results when applied to cycloalkanes free of the type of skew interactions found in acyclic alkanes. The Tatevskii, Laidler, and Franklin schemes are conspicuously bad in this respect and should not be used for estimating the strain in adamantane. In conformational analysis terminology, the failure of such schemes is due to the lack of corrections for varying numbers of skew conformations present in different systems.

2. Schemes which correct for the number of skew interactions give excellent results for both acyclic and cyclic molecules. From a somewhat more sophisticated point of view, though, strain should be defined using schemes which have been corrected for the existence of skew-containing conformers present at equilibrium in the strain-free acyclic alkanes. We call our scheme a single-conformation one.

3. Using such single-conformation increments, as strain free as possible, adamantane is found to be appreciably strained—6.48 kcal/mol—relative to acyclic alkanes in *gauche*-free staggered conformations. Similarly, cyclohexane (1.35 kcal/mol) and *trans*-decalin (1.79 kcal/mol) possess modest strain energies.

4. The strain energy in adamantane is explicable in terms of angle strain and nonbonded interactions—predominantly C···C repulsions. These C···C repulsions are unexceptional and are common to all structures containing cyclohexane rings in chair conformations. In *trans*-decalin and larger molecules consisting of fused cyclohexanes, attractive C···C interactions are significant and even reduce the strain on a "per ring" basis. This is not so for polycyclic cage structures, *e.g.*, adamantane.

5. The strain in adamantane can be accounted for quantitatively once the C···C underweighting present in most sets of nonbonded potentials derived from properties whose values are fixed predominantly by H···H interactions is recognized and corrected.

6. The introduction of "cage" or other special effects to explain data for adamantane and other polycyclic molecules is not warranted at this time.

Acknowledgments. We would like to thank Mr. Richard C. Bingham for performing some of the calculations and Professor Edgar F. Westrum, Jr., and Professor Richard H. Boyd for providing thermodynamic data prior to publication. Some of the computing time was provided by Princeton University.

Carbon-13 Magnetic Resonance. XV.[1] Nonalternant Hydrocarbons

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Abstract: Carbon-13 chemical shifts have been determined for the nonalternant hydrocarbons, azulene, acenaphthylene, fluoranthene, and benzo[*ghi*]fluoranthene. In addition supporting data on acenaphthene and 1,8-dimethylnaphthalene are presented. Spectral assignments were made using selective decoupling techniques and nuclear Overhauser effects. The large chemical-shift range observed in the nonalternant systems (14–22 ppm) compared to the alternant systems (<10 ppm) is considered to provide a marked distinction between these categories of compounds. A discussion of the factors contributing to these shifts including both π- and σ-electronic contributions, obtained using the CNDO/2 method, is presented. It is emphasized that the chemical shifts are not simply related to π-electron charge but that both π- and σ-electronic variations must be considered for the majority of alternant *and* nonalternant hydrocarbons.

The value of the carbon-13 chemical shifts in providing an insight into the electronic structure of aromatic compounds has been clearly indicated.[3–11] Lauterbur,[3] Spiesecke and Schneider,[4] LaLancette and Benson,[5] and Lippmaa and coworkers[6] have shown that carbon-13 shifts vary by approximately 160–200 ppm per unit of π-electron charge in substituted benzenes,[3] nonalternant hydrocarbons,[3] in the series $C_5H_5^-$, C_6H_6, $C_7H_7^+$,[4] and $C_9H_9^-$,[5] and in the mesitylenonium ion.[6] Similar charge dependence has been observed in nitrogen heteroaromatic systems[7–11] provided σ-polarization terms are also considered.

Theoretical considerations[7–12] have provided some justification for the chemical-shift dependence on π-electron density, though a dependence on mobile bond orders[8,12] and σ-electronic variations[8–11] has also been stressed. However, a note of caution has very recently been added.[13] In the isoelectronic series

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[1] Previous paper in this series: R. J. Pugmire, D. M. Grant, M. J. Robins, and R. K. Robins, *J. Amer. Chem. Soc.*, **91**, 6381 (1969).

