several molecules using both Pariser–Parr and theoretical integrals. It is seen that the results when the same integrals are used are essentially the same. The differences between the localization energies from the present program and the previous work are essentially constant at 0.3–0.4 ev. The bulk of this difference is due to the fact that the previous program included a compensation for the distortion of the bond lengths in the molecule from the value for an isolated carbon–carbon bond.[17] The principal point is that the localization energy differences, both within a given molecule and within the series, are the same in the two cases using the same integrals.

Conclusions

It has been shown that qualitative agreement between open-shell calculations and CI calculations of excited triplet-state localization energies is obtained. This agreement is far from quantitative, however. The methods do not predict the same positions of reaction within a molecule or even the same over-all reactivity within a series. The excited singlet-state basicities calculated by the CI method give satisfactory agreement with experiment; hence, this implies that the CI results might be preferable to the open-shell results for the triplet states. This, however, can only be conjecture, in the absence of confirming experimental evidence.

It has also been shown that the predicted position of attack in SCMO calculations is dependent upon the method of evaluating two-center, two-electron repulsion integrals. This is a factor which should be investigated in detail.

Acknowledgments. The author expresses his appreciation to the Louisiana State University in New Orleans Computer Research Center (supported in part by NSF Grant No. GP 2964) for generous provision of computer time. He also thanks Dr. O. W. Adams of Abbott Laboratories for making available his SCMO program from which the present program evolved.

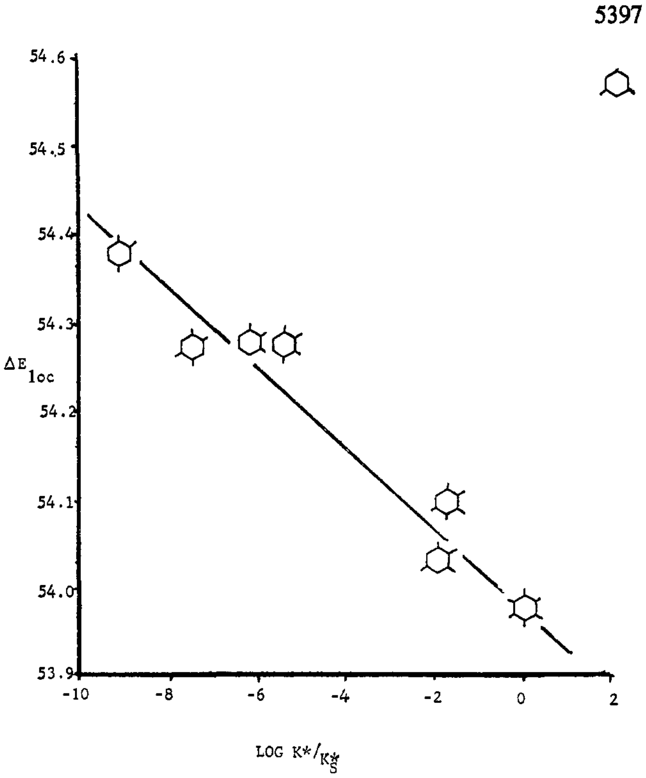

Figure 3. Plot of ΔE_{loc} for excited singlet states calculated by the CI method with experimental relative excited singlet-state basicities[4] (localization energies corrected for the number of equivalent reactive positions and for attack at a methyl-bearing position where appropriate; basicities referred to hexamethylbenzene as a standard).

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[17] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, 11, 96 (1960).

Carbon-13 Magnetic Resonance. VI.[1a] Theory of Carbon-13 Magnetic Resonance Shifts in Aromatic Molecules[1b]

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Abstract: The 15.1-Mcps carbon-13 nuclear magnetic resonance spectra of biphenyl, naphthalene, phenanthrene, and pyrene have been obtained, and with the exception of the two bridgehead peaks in phenanthrene all of the resonance peaks have been assigned. An extension to the theory of chemical shifts for aromatic carbons is proposed which considers both σ- and π-electron density terms as they alter a proposed effective nuclear charge parameter for each bond. The theory is applied to toluene, chlorobenzene, and the above four alternant aromatic compounds.

Carbon-13 chemical shift values of aromatic compounds have been studied[2–5] with the purpose of illucidating additional details of the electronic structure in this interesting class of compounds. Empirically, it has been found that carbon-13 shifts vary

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[1] (a) Previous paper in this series: W. R. Woolfenden and D. M. Grant, *J. Am. Chem. Soc.*, 88, 1496 (1966); (b) taken in part from the Ph.D. dissertation of T. D. Alger, University of Utah, Aug. 1966.

[2] P. C. Lauterbur, *J. Chem. Phys.* 26, 217 (1957); *J. Am. Chem. Soc.*, 83, 1838 (1961).

[3] H. Spiesecke and W. G. Schneider, *Tetrahedron Letters*, 468 (1961).

[4] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, 35, 731 (1961).

[5] P. C. Lauterbur, *ibid.*, 43, 360 (1965).

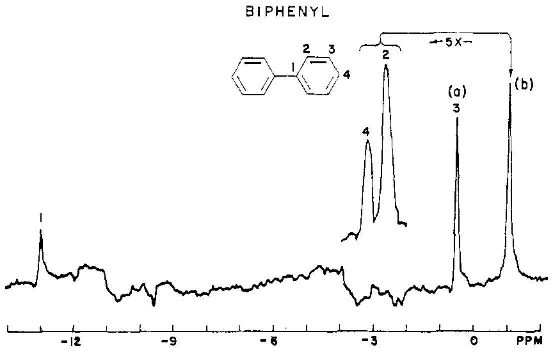

Figure 1. The proton-decoupled carbon-13 magnetic resonance spectra of biphenyl.

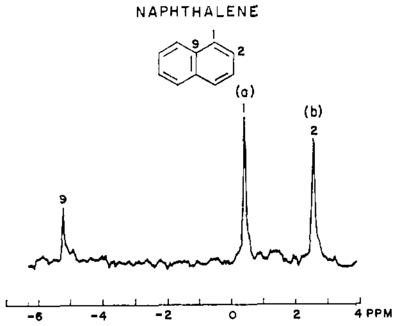

Figure 2. The proton-decoupled carbon-13 magnetic resonance spectra of naphthalene.

by approximately 160–200 ppm per unit of π-electron charge in substituted benzenes[2] and in the isoelectronic series $C_5H_5^-$, C_6H_6, and $C_7H_7^+$.[3] A similar dependence upon π-electron charge was also noted in selected nitrogen heteroaromatic systems[5] providing σ-polarization terms are considered in carbons adjacent to the heteroatom.

Theoretical considerations[6–9] have emphasized the importance in aromatic chemical shifts of variations in the π-electron charge density and in mobile bond-order terms. The final expression of Karplus and Pople[8] is convenient for estimating the magnitude of variations in the chemical shift resulting from either of these two terms. This paper extends the previous formulation of the chemical shift terms arising from charge polarization to include variations in the σ-electronic structure. Two-electron terms of the type which reflect changes in the mobile bond orders are essentially those derived by Karplus and Pople.[8]

More complete data are obtained with greater precision for several alternant aromatic hydrocarbons by the proton-decoupling technique.[10] In previous rapid-passage work[2] it was possible only to differentiate bridgehead carbons from the other ring carbons, whereas in this work the resonance peaks in the decoupled spectra have been observed for all of the nonequivalent carbons with the exception of the unresolved peaks due to C-2 and C-3 in phenanthrene.

