where the diamagnetic ring moment has very little effect, except that of course each aromatic proton feels the effect of its own ring. We report the chemical shifts here because of their anomalous size, presumably connected with the presence of strain. The benzene rings are known to be non-planar,<sup>10</sup> the substituted carbon atoms being  $0.13 \text{ \AA}$ . out of the plane of the other four. The circulation of the  $\pi$  electrons is thus apparently sufficiently impaired so that  $\delta_{\text{arom.}}$  is about midway between that in *p*-xylene and that characteristic of conjugated non-aromatic systems such as cyclo-

(9) D. J. Cram and H. Steinberg, *ibid.*, **73**, 5691 (1951).

(10) C. J. Brown and A. C. Farthing, *Nature (Lond.)*, **164**, 915 (1949).

hexadiene-1,3. On the basis of our simple free electron model this would correspond to a  $\pi$ -current only half as large as normal.

$\delta_{CH}$  is also smaller than might be expected on purely chemical grounds. The corresponding value in dibenzyl, which might be expected at first sight to be about the same, is  $-2.0$  p.p.m. The large deviation from this value in (2,2)-*p*-cyclophane must be attributed to the effect of strain on C-H bond hybridization. The aliphatic C-C-C bond angle in this substance is  $115^\circ$ .<sup>9</sup> It seems unlikely to us, however, that the effect can be ascribed completely to the contribution of hyperconjugated structures which give aliphatic double bond character to the bridges. It is interesting that the chemical shift anomaly here is opposite to that found in small (cyclopropane) rings, in which the C-C-C angles are constrained to have *less* than their ideal values.

### Conclusions

We feel that the investigations described above constitute strong support for Pople's suggestion that the field due to freely precessing  $\pi$  electrons in six-membered aromatic rings is important in determining chemical shifts in molecules containing such rings. Agreement between experiment and calculations from Pople's model is often not entirely quantitative, but is good enough so that one may entertain the notion that the deviations observed may be due to the operation of more conventional "chemical" effects of an incompletely predictable variety. While the model may be somewhat oversimplified, we have not felt it desirable at this time to add further refinements, such as the ascription of different  $\pi$ -currents to different rings in condensed aromatic systems.<sup>2</sup> We suggest, however that it would be interesting to obtain comparisons between the ethylenic chemical shifts in substituted conjugated cyclic polyenes and in the corresponding substituted benzenes. Such data might suggest whether any part of the observed wide range of substituent effects on aromatic proton shifts is to be ascribed to modification of the  $\pi$ -current by the substituents.

We have a few preliminary data which suggest that  $\pi$  electron effects in five-membered aromatic rings may not be entirely describable on the basis of the above model. A later communication will deal with this problem.

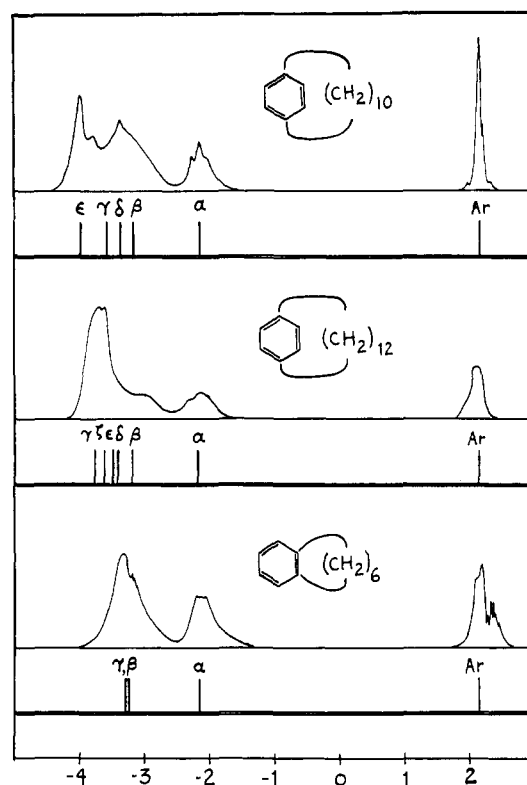


Fig. 2.—Experimental and predicted spectra of three polymethylenebenzenes. The horizontal scale is as in Fig. 1. The  $\pi$  currents are separated by  $0.9 \text{ \AA}$ ., but only the lines marked Ar are sensitive to this spacing. The symbols  $\alpha, \beta, \dots$  designate  $\text{CH}_2$  groups at progressively greater distances from their points of attachment to the aromatic ring.

**Acknowledgment.**—We would like to express our indebtedness to Mr. D. Knutson, Mrs. P. T. Moore and Professor D. J. Cram for their kindness in preparing and donating some of the more exotic compounds we have studied. This work was supported in part by the Army (Signal Corps), the Air Force (Office of Scientific Research, Air Research and Development Command), and the Navy (Office of Naval Research); and in part by the Petroleum Research Fund of the American Chemical Society. In addition, R. W. F. wishes to state his appreciation for support under a National Science Foundation Predoctoral Fellowship.

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