[2] Author to whom correspondence may be addressed at the Department of Chemistry, Colorado State University, Fort Collins, Colo. 80521.

[3] P. C. Lauterbur, *J. Amer. Chem. Soc.*, **83**, 1838 (1961).

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

[5] E. A. LaLancette and R. E. Benson, *J. Amer. Chem. Soc.*, **87**, 1941 (1965).

[6] V. Koptyua, A. Rezvukhin, E. Lippmaa, and T. Pehk, *Tetrahedron Lett.*, 4009 (1968).

[7] P. C. Lauterbur, *J. Chem. Phys.*, 43, 360 (1965).

[8] R. J. Pugmire and D. M. Grant, *J. Amer. Chem. Soc.*, **90**, 697 (1968).

[9] J. E. Bloor and D. L. Breen, *ibid.*, **89**, 6835 (1967).

[10] W. Adam, A. Grimison, and A. Rodrigues, *Tetrahedron*, **23**, 2513 (1967).

[11] R. J. Pugmire and D. M. Grant, *J. Amer. Chem. Soc.*, **90**, 4232 (1968).

[12] M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).

[13] A. J. Jones, D. M. Grant, J. G. Russell, and G. Fraenkel, *J. Phys. Chem.*, 73, 1624 (1969).

pyridine, phenyllithium, and phenylmagnesium bromide the "average energy" contribution to the paramagnetic term in the Saika and Slichter equation[12,14] has been shown to dominate the charge contribution.[13] Further, the observed carbon-13 shifts in pyrene[15] and biphenylene[16] suggest that the magnetic screening anisotropies associated with ring currents also warrent consideration.

The present study was undertaken in an attempt to differentiate between the electronic features which distinguish the alternant from the nonalternant hydrocarbons.[17] In previous carbon-13 studies[3] this classification appears to have gained some justification from the observed range of chemical shifts, which for the nonalternant hydrocarbons studied was substantially larger than that observed for the alternant molecules, and which was interpreted as a consequence of the larger charge migrations that are possible in the nonalternant category.[3,17]

Implicit in the classification of hydrocarbons into alternant and nonalternant[17,18] is that for the former the π-electron charge density will be evenly distributed throughout the molecule, while for the latter this distribution will be uneven. In addition, classical type bond structures place π electrons with like spins on adjacent carbons in nonalternant systems. Such spin–spin interactions are expected to lead to decreases in mobile bond orders and π conjugation between such carbons. As these effects are relatively large in the nonalternants they can be expected to have an effect upon the carbon-13 chemical-shift values.

In previous rapid passage carbon-13 studies[3] of nonalternant systems, it was only possible to differentiate between the quaternary and other ring carbon atoms. However, with the improved proton decoupling techniques[19] and availability of accurate proton assignments it has been possible to unequivocably assign the resonance peaks for almost all nonequivalent carbon atoms. Carbon-13 shift data are presented for the nonalternant hydrocarbons, azulene, acenaphthylene, fluoranthene, and benzo[*ghi*]fluoranthene. Supporting data for 1,8-dimethylnaphthalene and acenaphthene are also included. Using the CNDO-2 method[20] we have attempted to determine the contributions to the carbon-13 shifts in these systems taking into consideration changes in π- and σ-electron densities and mobile bond orders. (The limited dimensions of our computer program prevented extension of these calculations to fluoranthene and benzo[*ghi*]-fluoranthene.)

Experimental Section

Carbon-13 spectra were obtained using a Varian AFS-60 analog frequency sweep high-resolution spectrometer operating at 15.1 MHz. The 10-mm sample tubes were spun in a Varian V-4331A probe, double tuned to 15 and 60 MHz. The field was locked by conventional techniques to the protons in a water sample positioned just behind the analytical sample. Proton decoupling was accomplished using a Hewlett-Packard 5105A frequency synthesizer in conjunction with a white noise generator, with a band width in excess of 500 Hz. Due to the limited solubility of some of the compounds it was necessary to accumulate at least some part of the spectra on a Varian C-1024 time-averaging device. The chemical shift relative to benzene for a suitable reference carbon atom in the system was determined from the relationship[21]

$$\delta_{^{13}\mathrm{C}_{\mathrm{REF}}} = \frac{\Gamma_i - \Gamma_0}{\Gamma_i} + \frac{\Gamma_0}{\Gamma_i}\delta_{\mathrm{H}} \simeq \frac{\Gamma_i - \Gamma_0}{\Gamma_i} + \delta_{\mathrm{H}}$$