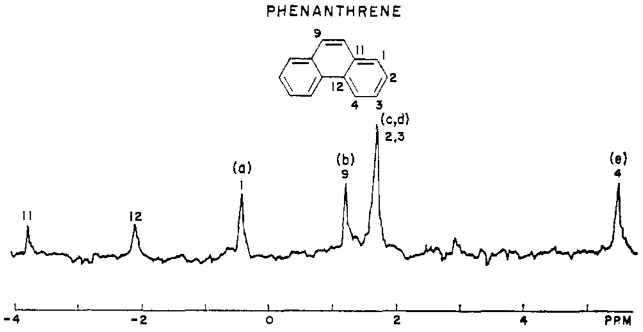

Figure 3. The proton-decoupled carbon-13 magnetic resonance spectra of phenanthrene.

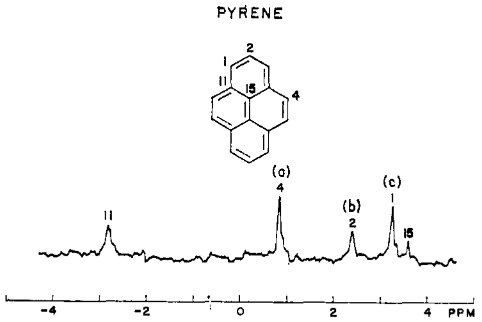

Figure 4. The proton-decoupled carbon-13 magnetic resonance spectra of pyrene.

Experimental Section

A. Equipment. A Varian high-resolution spectrometer equipped with a V-4311 transmitter operating at 15.1 Mcps is used to obtain the carbon-13 magnetic resonance spectra. Proton decoupling is accomplished with a Varian V-4320 spin decoupler operating at 60 Mcps. The Varian V-4331 probe used in this work is fitted with a 15-mm insert. Sample tubes (12 mm) are spun with a Wilmad spinner assembly.

The frequencies of both the transmitter and the proton decoupler are measured with a Hewlett-Packard 524C electronic counter equipped with a 524-A frequency converter capable of counting with a precision of ±0.1 cps. Instabilities in the decoupler frequency limit this measurement to an accuracy of about ±1 cps. Chemical shift data are obtained by continuously monitoring the decoupler frequency as the decoupler setting is varied in accordance with the method described previously.[10] The transmitter frequency is determined with a precision of about ±0.5 cps.

B. Carbon-13 Chemical Shift Values. The following equation[1a] is used to calculate the experimental chemical shifts.

$$\delta_{C^{13}} = \frac{\Gamma_i - \Gamma_0}{\Gamma_i} + \frac{\Gamma_i}{\Gamma_0}\delta_H \cong \frac{\Gamma_i - \Gamma_0}{\Gamma_i} + \delta_H \qquad (1)$$

For the ith carbon shift, $\Gamma_i = (f_i/v_i)$, f_i is the frequency of the decoupler, v_i is the frequency of the transmitter, and δ_H is the proton shift referenced to benzene. The value for Γ_0 is 3.97644916 when benzene is used as the reference compound.

C. Samples. All compounds were obtained from standard commercial sources and were run as solutions (20–40 mole %) in CS_2. Some were also run in furan to obtain chemical shift data from calibrated sweep rates. The two furan peaks were used as fiducial marks in these spectra.

Results

Proton and carbon-13 chemical shifts are presented in Table I for the compounds under study, and the slow-sweep, proton-decoupled carbon-13 spectra for biphenyl, naphthalene, phenanthrene, and pyrene are given in Figures 1 to 4, respectively. Shift values for chlorobenzene[4] and toluene[11] compounds studied by

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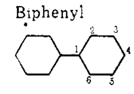
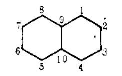
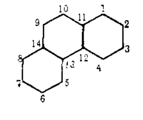
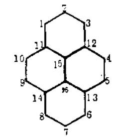
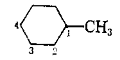
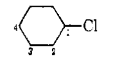
(6) C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, **40**, 1714 (1964).
(7) M. Karplus and T. P. Das, *ibid.*, **34**, 1683 (1961).
(8) M. Karplus and J. A. Pople, *ibid.*, **38**, 2803 (1963).
(9) F. Prosser and L. Goodman, *ibid.*, **38**, 374 (1963).
(10) E. G. Paul and D. M. Grant, *J. Am. Chem. Soc.*, **86**, 2977 (1964).

Table I. Carbon-13 Chemical Shifts of Selected Aromatic Hydrocarbons in CS_2 Solution

Item no.	Compound	Carbon position	Γ_i	$(\Gamma_i - \Gamma_0)/\Gamma_i$, ppm	δ_H, ppm[a,b]	$\delta_{C^{13}}$, ppm[a]
1	Biphenyl	1	...	...	...	−13.0[c]
2		2,6	3.97645474	+1.40	−0.27	+1.13
3		3,5	3.97644766	−0.38	−0.08	−0.46
4		4	3.97645309	+0.98	+0.04	+1.02
	Naphthalene					
5		1,4,5,8	3.97645179	+0.67	−0.23	+0.44
6		2,3,6,7	3.97645889	+2.45	+0.11	+2.56
7		9,10	...	...	...	−5.2[c]
8	Phenanthrene	1,8	3.97644926	+0.02	−0.40	−0.38
9		(2,7)[d]	(3.97645656)[d]	(+1.86)[d]	(−0.07)[d]	(+1.76)[d]
10		(3,6)	(3.97645656)	(+1.86)	(−0.13)	(+1.76)
11		4,5	3.97647541	+6.60	−1.13	+5.47
12		9,10	3.97645481	+1.42	−0.21	+1.21
13		(11,14)[e]	...	...	...	(−3.8)[c,e]
14		(12,13)	...	...	...	(−2.0)
15	Pyrene	1,3,6,8	3.97646489	+3.95	−0.69	+3.26
16		2,7	3.97646078	+2.92	−0.54	+2.38
17		4,5,9,10	3.97645474	+1.40	−0.57	+0.83
18		11,12,13,14	...	...	...	−2.8[c]
19		15,16	...	...	...	+3.6[c]
20	Toluene[f]	1	...	...	...	−9.1[c]
21		2,6	3.9764460	−0.80	0.18	−0.62
22		3,5	3.9764496	0.01	0.18	+0.19
23		4	3.9764605	2.87	0.18	+3.05
24	Chlorobenzene[g]	1	...	...	...	−5.9[c]
25		2,6	3.97644820	−0.23	+0.01	−0.22
26		3,5	3.97644334	−1.47	+0.07	−1.40
27		4	3.97645623	+1.78	+0.22	+2.00

[a] Referenced to benzene; positive values indicate higher field values. [b] Proton assignments: chlorobenzene (ref 3); biphenyl [R. C. Hirst, unpublished work, University of Utah]; naphthalene, pyrene [N. Jonathan, S. Gordon, and B. P. Dailey, *J. Chem. Phys.*, **36**, 2443 (1962)]; phenanthrene [T. Batterham, L. Tsai, and H. Ziffer, *Australian J. Chem.*, **17**, 163 (1964)]. [c] These values are obtained under slow sweep conditions from calibrated sweep rates. Error is estimated at ±0.1 ppm. [d] These two peaks could not be resolved. The average of the proton values was used to obtain $\delta_{C^{13}}$. [e] Tentative assignment based upon theoretical consideration. [f] Taken from W. R. Woolfenden, Ph.D. Thesis, University of Utah, 1965. [g] Literature values in ppm from ref 4 are C-1, −6.4; C-2, −0.6; C-3, −1.0; C-4, +2.0.

others have been included in Table I to provide additional checks on the validity of the theoretical treatment used to analyze the data on the simple alternant aromatic hydrocarbons.