The remaining carbon-13 resonance signals were measured relative to this reference according to the equation

$$\delta_{^{13}\mathrm{C}} = \delta_{^{13}\mathrm{C}_{\mathrm{REF}}} - \left(\frac{\nu_i - \nu_{\mathrm{REF}}}{\nu_{\mathrm{REF}}}\right)$$

Proton spectra were determined on a Varian Associates A56/60 spectrometer in the usual manner. Where the multiplets at this field strength were too closely coupled, literature analyses of 100-MHz spectra assisted in an approximate assignment. In general, the splitting patterns observed at 60 MHz were commensurate with those obtained at 100 MHz.

1,8-Dimethylnaphthalene was synthesized by the method of Mitchell, Topsom, and Vaughan[22] mp 61–63° (lit.[22] mp 62.5°). All other compounds were obtained from commercial sources and were recrystallized using the appropriate solvents. The carbon-13 spectra were determined as (*ca.* 3–5 mol %) solutions in CS_2 and/or dioxane:CS_2.

Results

Proton and carbon-13 chemical shifts for the compounds studied are presented in Table I, and the proton-decoupled carbon-13 spectra of azulene, acenaphthylene, fluoranthene, and benzo[*ghi*]fluoranthene given in Figures 1 to 4, respectively. Due to the relative insolubility of fluoranthene and benzo[*ghi*]fluoranthene, the spectra for these compounds (Figures 3 and 4) were obtained after successive scans and accumulation using a time-averaging device.

The quaternary carbon atoms in all of the systems given in Table I were readily distinguished due to the absence of large proton-induced splittings on the observed resonance peaks. The single absorption of this type in the spectrum of azulene (item 6) was assigned solely on this basis. Similarly, the unit intensity quaternary carbon atom signals in acenaphthylene (item 12 and 13), fluoranthene (items 21 and 22), benzo[*ghi*]fluoranthene (items 28 and 29), acenaphthene (items 38 and 39), and in 1,8-dimethylnaphthalene (items 44 and 45) were distinguished from the double intensity signals due to the quaternary carbon atoms C-9,10 in acenaphthylene (item 11), C-11,12 and C-13,14 in fluoranthene (items 19 and 20), C-13,14, C-15,16, and C-17,18 in benzo[*ghi*]fluoranthene (items 30,31, and 32), C-9,10 in acenaphthene (item 37), and C-1,8 in 1,8-dimethylnaphthalene (item 40), respectively. The latter signal was also distinguished by the enhancement observed on irradiation of the substituent methyl groups.

The distinction between the quaternary carbon atoms which are magnetically nonequivalent but which are of similar intensity was made using nuclear Over-

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

[15] T. D. Alger, D. M. Grant, and E. G. Paul, *J. Amer. Chem. Soc.*, **88**, 5397 (1966).

[16] A. J. Jones and D. M. Grant, *Chem. Commun.*, 1670 (1968).

[17] C. A. Coulson and G. S. Rushbrooke, *Proc. Cambridge Phil. Soc.*, **36**, 193 (1940); C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc., Ser. A*, **191**, 39 (1947); *ibid., Ser. A*, **192**, 16 (1947); *J. Chem. Phys.*, **18**, 265 (1950).

[18] For a detailed discussion see: A. J. Jones, *Rev. Pure Appl. Chem.*, **18**, 253 (1968).

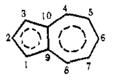
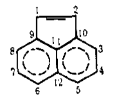
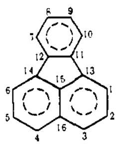
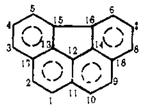
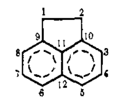
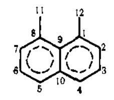
[19] E. G. Paul and D. M. Grant, *J. Amer. Chem. Soc.*, **86**, 2977 (1964).

[20] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, 3129 (1965); J. A. Pople and G. A. Segal, *ibid.*, **43**, 5136 (1965); **44**, 3289 (1966); J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).

[21] W. R. Woolfenden and D. M. Grant, *ibid.*, **88**, 1496 (1966).

[22] W. J. Mitchell, R. D. Topsom, and J. Vaughan, *J. Chem. Soc.*, 2526 (1962).

Table I. Carbon-13 Chemical Shifts of Selected Nonalternant Hydrocarbons and Supporting Data

Item no.	Compd	Carbon position	H, ppm[a-c]	^{13}C, ppm[a]	^{13}C chemical-shift range
	Azulene				
1		1,3	−0.07	+9.53	21.67
2		2	−0.58	−9.17	
3		4,8	−0.95	−8.23	
4		5,7	+0.28	+5.47	
5		6	−0.17	−8.74	
6		9,10		−12.14	
	Acenaphthylene				
7		1,2	+0.29	−1.17	15.71
8		3,8	−0.24	+4.21	
9		4,7	−0.11	+0.67	
10		5,6	−0.36	+1.16	
11		9,10		−11.50	
12		11		−0.17	
13		12		+0.11	
	Fluoranthene				
14		1,6	−0.62	+5.61	19.47
15		2,5	−0.33	−0.01	
16		3,4	−0.52	+1.23	
17		7,10	−0.60	+7.84	
18		8,9	−0.08	+0.28	
19		11,12		−11.63	
20		13,14		−9.13	
21		15		−4.41	
22		16		−2.19	
	Benzo[*ghi*]fluoranthene				
23		1,10	(−0.73	(+3.06	14.12
24		2,9	−0.73)	+1.45	
25		3,8	−0.42	+1.80)	
26		4,7	−0.45	−0.23	
27		5,6	−0.88	+4.87	
28		11		(−4.90	
29		12		+1.66)	
30		13,14		(+0.43	
31		15,16		−9.25	
32		17,18		−5.16)	
	Acenaphthene				
33		1,2	+3.93	+98.27	
34		3,8	+0.06	+9.06	26.43
35		4,7	−0.14	+0.33	
36		5,6	−0.29	+5.83	
37		9,10		−17.37	
38		11		−11.14	
39		12		−3.56	
	1,8-Dimethyl-naphthalene				
40		1,8		−7.12	
41		2,7	(+0.01	(+0.12	
42		3,6	−0.01)	−1.32)	
43		4,5	−0.38	+3.16	
44		9		−5.07	
45		10		−7.83	
46		11,12	+3.69	+102.54	

[a] Relative to benzene. [b] Benzene proton reference 7.17 ppm: W. M. Litchman and D. M. Grant, *J. Amer. Chem. Soc.*, **90**, 1400 (1968). [c] Proton assignments: azulene (ref 3); acenaphthylene and acenaphthane (M. J. S. Dewar and R. C. Fahey, *J. Amer. Chem. Soc.*, **85**, 2704 (1965); fluoranthene and benzo[*ghi*]fluoranthene (M. L. Heffernan, A. J. Jones, and P. J. Black, *Aust. J. Chem.*, **20**, 589 (1967); K. D. Bartle, D. W. Jones, and J. E. Pearson, *J. Mol. Spectrosc.*, **24**, 330 (1967)); 1,8-dimethylnaphthalene (present work).

hauser effects.[23,24] This phenomenon relies on the observation that the carbon-13–proton relaxation mechanism is usually dominated by the dipole–dipole coupling term,[23] especially when a hydrogen is directly bonded to the carbon-13 atom. This term is distance dependent ($1/r_{\mathrm{CH}}^6$) and falls off rapidly as the carbon–proton distance increases. Thus distinction was made[24] between C-11 and C-12 in acenaphthylene, acenaphthene, C-9, and C-10 in 1,8-dimethylnaphthalene, and C-15 and C-16 in fluoranthene on the basis of the greater signal intensity observed for C-12, C-10, and C-16 compared to C-11, C-9, and C-15 in these cases. This technique could not be extended to benzo[*ghi*]fluoranthene due to the superimposition of the line C-11 or C-12 with C-2,9.