One method used to make some of the spectral assignments given in Table I rests upon the absence in the rapid passage spectra of large proton induced splittings in the resonance of the bridgehead carbons. On this basis the lone quaternary carbons (items 1, 7, 20, and 24 in Table I) contained in four of the compounds were assigned with no difficulty. Items 18 and 19 for pyrene also can be recognized as quaternary peaks and distinguished from one another by the 2:1 intensities observed (see Figure 4) for C-11,12,13,14, and C-15,16, respectively. In phenanthrene the equally intense peaks due to C-11,14 and C-12,13 (items 13 and 14 in Table I) are easily characterized as arising from quaternary carbons, but no additional characteristic spectral feature permits an unequivocal assignment to be made. At the present time these two peaks can be assigned only tentatively on the basis of theoretical considerations. Different values[8] for the theoretical bond orders at the two nonequivalent bridgeheads in phenanthrene predict that the higher field peak (−2.0 ppm) should be due to C-12,13, whereas the lower field peak (−3.8 ppm) is assigned to C-11,14. The similarity of the chemical shift of this lower field peak with the corresponding peak resulting from the bridgehead in naphthalene (−5.2 ppm) is expected as the additional ring in phenanthrene is rather remote from positions C-11,14, and it is reasonable that the electronic environment at C-11,14 would be similar to that in naphthalene.

The spectral features of a larger number of ring carbons in the compounds considered in this work exhibit the same multiplicity and the same intensity, and thus, the assignment of many of these peaks proceeds with some difficulty. Only four peaks (items 4, 16, 23, and 27 in Table I) can be assigned on the basis of unique peak intensities, and this leaves all five different ring carbons in phenanthrene and two ring carbons in each of the other five compounds to be assigned by means other than intensity arguments. The *ortho* and *meta* ring positions (items 21 and 22) in toluene have been assigned[11] from an observable long-range methyl-proton splitting in the *ortho* position, and the corresponding assignments for chlorobenzene (items 25 and 26) were taken from ref 5 in which data on appropriately deuterated compounds were reported.

The remaining assignments are made by comparing the carbon-13 chemical shifts, $\delta_{C^{13}}$, determined from sweep-rate data with $(\Gamma_i - \Gamma_0)/\Gamma_i$, a term referred to as a *decoupling shift*. Equation 1 gives the linear relationship existing between these two quantities and δ_H, the chemical shift of the proton being perturbed by the second radiofrequency field. Normally, one uses the decoupling information with known values of

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(11) W. R. Woolfenden, Ph.D. Thesis, University of Utah, 1965.

Table II

Compound	Peak	Carbon-13 shift sweep data, ppm	$(\Gamma_i - \Gamma_0)/\Gamma_i$, ppm[a]	Position of decoupler frequency, ppm[b]	Proton shifts, ppm[a,c]	Assignment of proton shift
Biphenyl	a	−0.39	−0.35	−0.04	−0.07	C-3,5
	b	+1.18	+1.47	−0.29	−0.25	C-2,6
Naphthalene	a	+0.46	+0.85	−0.39	−0.45	C-1,4,5,8
	b	+2.60	+2.65	−0.05	−0.11	C-2,3,6,7
Phenanthrene	a	−0.22	+0.28	−0.50	−0.51	C-1,8
	b	+1.44	+1.77	−0.33	−0.33	C-9,10
	c[d]	+1.92	+2.13	−0.21	−0.18	C-2,7
	d				−0.24	C-3,6
	e	+5.63	+6.88	−1.25	−1.28	C-4,5

[a] Relative to benzene; positive values indicate higher field values. [b] Calculated from eq 1; error in these values may be as large as ±0.1 ppm. [c] Obtained on a Varian A-60 spectrometer for the same furan solution; see footnote *b* in Table I for assignments. [d] These two peaks were unresolved in the carbon-13 spectrum.

δ_H to calculate $\delta_{C^{13}}$. To do this the proton shift values must be properly paired up with the decoupling shifts of the several carbon-13 singlets. This is possible only if the carbon-13 peaks are correctly assigned. Working in reverse, the positions of the proton decoupler frequency required to give a maximized carbon-13 singlet can be calculated with eq 1 from calibrated sweep data and the decoupling shifts. These values then can be compared with existing proton chemical shift values, and often it is possible to match up these two sets of proton shifts to assign otherwise equivalent carbon-13 peaks.

Table II contains decoupling shifts and calibrated sweep data for biphenyl, naphthalene, and phenanthrene obtained in furan solutions. The peaks are labeled in Table II to correspond with the same labeling in Figures 1–3. As can be observed in Table II the position of the proton-decoupling frequency, calculated from eq 1, agrees within experimental error with recorded proton chemical shifts in all three compounds, and these assignments are indicated in the last column of Table II. In both biphenyl and naphthalene, the separation of the two proton shifts is sufficiently large that only for the assignment given in Table II is agreement realized between the value for δ_H and the calculated position of the two proton-decoupling frequencies. Thus, items 2, 3, 5, and 6 in Table I can be assigned unequivocally by comparing the decoupling shifts with the sweep data in the manner indicated. In phenanthrene at least two assignments (peak a to C-1,8 and peak e to C-4,5) also can be made with confidence as the proton shifts at positions 1,8 and 4,5 are isolated from those arising from the other ring protons. The remaining three assignments are less certain because of the relatively small separations existing between the proton shifts at C-9,10, C-2,7, and C-3,6. However, it should be noted that the possible ways of pairing up the decoupling shifts with proton shifts is reduced greatly from 60 permutations (5!/2!) to three alternatives (3!/2!) as a result of making the two certain assignments (items 8 and 11 in Table I) in phenanthrene. A slightly more accurate analysis of sweep and decoupling data is employed to corroborate the tentative assignment given in Table II for peaks b, c, and d. The relatively low solubility of pyrene in furan prevented the application of the above method of analysis to this compound. Fortunately the one peak of double intensity due to ring carbons C-2,6 can be used as a reference peak in the analysis of the two unassigned ring-carbon peaks of fourfold intensity.

It was shown earlier[12] that only relative peak positions and not absolute values could be compared with decoupling shifts to make unequivocal assignments providing at least three spectral peaks are considered. The relative separations between the intermediate peak and the two outer peaks are measured precisely in the uncalibrated spectrum, and then the ratio of these two quantities is computed. Dividing one quantity into the other eliminates the sweep-rate parameter from this ratio of peak separations and thereby relaxes the requirement that the sweep rate be known. This reduced quantity can then be compared with the same ratio of peak separations as computed for all possible combinations of decoupling shifts with proton chemical shifts. This has been done in Table III for the remaining three possible assignments in phenanthrene using the peaks labeled a, b, and c, in Figure 3. Also included are the two possible permutations in peak assignments for pyrene, using peaks labeled a, b, and c in Figure 4. It should be remembered that peaks a and e in phenanthrene and peak b in pyrene are already assigned and only those permutations involving changes in the unassigned peaks are considered in this analysis. The statistical analysis given in Table III supports the tentative assignments made in Table II for phenanthrene that peak b is due to C-9,10, and therefore the degenerate peak (c,d) must arise from C-2,7 and C-3,6. Furthermore, it is evident that peaks a and c in pyrene can be assigned, respectively, to C-4,5,9,10 and to C-1,3,6,8 on the basis of the agreement between the sweep and decoupling values given in Table III.

Theory

The chemical shift parameter has been subdivided into the following three terms[8,13]

$$\sigma = \sigma_d + \sigma_p + \sigma' \qquad (2)$$

where σ_d arises from diamagnetic electron currents on the observed nucleus, σ_p is the paramagnetic contribution arising from orbitals with intrinsic angular momentum centered on the atom of interest, and σ' includes all remaining terms for interatomic ring currents and electron circulation on other atoms. The paramag-

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(12) T. Page, T. Alger, and D. M. Grant, *J. Am. Chem. Soc.*, **87**, 5333 (1965).

(13) A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954).