The above assignments were made using white-noise decoupling techniques[24] and consequently all protons were irradiated simultaneously. Relative peak intensities also provided initial considerations in making further spectral assignments. For example, in azulene the unit intensity peaks corresponding to C-2 and C-6 (items 2 and 5) are distinguished from the

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(23) K. F. Kuhlmann and D. M. Grant, *J. Amer. Chem. Soc.*, 90, 7355 (1968).

(24) A. J. Jones, D. M. Grant, and K. F. Kuhlmann, *ibid.*, 91, 5013 (1969).

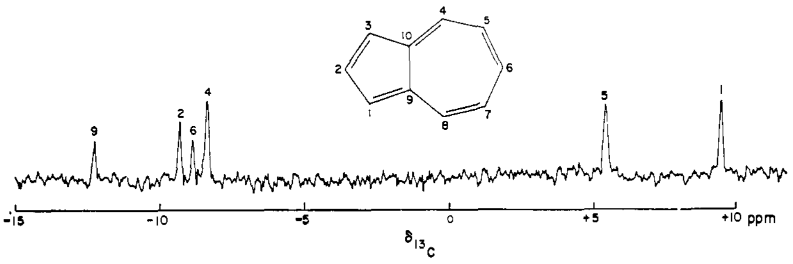

Figure 1. The proton-decoupled carbon-13 magnetic resonance spectrum of azulene.

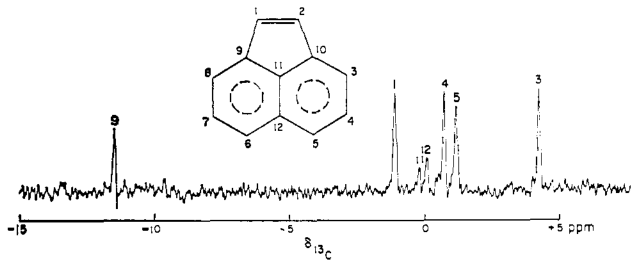

Figure 2. The proton-decoupled carbon-13 magnetic resonance spectrum of acenaphthylene.

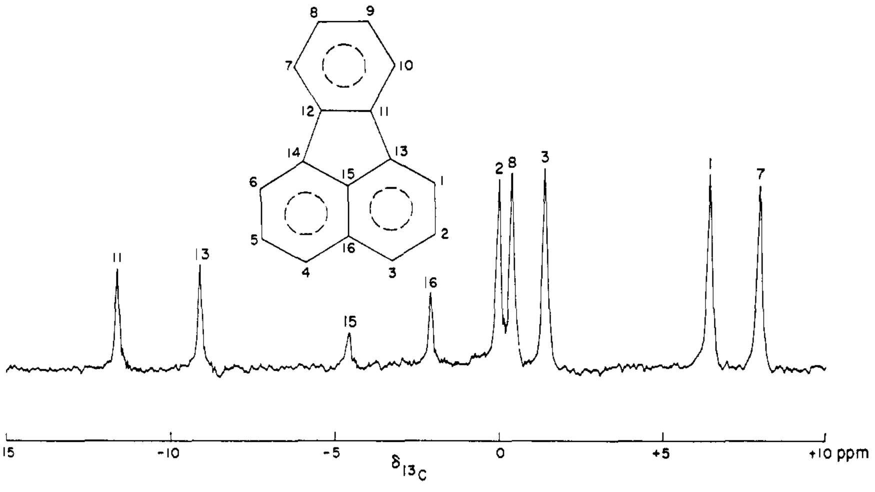

Figure 3. The proton-decoupled carbon-13 magnetic resonance spectrum of fluoranthene.

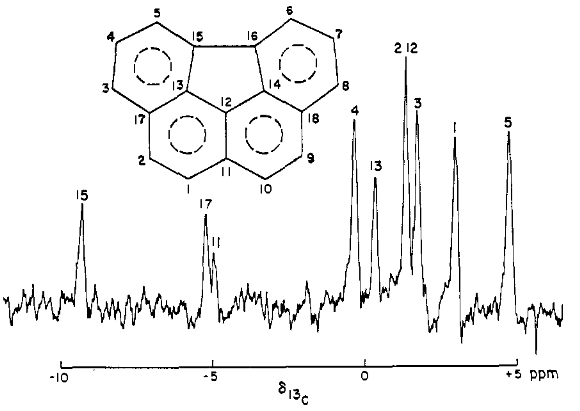

Figure 4. The proton-decoupled carbon-13 magnetic resonance spectrum of benzo(ghi)fluoranthene.

double intensity peaks of C-1,3, C-4,8, and C-5,7 (items 1, 3, and 4). The carbon C-1,3 was assigned by Lauterbur[3] from studies on the 1,3-dideuterium derivative. This assignment has been confirmed in the present work. Remaining assignments were made by directly relating each carbon-13 decoupled singlet with an assigned proton-resonance position through *selective* spin decoupling.

In the selective decoupling experiment the irradiating rf (decoupler frequency) is aligned with the center of a selected multiplet of protons directly bonded to the carbon atom to be assigned. When the proton spectrum is sufficiently spread out (>3 Hz separation between any two proton multiplets) only the carbon-13 peak arising from the directly bonded carbon maximizes relative to all other carbon peaks in the spectrum. The other peaks are assigned in the same way by successively stepping the decoupler frequency through the known proton chemical-shift values. For azulene the proton assignment of Spiesecke and Schneider[4] was used and all the carbons directly bonded to protons were distinguished by selective irradiation. Similarly for acenaphthylene and acenaphthene the proton assignments of Dewar and Fahey[25] provided the mechanism for assignment of C-1,2, C-3,8, C-4,7, and C-5,6 in these compounds. To illustrate this technique we have chosen the more complex spectrum of fluoranthene (Figure 3). The 60-MHz pmr spectrum of fluoranthene in carbon disulfide resembles that in carbon tetrachloride for which analyses at 100 MHz[26] and 60 MHz[27] have been obtained.

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(25) M. J. S. Dewar and R. C. Fahey, *J. Amer. Chem. Soc.*, **85**, 2704 (1965).

(26) M. L. Heffernan, A. J. Jones, and P. J. Black, *Aust. J. Chem.*, **20**, 589 (1967).

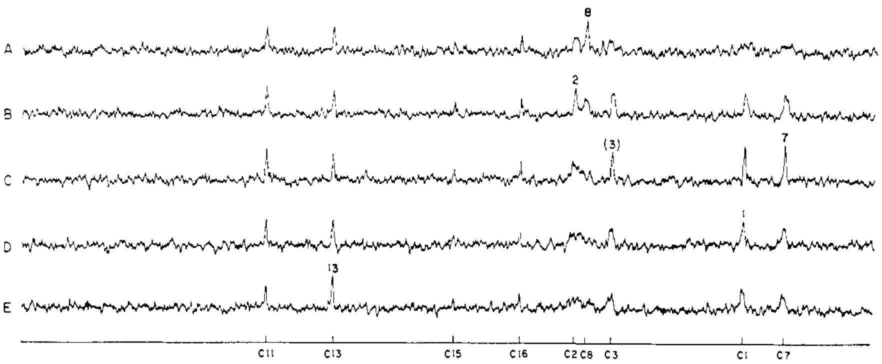

Figure 5. Selective decoupling experiments on fluoranthene. Figures A to E show the effects of stepping up the decoupler through the proton resonance frequencies.