Table III. Comparison of Chemical Shift Data as Determined by Decoupling and Calibrated Sweep Methods in CS_2 Solution

	Decoupling values[a]							Sweep values[b]
	Low-field peak		Mid-field peak		High-field peak			
Compound	Carbon no.	δ_L	Carbon no.	δ_M	Carbon no.	δ_H	$\dfrac{\delta_H - \delta_M}{\delta_M - \delta_L}$	$\dfrac{\delta_H - \delta_M}{\delta_M - \delta_L}$
Phenanthrene	1	−0.38	2	+1.35	4	+5.47	2.38	
	1	−0.38	3	+1.29	4	+5.47	2.50	
	1	−0.38	10	+1.21	4	+5.47	2.68	2.65 ± 0.06
Pyrene	4	+0.83	2	+2.38	1	+3.26	0.566	0.565 ± 0.009
	1	+0.71	2	+2.38	4	+3.38	0.598	

[a] Referenced to benzene. [b] Ratio determined from experimentally measured separation of the proton-decoupled singlets obtained under slow-sweep conditions. Error limits are expressed as one standard deviation in the determination of this value from a large number of spectra.

netic term may be further subdivided for convenience into two additional terms[8]

$$\sigma_p = \sigma_p^{(1)} + \sigma_p^{(2)} \tag{3}$$

The term $\sigma_p^{(1)}$ involves only integrals composed of orbitals on the atom of interest and reflect variations in the π and σ densities.[5,8] Integrals in the $\sigma_p^{(2)}$ term involve orbitals on the atom of interest with other orbitals on directly bonded atoms. This latter term[8] is dependent upon both π- and σ-bond orders or overlap population densities. While $\sigma_p^{(2)}$ resembles σ', it differs in that it always involves an orbital on the carbon atom under study. On the other hand, σ' is reserved for shielding fields arising solely on atoms removed by one or more bonds.

The main contribution in C^{13} chemical shifts appears to come from variations in the paramagnetic expression,[6–9] and therefore only this part of eq 2 is considered in this study. Equation 21 of Karplus and Das[7] gives a general expression for the paramagnetic terms, and this is reproduced here as a starting point

$$\bar{\sigma}_p = \bar{\sigma}_p^{(1)} + \bar{\sigma}_p^{(2)} = \frac{-e^2}{\Delta E m^2 c^2}\sum_j 2\left\{\left\langle \psi_j(k)\left|\frac{\bar{l}_k\bar{l}_k}{r_k^{\,3}}\right|\psi_j(k)\right\rangle - \sum_{j'}\left\langle \psi_j(k)\left|\frac{\bar{l}_k}{r_k^{\,3}}\right|\psi_{j'}(k')\right\rangle\left\langle \psi_{j'}(k')\middle|\bar{l}_{k'}\middle|\psi_j(k')\right\rangle\right\} \tag{4}$$

where j and j' are indices which run over all occupied molecular orbitals, ψ_j, for the two electrons k and k'. ΔE is the average excitation energy and the angular momentum operators are $\bar{l}_k$. The rapid tumbling motion of molecules in liquid samples averages the nuclear shielding contributions over all orientations of the molecule. This averages the off-diagonal tensor terms in eq 4 to zero and preserves only the diagonal elements in the paramagnetic tensor which, with averaging, are reduced by a factor of 3 into the following form (see eq 27 of ref 7).

$$\sigma_p = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) \tag{5}$$

Equation 4 transformed into the form of eq 5 is further reduced to a more applicable equation if simple molecular orbitals (LCAO) are constructed for the planar system in the following manner

$$\begin{aligned}\psi_i^{\sigma} &= 2^{-1/2}[(1 + \lambda_I)^{1/2}(c_{si}^{A}\,s^{A} + c_{xi}^{A}p_x^{A} + c_{yi}^{A}p_y^{A}) + (1 - \lambda_I)^{1/2}(c_{si}^{I}s^{I} + c_{xi}^{I}p_x^{I} + c_{yi}^{I}p_y^{I})]\\ \psi_n^{\pi} &= N_n^{-1/2}[c_{n\pi}^{A}p_z^{A} + c_{n\pi}^{B}p_z^{B} + c_{n\pi}^{C}p_z^{C} + \ldots]\end{aligned} \tag{6}$$

where the three σ orbitals are given by ψ_i^{σ}, with i representing the bond between the atom of interest, A, and the directly bonded atom, I. When i is a C–H bond, $c_{xi}^{I} = c_{yi}^{I} = 0$, and s^I is the hydrogen 1s orbital. The identity of each bond is maintained throughout the derivation with the indexes i and n. The π-molecular orbitals are represented by ψ_n^{π} and index n runs over all occupied orbitals (*e.g.*, three in benzene, five in naphthalene, etc.). The bond angles and hybridization of the σ system are unspecified at this point in order to make the derivation more general.

The equation obtained by substituting the molecular orbitals of eq 6 into the modified eq 4 are simplified by means of the following general assumptions for the operators l_x, l_xl_x, etc.

$$\langle \phi_{yi}^{A}|\phi_{yi}^{B}\rangle = \langle \phi_{yi}^{A}|l_x|\phi_{zj}^{B}\rangle = 0 \tag{7}$$

$$\left\langle \phi_{yi}^{A}\left|\frac{l_xl_x}{r^3}\right|\phi_{yi}^{B}\right\rangle = \left\langle \phi_{yi}^{A}\left|\frac{l_x}{r^3}\right|\phi_{zj}^{B}\right\rangle = 0 \tag{8}$$

$$\left\langle \phi_{yi}^{B}\left|\frac{l_xl_x}{r^3}\right|\phi_{yi}^{B}\right\rangle = \left\langle \phi_{yi}^{B}\left|\frac{l_x}{r^3}\right|\phi_{zj}^{B}\right\rangle = 0 \tag{9}$$

where ϕ_{yi}^{A} is the atomic p_y orbital on atom A in bond i coming from the LCAO molecular orbitals of eq 6. Identical equations for l_y and l_z operators are also represented by eq 7–9. Equation 7 corresponds to neglect of overlap, while eq 8 is taken to be zero because of its overlap character and the reduction resulting from the $1/r^3$ dependence. The rapid attenuation due to the r^3 term in eq 9 is given as the rationale for neglecting this integral. There is only one integral which survives the assumptions embodied in eq 7–9 that does not place all orbitals on atom A. It is a two-electron integral of the form

$$\left\langle \phi_{yi}^{A}\left|\frac{l_x^{A}}{r^3}\right|\phi_{zj}^{A}\right\rangle\left\langle \phi_{yi}^{B}\middle|l_x^{A}\middle|\phi_{zj}^{B}\right\rangle \tag{10}$$

Since the origin of the angular momentum operator is on atom A, the integral $\langle \phi_{yi}^{B}|l_x^{A}|\phi_{zj}^{B}\rangle$ requires a translation of coordinates $l_x^{A} = L_x^{AB} + l_x^{B}$ in order to be evaluated. The term arising from the L_x^{AB} portion of l_x^{A} can be shown to be zero and transformations in l_x, l_y, l_z of the following type are allowed.

$$\langle \phi_{yi}^{B}|l_x^{A}|\phi_{zj}^{B}\rangle = \langle \phi_{yi}^{B}|l_x^{B}|\phi_{zj}^{B}\rangle \tag{11}$$

Thus, integrals of the type given in eq 10 involve orbitals on the atom of interest and atoms directly bonded to it and give rise to the $\sigma_p^{(2)}$ term. All other nonzero integrals appear in the $\sigma_p^{(1)}$ term.