In Figure 5 the results of a selective spin-decoupling experiment on fluoranthene are shown. The decoupler frequency was initially aligned with the highest field proton multiplet associated with carbon atoms C-8,9. Figure 5A clearly shows the peaks arising from the quaternary carbon atoms, the sharp, highest intensity peak due to C-8,9, and broad, partially decoupled lines for the other carbon atoms. By setting the decoupler frequency at the value corresponding to the H-2,5 chemical shift, C-2,5 was decoupled as shown in Figure 5B. Successive stepping up of the decoupler frequencies through the proton shift values gave the spectra shown in Figure 5C and D. The highest field peak is assigned to C-7,10, Figure 5C (Table I, item 17), while the peak requiring the highest decoupler frequency must be assigned to C-1,6 (+5.6 ppm) as shown in Figure 5D. Carbon atoms C-3,4 were assigned on the basis of the intensity enhancement observed as the decoupler frequency was increased, 5A through C. The only remaining ambiguities are in the assignment of the lines associated with the quaternary carbons C-11,12 and C-13,14. The small difference between the proton chemical shifts of H-1,6 and H-7,10 does not permit unequivocable observation, by selective decoupling, of the expected nuclear Overhauser enhancement for the nearest neighbor quarternary carbon atoms C-13,14 and C-11,12, respectively. However, it is clear from Figure 5E that irradiation downfield (~20 Hz) of H-1,6 produces an enhancement of the higher field quaternary carbon atom signal. It should also be noted that this experiment also leaves C-1,6 enhanced relative to all other carbon signals. The line at −9.13 ppm is therefore tentatively assigned to C-13,14.

The proton chemical shifts in benzo[*ghi*]fluoranthene are not sufficiently separated to enable distinction between C-1,10, C-2,9, or C-3,8. As expected, irradiation at the proton frequency corresponding to H-1,2 produced enhancement of three peaks (Table I, items 23–25). Selective decoupling of H-4,7 and H-5,6, however, enables assignment of the corresponding carbon signals (items 26,27). It is particularly significant that C-5,6 occurs at highest field since the van der Waals interaction between the corresponding protons in this system would be expected to be analogous to the H-4–H-5 interaction observed in phenanthrene.[15] Due to the low solubility of this material, the quaternary carbon atoms were only easily observed after successive accumulations using a TAD. This factor also prevented establishment of the ordering of the unit or doubly intense quaternary carbon atom peaks using Overhauser enhancement techniques. The ordering of the nuclei shown in Table I is based upon qualitative arguments to be discussed.

The carbon-13 spectrum of 1,8-dimethylnaphthalene in 50:50 dioxane:carbon disulfide is somewhat less complex. The proton assignment is given in Table I. The low-field quartet of the ABC system arising from protons H-2,3, and 4 was assigned to proton H-4,5 by analogy with the corresponding protons in acenaphthylene, acenaphthene, and naphthalene,[25,28] ($J_{3,4}$ = 6.5 Hz, $J_{2,4}$ = 3.5 Hz). The quartets associated with the AB part of this 60-MHz spectrum overlap to the extent that the chemical shifts of H-2 and H-3 cannot be clearly determined. Thus selective decoupling of the carbon-13 spectrum enables assignment of the carbons C-11,12 and C-4,5 but C-2,7 and C-3,6 are not distinguished from each other. The distinction between the quaternary carbon atoms C-9 and C-10 was made by the observed Overhauser enhancement at C-10 on irradiating H-4,5.

Discussion

As indicated in the previous study[3] of the carbon-13 spectra of nonalternant systems, the chemical-shift ranges are much larger than in alternant systems.[4] It is clear that in unsubstituted $4n + 2$ benzenoid-alternant hydrocarbons this range is usually less than 10 ppm whereas in the nonalternant systems described herein the range varies from 14 to 22 ppm. It was suggested[3] that variations in π-electron densities were primarily responsible for such shifts in aromatic rings and consequently it is inferred that the observed chemical-shift ranges provide at least a qualitative justification for the classification of hydrocarbons as alternant and nonalternant.

A. Correlations with Molecular Orbital Parameters. The above generalization is best tested using the improved chemical-shift data obtained in the present work in conjunction with currently available theoretical models for aromatic systems. The CNDO/2-SCF–MO method[20] has been used to estimate the charge-density and bond order (summarized in terms of free valences) parameters given in Figure 6, for naphthalene, azulene,

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(27) K. D. Bartle, D. W. Jones, and J. E. Pearson, *J. Mol. Spectrosc.*, 24, 330 (1967).