The integrals which have not been set equal to zero with the assumptions embodied in eq 7–9 can be put into an integrable form using the information given in Table I of ref 6. If a product wave function of the general form $\phi_i^{\mathrm{A}} = R_i(\xi_i)Y_i\,(\theta,\phi)$ is used for the atomic orbitals, the following typical results are obtained.

$$\left\langle R_i(\xi_i)Y_{yi}(\theta,\phi)\left|\frac{l_xl_x}{r^3}\right|R_i(\xi_i)Y_{yi}(\theta,\phi)\right\rangle = \hbar^2\left\langle\frac{1}{r^3}\right\rangle = \frac{\hbar^2}{24a_0^{\,3}}\xi_i^{\,3} \quad (12)$$

$$\left\langle R_i(\xi_i)Y_{yi}(\theta,\phi)\left|\frac{l_x}{r_3}\right|R_j(\xi_j)Y_{zj}(\theta,\phi)\right\rangle = \frac{\hbar}{i}\left\langle R_i(\xi_i)\left|\frac{1}{r_3}\right|R_j(\xi_j)\right\rangle = \frac{\hbar}{i}\frac{\xi_i^{\,5/2}\xi_j^{\,5/2}}{6a_0^{\,3}(\xi_i + \xi_j)^2} \quad (13)$$

$$\langle R_i(\xi_i)Y_{yi}(\theta,\phi)|l_x|R_j(\xi_j)Y_{zj}(\theta,\phi)\rangle = \frac{h}{i}\langle R_i(\xi_i)|R_j(\xi_i)\rangle = \frac{\hbar}{i}\frac{32\xi_i^{\,5/2}\xi_j^{\,5/2}}{(\xi_i + \xi_j)^5} \quad (14)$$

Equations 12–14 represent also the analogous expressions containing the l_y and l_z operators, and ξ_i and ξ_j are the effective nuclear charges in bonds i and j, respectively. These results are similar to those given by Prosser and Goodman.[9] Thus the application of eq 5–9 and 12–14 transforms eq 4 into the following two equations:

$$\sigma_{\mathrm{p}}^{(1)} = -\frac{2e^2\hbar^2}{3m^2c^2a_0^{\,3}\Delta E}\left\{\frac{1}{12}\sum_n\left(\frac{c^2{}_{n\pi}}{N_n}\right)\xi_\pi^{\,3} + \frac{1}{24}\sum_i(1 + \lambda_{\mathrm{I}})(c_{xi}^{\,2} + c_{yi}^{\,2})\xi_i^{\,3} - \frac{16}{3}\sum_i\sum_n\left(\frac{c^2{}_{n\pi}}{N_n}\right)(1 + \lambda_{\mathrm{I}})(c_{xi}^{\,2} + c_{yi}^{\,2})\frac{\xi_\pi^{\,5}\xi_i^{\,5}}{(\xi_\pi + \xi_i)^7} - \frac{8}{3}\sum_{i<j}(1 + \lambda_{\mathrm{I}})(1 + \lambda_j)(c_{xi}^{\,2}c_{yj}^{\,2} + c_{xj}^{\,2}c_{yi}^{\,2} - 2c_{xi}c_{xj}c_{yi}c_{yj})\frac{\xi_i^{\,5}\xi_j^{\,5}}{(\xi_i + \xi_j)^7}\right\} \quad (15)$$

$$\sigma_{\mathrm{p}}^{(2)} = \frac{32e^2\hbar^2}{9m^2c^2a_0^{\,3}\Delta E}\sum_i\left\{\sum_n\left(\frac{c_{n\pi}{}^{\mathrm{A}}c_{n\pi}{}^{\mathrm{I}}}{N_n}\right)(1 - \lambda^2)^{1/2}(c_{xi}{}^{\mathrm{A}}c_{xi}{}^{\mathrm{I}} + c_{yi}{}^{\mathrm{A}}c_{yi}{}^{\mathrm{I}})\frac{(\xi_\pi{}^{\mathrm{A}}\xi_\pi{}^{\mathrm{I}}\xi_i{}^{\mathrm{A}}\xi_i{}^{\mathrm{I}})^{5/2}}{(\xi_\pi{}^{\mathrm{A}} + \xi_i{}^{\mathrm{A}})^2\,(\xi_\pi{}^{\mathrm{I}} + \xi_i{}^{\mathrm{I}})^5}\right\} \quad (16)$$

where Σ_i is a sum over the three σ bonds. In eq 16 the superscript I is also used, where appropriate, to denote parallel summation with the index i over the atoms I which are bonded to A by the ith bond. The absence of superscripts in eq 15 implies the label A. The $\Sigma_{i<j}$ indicates summation over all different combinations of the three σ bonds.

The following assumptions are made to simplify eq 15 and 16.

(a) Simple sp^2 hybrids are used for he σ system to give the following values for the c_i and c_j terms.

$$\begin{aligned}(c_{xi}^{\,2} + c_{yi}^{\,2}) &= {}^2/_3\\ (c_{xi}{}^{\mathrm{A}}c_{xi}{}^{\mathrm{I}} + c_{yi}{}^{\mathrm{A}}c_{yi}{}^{\mathrm{I}}) &= -{}^2/_3 \quad (17)\\ (c_{xi}^{\,2}c_{yj}^{\,2} + c_{xj}^{\,2}c_{yi}^{\,2} - 2c_{xi}c_{xj}c_{yi}c_{yj}) &= {}^1/_3\end{aligned}$$

(b) Parts of eq 15 and 16 are recognized as the π-electron density, Q_π, and the σ-polarization charges, Q_i, for the ith bond as follows.

$$\sum_n\frac{c_{n\pi}^{\,2}}{N_n} = \frac{Q_\pi}{2} \quad (18)$$

$$(1 + \lambda_{\mathrm{I}}) = Q_i \quad (19)$$

(c) The π-mobile bond order between the directly bonded atoms A and I is

$$\sum_n\frac{c_{n\pi}{}^{\mathrm{A}}c_{n\pi}{}^{\mathrm{I}}}{N_n} = \frac{P_i^{\,\pi}}{2} \quad (20)$$

Substitution of eq 17–20 into eq 15 and 16 along with the reasonable approximation that $(1 - \lambda^2) \approx 1$ yields the following expressions.

$$\sigma_{\mathrm{p}}^{(1)} = -\frac{965.3}{\Delta E}\left\{\frac{1}{24}Q_\pi\xi_\pi^{\,3} + \frac{1}{36}\sum_i Q_i\xi_i^{\,3} - \frac{16}{9}\sum_i Q_\pi Q_i\frac{\xi_i^{\,5}\xi_\pi^{\,5}}{(\xi_\pi + \xi_i)^7} - \frac{8}{9}\sum_{i<j}Q_iQ_j\frac{\xi_i^{\,5}\xi_j^{\,5}}{(\xi_i + \xi_j)^7}\right\} \quad (21)$$

$$\sigma_{\mathrm{p}}^{(2)} = -\frac{1716.1}{\Delta E}\sum_i P_i^{\,\pi}\frac{(\xi_\pi{}^{\mathrm{A}}\xi_\pi{}^{\mathrm{I}}\xi_i{}^{\mathrm{A}}\xi_i{}^{\mathrm{I}})^{5/2}}{(\xi_\pi{}^{\mathrm{A}} + \xi_i{}^{\mathrm{A}})^2(\xi_\pi{}^{\mathrm{I}} + \xi_i{}^{\mathrm{I}})^5} \quad (22)$$

If ξ_π and ξ_i are assumed to be independent of both σ and π charge, eq 21 indicates that the carbon-13 chemical shift will move downfield as Q_π and Q_σ increase, whereas it is the opposite trend which is observed experimentally. This difficulty can only be avoided by assuming that the effective nuclear charge varies with electron polarization. The following expression has been proposed to account for such effects.[8]

$$\xi_\pi = 3.25 - 0.35(Q_\pi - 1) \quad (23)$$

While this formulation predicts the correct dependence upon Q_π, one is left with the problem of explaining how changes in the π-electron density can lead directly to a change in the screening of the π electron itself. The inclusion[5] of σ-charge polarization in an expression like eq 23 does not pose this type of a problem if only the π electrons are considered. However, if one considers all electrons both σ and π, and applies screening concepts as originally proposed wherein an electron in a given orbital will screen all other electrons in the same principal quantum shell by 0.35, then an expression[14] of the following type should be used.

$$\xi_k = 3.25\beta_k - 0.35\sum_{j\neq k}(Q_j - 1) \quad (24)$$

The Coulson[15] parameter, β, is included to account for a general contraction in atomic orbitals with bond formation. The value for β has been estimated[15,16] to fall between 1.1 and 1.2 for a sp^3 C–H bond.

Raising ξ_k, given by eq 24, to the mth power and eliminating higher order terms yields

$$\xi_k^{\,m} \cong (3.25\beta)^m - 0.35m\,(3.25\beta)^{m-1}\sum_{j\neq k}(Q_j - 1) \quad (25)$$

Substitution[17] of eq 25 into eq 21 and 22 gives an expression of reduced complexity if similar terms are collected and if higher order terms in the Q_j's are not considered. Subtracting the corresponding expression for benzene then gives the following type of expression

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[14] D. M. Grant and W. M. Litchmann, *J. Am. Chem. Soc.*, **87**, 3994 (1965).

[15] C. A. Coulson, *Trans. Faraday Soc.*, **38**, 433 (1942).

[16] A β value of 1.166 was found in a variation treatment of H$_2$; see C. A. Coulson, "Valence," Oxford University Press, London, 1961, p 121.

[17] R. J. Pugmire, Ph.D. Thesis, University of Utah, June 1966.

for the chemical shift relative to benzene

$$\delta_{C^{13}} = \frac{1}{\Delta E}(A_\pi \Delta Q_\pi + B_\sigma \Delta Q_\sigma - C_P \Delta P) \qquad (26)$$

where ΔQ_π, ΔQ_σ, and ΔP are, respectively, the π charge, σ charge, and the sum of the mobile bond orders relative to the corresponding values in benzene. The values for A_π, B_σ, and C_P in units of ppm ev are given in Table IV for various representative values of β_k. The information given in Table IV indicates the sensitive dependence of eq 26 upon minor variations in β_k. The first three entries in Table IV have $\beta_\pi = \beta_\sigma$ and, with this assumption the σ coefficient is larger than the π. Both coefficients under these conditions increase as the value of β is raised. A sizable variation in the coefficients is realized when β_π is allowed to vary for the intermediate value of 1.15 for β_σ. It is reasonable to assume that $\beta_\pi < \beta_\sigma$ on the basis that the exchange interaction in a π bond is less than for a σ system. Pending the availability of better values for these β parameters, the values of $\beta_\pi = 1.05$ and $\beta_\sigma = 1.15$ are used as a working hypothesis along with a $\Delta E = 8$ ev to give the following equation.

$$\delta_{C^{13}} = 100\Delta Q_\pi + 67\Delta Q_\sigma - 76\Delta P \qquad (27)$$

Equation 27 will be used to explain general trends noted in the alternate aromatic chemical shifts. The numerous approximations and assumptions embodied in its derivation limit its usefulness in highly refined correlations between calculated and experimental chemical shifts.

Table IV. Polarization and Bond-Order Coefficients for Various β Values

β_π	β_σ	A_π	β_σ	C_P
1.10	1.10	536	632	608
1.15	1.15	600	688	688
1.20	1.20	648	752	792
1.00	1.15	744	352	568
1.05	1.15	800	536	608
1.10	1.15	712	608	656

Calculations and Discussion

A. The Mobile Bond-Order Term. In the alternant aromatic hydrocarbons zero-charge polarization is predicted by both simple molecular orbital (MO) and valence bond (VB) wave functions, and, therefore, the only way that differences in the carbon-13 chemical shift can be calculated with either of these simple theoretical treatments is through the bond-order term. As a means of checking the validity of such simplifying assumptions, a detailed analysis of the effect of variations in the mobile bond orders upon the carbon-13 chemical shift is given in Table V for three very simple wave mechanical treatments of naphthalene. While reasonable agreement exists between all treatments in the outer ring carbons which are similar to the reference benzene molecule, considerable variation in the predicted bridgehead values is noted for the several different wave functions. This diversity of results emphasizes very acutely the errors which can be introduced into the chemical shift calculation by simplifying assumptions inherent in various quantum mechanical treatments.

The simple HMO wave function (item 1 in Table V) gives a value which deviates from the experimental values by the greatest amount at the bridgehead position. The agreement is improved considerably when overlap is introduced into the simple HMO treatment as can be observed in the second line of Table V. Inclusion of an overlap integral with the value of 0.27 reduces the mobile bond orders by a significant amount in benzene and in all positions in naphthalene, but the relative decrease at the naphthalene bridgehead is greater than in the peripheral ring positions. The sum of bond orders decreases by almost a constant factor, 1.39, in benzene and in positions 1 and 2 in naphthalene, thereby giving rise to only slight changes in the chemical shifts. On the other hand, the total bond order at the bridgehead decreased by a factor of 1.48 (1.628 to 1.100), and, as all chemical shifts are referenced to benzene, this leads to a sizable change in the predicted shift value.

Introduction of overlap into the MO wave function leads to better agreement between the predicted and experimental chemical shifts. In addition, a set of MO bond orders is obtained with inclusion of overlap which correspond more closely with those obtained from simple VB theory. For comparison purposes, the VB bond orders are given in Table V along with the corresponding predicted chemical shifts. The VB approach predicts a considerably smaller shift value at the bridgehead than do either MO treatments. This result argues that the sizable total bond order terms obtained for bridgehead carbons from simple HMO methods may be in error even when overlap is included. If this is the case then the variations in mobile bond orders noted for MO treatments, especially those neglecting overlap, do not reflect faithfully the electronic features in these molecules. Free valence parameters determined from such bond-order values also will show the same discrepancies as noted in the predicted carbon-13 chemical shifts. This study suggests that care is needed in the use of free valence values when comparing bridgehead positions with normal ring carbons in aromatic systems. As much of the downfield shift of the bridgehead resonances can be explained from charge polarization effects to be discussed in the next section, it is felt that the −2.3-ppm shift predicted by the simple VB treatment represents a slightly better estimate of the magnitude of this term than does the −10.6-ppm shift calculated from an overlap corrected MO function.

Table VI compares experimental chemical shifts with values predicted by HMO wave functions for the four alternate aromatic hydrocarbons considered in this study. To compensate for neglect of overlap the bond order sums were reduced by 1.39 and 1.48 for ring and bridgehead carbons, respectively, in the manner described above for naphthalene. Agreement for biphenyl is unusually good and general spectral features are reflected in the other compounds. As with naphthalene the bridgeheads in phenanthrene and pyrene exhibit chemical shifts which are upfield from the predicted values, indicating that the same errors found in naphthalene probably also exist in phenanthrene and pyrene. In all compounds, theory pre-

Table V. Naphthalene Carbon-13 Chemical Shifts (ppm) Calculated from Mobile Bond Orders

		Naphthalene					
	Benzene	Carbon-1		Carbon-2		Carbon-9	
Method	P	P	$\Delta\sigma_p^{(2)}$	P	$\Delta\sigma_p^{(2)}$	P	$\Delta\sigma_p^{(2)}$
1 Simple HMO[a] (no overlap)	1.332	1.280	+3.9	1.328	+0.3	1.628	−22.5
2 Simple HMO[b] (overlap included)	0.960	0.920	+3.0	0.957	+0.2	1.100	−10.6
3 Simple VB[c]	0.920	0.850	+5.3	0.900	+1.5	0.950	−2.3
Experimental			+0.4		+2.6		−5.2

[a] A. Streitwieser and C. A. Coulson, "Dictionary of π-Electron Calculations," W. H. Freeman, Co., San Francisco, Calif., 1965. [b] Authors' treatment, using $S = 0.27$ is based on the method described by Streitwieser and Coulson, footnote *a*, p xii. Results are similar to ref 20 and R. McWeeny, *J. Chem. Phys.*, **19**, 1614 (1951). [c] C. A. Coulson, "Valence," 2nd ed, Oxford University Press, London, 1961, p 267.

dicts that carbons α to a bridgehead are upfield from β carbons. Experimentally, the opposite ordering is found for C-1 and C-2 in naphthalene, C-1 and C-2 in phenanthrene, and C-2 and C-4 in pyrene. This failure to predict the correct ordering of several α and β peaks is taken as an indication that other terms arising from charge polarization are important. It is interesting to note for the bridgehead positions in phenanthrene that theory predicts a 1.4-ppm separation between the two bridgehead peaks, and this compares favorably with the 1.8-ppm separation found experimentally. Even so, the magnitude of the predicted and experimental values are in disagreement by approximately 6 ppm.

Table VI. Aromatic Carbon-13 Chemical Shifts Calculated from Mobile Bond Orders

Compound		Sum of bond orders *a*	Corrected	$\Delta\sigma_p^{(2)}$, ppm	$\delta_{C^{13}}$ (exptl), ppm
Benzene		1.332	0.960	0	0
Naphthalene	1	1.280	0.920	+3.0	+0.4
	2	1.328	0.957	+0.2	+2.6
	9	1.613	1.100	−10.6	−5.2
Biphenyl	1	1.607	1.086	−9.5	−13.0
	2	1.295	0.932	+2.1	+1.1
	3	1.337	0.962	−0.1	−0.5
	4	1.320	0.950	+0.8	+1.0
Phenanthrene	1	1.282	0.922	+2.9	−0.4
	2	1.330	0.956	+0.3	+1.8
	3	1.324	0.952	+0.6	+1.8
	4	1.292	0.930	+2.2	+5.5
	10	1.281	0.921	+2.9	+1.5
	11	1.623	1.097	−10.4	−3.8
	12	1.593	1.077	−8.9	−2.0
Pyrene	1	1.264	0.911	+3.7	+3.3
	2	1.339	0.963	−0.2	+2.4
	4	1.280	0.922	+2.9	+0.8
	11	1.622	1.096	−10.3	−2.8
	15	1.583	1.070	−8.3	+3.6

[a] Taken from Streitwieser and Coulson, footnote *a*, Table V.

Attention is focused on the unusually large upfield shift for C-15,16 in pyrene. As theory predicts that C-15,16 should have a similar chemical shift with the other bridgehead positions (C-11,12,13,14), the observed separation of 6.4 ppm (see Figure 4) is felt to be anomalous. In the methyl resonance of 15,16-dimethylpyrene, Blattmann, *et al.*,[18] observed a similar 5.7-ppm shift to higher fields relative to the methyl peak in the corresponding metacyclophane. It is reasonable to explain both of these upfield shifts with an anisotropic ring current in the peripheral ring carbons. The effect of such ring currents on the chemical shifts of peripheral carbons, if at all important, must be similar with that found in the benzene reference as it has not been necessary to consider such terms in explaining the essential features of the chemical shift data.

B. The Effect of Charge Polarization. Equation 27 emphasizes the importance in carbon-13 chemical shifts of variations in both σ- and π-electron charge densities. Only two σ-electron treatments[19,20] have been found in the literature for the molecules considered in this study even though numerous theoretical studies exist for the π-electron systems. These treatments indicate that σ-polarization charges are comparable to π-electron densities especially at bridgehead positions in fused polycyclic molecules. Hoffmann's treatment has the advantage that both σ- and π-electrons are considered simultaneously, whereas Fukui, *et al.*, considered only the σ systems. However, it appears that Fukui, *et al.*, may have used slightly more refined exchange and coulombic integrals in their calculation, and their σ values are used wherever possible along with values from existing π-electron treatments to calculate the carbon-13 chemical shifts. Only Hoffmann has treated the σ structure in biphenyl and phenanthrene, and both his σ- and π-electron parameters are used in these two molecules. Table VII contains an accumulation of σ- and π-electron densities along with bond orders properly corrected for overlap when necessary. The predicted carbon-13 chemical shifts obtained from eq 27 are subdivided into the several terms for comparison purposes. Only the simple HMO treatment is available for pyrene, and therefore the discussion given in the last section for this molecule must suffice for the present.

The agreement between calculated and experimental shift values in Table VII might be considered to be unusually good if one considers the general limitations of approximate wave mechanical treatments. The greatest discrepancies between the calculated and experimental results is found at the bridgehead positions in the fused aromatic systems and at C-1 in chlorobenzene. The problem of bridgehead carbons was considered at length in the preceding section; and, as errors in the bond-order terms are probably larger than

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(18) H. R. Blattmann, D. Meuche, E. Heilbronner, R. J. Molyneux, and V. Boekelheide, *J. Am. Chem. Soc.*, **87**, 130 (1965).

(19) K. Fukui, H. Kato, T. Yonezawa, K. Morokuma, A. Imamura, and C. Nagata, *Bull. Chem. Soc. Japan*, **35**, 38 (1962).

(20) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

Table VII. Calculated Chemical Shifts for Selected Aromatic Compounds

Compound	Position	Lit. bond order	Bond-order[a] overlap corrected	π density	σ density	$\Delta\sigma_p^{(1)}$		$\sigma_p^{(2)}$ bond order	$\Delta\sigma$	
						π term	σ term		Total	Exptl
Benzene[b]	1	0.960		1.000	3.101					
Biphenyl[b]	1	1.032		0.971	2.998	−2.9	−7.3	−5.6	−15.8	−13.0
	2	0.942		1.011	3.124	1.1	1.6	1.4	4.1	1.1
	3	0.962		0.999	3.098	−0.1	−0.2	−0.1	−0.4	−0.5
	4	0.952		1.009	3.101	0.9	0.0	0.6	1.5	1.0
Phenanthrene[b]	1	0.918		1.014	3.111	1.4	0.7	3.2	5.3	−0.4
	2	0.952		1.011	3.102	1.1	0.1	0.6	1.8	1.8
	3	0.948		1.011	3.099	1.1	−0.1	1.0	2.0	1.8
	4	0.928		1.014	3.137	1.4	2.5	2.5	6.4	5.5
	10	0.912		1.014	3.112	1.4	0.8	3.6	5.8	1.2
	11	1.094		0.968	2.982	−3.2	−8.3	−10.2	−21.7	−3.8
	12	1.070		0.969	2.989	−3.1	−8.0	−8.3	−19.4	−2.0
Benzene[c]	1	1.332	0.960	1.000	3.1037					
Naphthalene[c,d]	1	1.277	0.921	0.986	3.0970	−1.4	−0.5	3.0	1.1	0.4
	2	1.320	0.950	1.007	3.1020	0.7	−0.1	0.8	1.4	2.6
	9	1.601	1.080	1.012	3.0180	1.2	−6.0	−9.1	−13.9	−5.2
Toluene[c,e]	1	1.5082	1.020	0.9950	3.0342	−0.5	−4.7	−4.6	−9.8	−9.1
	2	1.3216	0.952	1.0051	3.0924	0.5	−0.7	0.6	0.4	−0.6
	3	1.3343	0.962	0.9997	3.1032	0.0	0.0	−0.1	−0.1	0.2
	4	1.3306	0.959	1.0038	3.1154	0.4	0.8	0.1	1.3	3.0
Chlorobenzene[c,f]	1	1.480	1.000	1.012	2.7858	−1.2	−21.3	−3.0	−23.1	−5.9
	2	1.322	0.952	1.010	3.0760	1.0	−1.8	0.6	−0.2	−0.2
	3	1.332	0.960	1.000	3.1014	0.0	−0.2	0.0	−0.2	−1.4
	4	1.328	0.957	1.007	3.1037	0.7	0.0	0.2	0.9	2.0

[a] Ratios of 1.39 and 1.48, respectively, were used to reduce bond orders of ring and bridgehead carbons in order to correct for overlap. Bond orders for biphenyl and phenanthrene were obtained from calculations utilizing overlap. [b] Reference 20. [c] Reference 19. [d] Reference 25. [e] Y. I'Haya, *Bull. Chem. Soc. Japan*, **28**, 369 (1955). [f] M C. Sandorfy, *Bull. Soc. Chim. France*, 615 (1949).

corresponding errors in the charge density terms, no further discussion is felt to be necessary. The poor agreement at C-1 in chlorobenzene may reflect errors introduced into the calculation by the divided σ and π treatment of this compound or by neglect of back polarization of the chlorine's free-pair electrons into the π system of the benzene ring.

It is interesting to note that the upfield shift at C-4,5 in phenanthrene (see Figure 3) is predicted in part by the higher σ-electron densities recorded[20] for this position. The two hydrogen atoms at positions 4 and 5 are required to occupy spatial positions separated by approximately 1.75 A assuming normal bond angles and distances. It has been proposed[21] for such proximate hydrogens that nonbonded repulsions can induce charge polarization along the perturbed C–H bonds. The following semiempirical expression was found[21] to rationalize the conformationally dependent *ortho*-substituent parameters recorded[1] for the methylbenzenes

$$\delta_{\mathrm{C}^{13}} \text{ (in ppm)} = 307 \cos \theta \; e^{-1.96r} \qquad (28)$$

where θ is the angle between the H–C bond axis and a line of length r connecting the two proximate hydrogen atoms. For phenanthrene ($\theta = 60°$, $r = 1.75$ A) equation 28 predicts a steric shift at C-4,5 of +5.1 ppm which is in fair agreement with the +5.9-ppm separation of resonance peaks due to C-1 and C-4 in phenanthrene (see Figure 3).

It should be noted that Hoffmann also finds the same increase in σ charge in 2-methylbutane for the proximate *gauche*-methyls but not at the *trans*-methyl carbon which is not sterically perturbed. Pending additional work and more accurate calculations, extended HMO treatment and the shift data on phenanthrene appear to support the tentative proposal that charge polarization is induced in a sterically perturbed C–H bond.

A completely planar biphenyl molecule would have a similar geometry for *o,o'*-hydrogens as exists between H-4 and H-5 in phenanthrene. The increase in the theoretical σ charge at C-2 (see Table VII) in biphenyl reflects the assumption of planarity in the MO treatment. Failure to observe an expected upfield shift in C-2 of biphenyl comparable with that observed in phenanthrene (compare Figures 1 and 3) therefore argues strongly for a nonplanar biphenyl molecule in the liquid state in agreement with the proposal of Dale[22] and Suzuki.[23] Thus, it would appear that liquid biphenyl resembles more the structure of the nonplanar, gaseous molecule[24] (42° angle between planes) than it does the planar solid compound.[25]

It is well known that a number of π-electron treatments exist for a molecule such as naphthalene, and that considerable diversity is found between the various calculations. In selecting the results of Julg, *et al.*,[26] for the structural parameters obtained by X-ray techniques,[27] a treatment is selected which predicts the proper order of shifts for the α and β carbons in naphthalene, whereas many other wave functions would have predicted the reverse ordering of these two peaks. This fact emphasizes the importance of using carbon-13 chemical shift data as means for veri-

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fying specific structural features suggested by a given approximate molecular wave function. For example, in selecting a wave function for naphthalene which gives the most favorable agreement between the calculated and experimental carbon-13 chemical shift values, one has a description of this molecule which predicts that the highest charge density (both σ and π) is at the β carbon. As the α position is more chemically reactive than the β, it is concluded that the free valency term, which is largest in the α position, dominates charge-density considerations in the chemistry of naphthalene. The σ and π charges obtained from the extended HMO treatment of phenanthrene failed to give the correct ordering of shifts at C-1 and C-2, and one can only hope that use of more refined treatments of this molecule will lead to the better agreement noted in the naphthalene case.

Summary

The relatively narrow range of values (−13.0 to +5.5) noted for the several aromatics studied in this work is in itself an unusual observation when one considers that the shifts in simple aliphatic hydrocarbons extend over a range of more than 50 ppm.[28] This emphasizes that the electronic environment of a carbon atom in various aromatic systems is remarkably similar and that variations are minor when compared to changes noted in other classes of compounds. Furthermore, the reasonable theoretical correlation of these small differences lends support to the accuracy of even simple wave mechanical treatments for these molecules. Recent inclusion of σ electrons into such theoretical treatments appears to result in even better agreement. The use of carbon-13 chemical shift data as a means of selecting between alternative approximate wave functions indicates that these data are superior to the corresponding proton values in ellucidating the details of the electronic structure of molecules.

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Microwave Spectrum of Cyclohexyl Fluoride. Structure and Dipole Moment of the Axial Isomer, and the Axial–Equatorial Ratio

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Abstract: The microwave spectrum of axial cyclohexyl fluoride has been investigated in the frequency region 10 to 37 Gc/sec. Twenty-four absorption frequencies are reported which can be attributed to rotational transitions of a-$C_6H_{11}F$ in its ground vibrational state; rotational constants derived from the measured frequencies are $A = 3562.962$, $B = 2628.608$, $C = 1980.869$ Mc/sec. Assuming that the bonded CC and CH distances are the same in a-$C_6H_{11}F$ as they are in propane and that the ring structure has the same symmetry as cyclohexane, the following structural parameters are obtained: CF = 1.399, CC = 1.526, CH = 1.096 A, $\angle$CCC = 111° 42′, $\angle$HCH = 107° 21′, $\angle$HCF = 107° 51′, $\angle$CCF = 110° 0′, $\angle$CCH = 109° 24′, $\beta = 54° 5'$, where β = the dihedral angle for alternate CC bonds. Stark effect measurements yield $|\mu_a| = 1.05 \pm 0.02$, $|\mu_c| = 1.47 \pm 0.03$, and $\mu(\text{total}) = 1.81 \pm 0.03$ D. These data together with Stark effect measurements previously reported for the equatorial isomer establish that the dipole moment vector makes an angle of approximately 10° with the C_1F bond. (This vector lies between the C_1F and C_1H bond directions in both isomers.) Neither the difference in dipole moments of the two isomers (2.11 D. for e-$C_6H_{11}F$ and 1.81 D. for a-$C_6H_{11}F$) nor their orientations can be accounted for by the much used "bond moment" model. However, the "semiclassical" model of inductive effects proposed by Smith, Ree, Magee, and Eyring as applied to the present data is found to be in good agreement with experiment. This accord is not accidental as the same model is shown to account successfully for magnitudes and orientations of the dipole moments of several other fluoroalkanes. Comparison of the relative intensities of e-$C_6H_{11}F$ and a-$C_6H_{11}F$ rotational transitions indicate that the equatorial isomer is more stable than the axial isomer by 400 ± 300 cal/mole.

In a previous paper,[2] the results of an investigation of the rotational spectrum of the ground vibrational state of equatorial cyclohexyl fluoride were presented and analyzed for structural and dipole moment information. The present work is concerned with a parallel investigation of the microwave spectrum of the axial isomer. The experimental data not only provide the same kind of information concerning the axial form of the molecule, but when they are combined with data for the equatorial form additional information is obtained. Specifically, a comparison of Stark effect measurements allows the orientation of the dipole moment vector to be uniquely determined in both forms, and relative intensity measurements provide the means for estimating their energy difference.

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