(28) N. Jonathan, S. Gordon, and B. P. Dailey, *J. Chem. Phys.*, **36**, 2443 (1962).

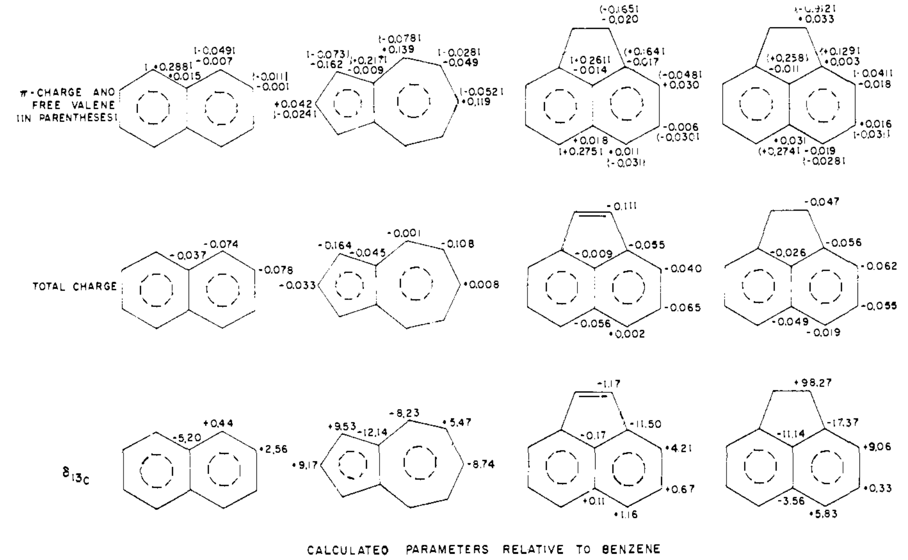

Figure 6. Calculated molecular orbital parameters (CNDO/2) and carbon-13 chemical shifts for naphthalene, azulene, acenaphthylene, and acenaphthene, shown relative to benzene.

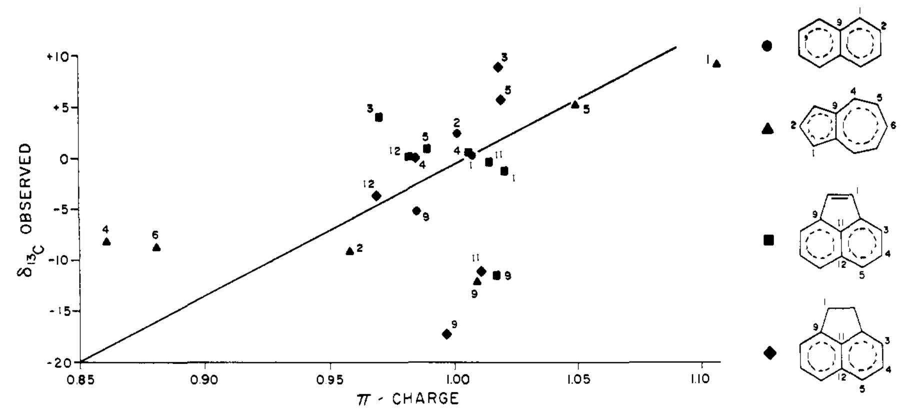

Figure 7. Observed carbon-13 chemical shifts for naphthalene, azulene, acenaphthalene, and acenaphthene are plotted against π-charge densities derived using the CNDO/2 method.

acenaphthylene, and acenaphthene. These parameters are given relative to benzene and compared to the carbon-13 shifts in these molecules. It is clear that the π- and total-charge distributions and the free valences in azulene and acenaphthylene exhibit a greater range of values than observed in naphthalene. Furthermore, and in compliance with the requirements set by "like spins on adjacent carbon atoms," the magnitude of the mobile bond order (not shown) in the nonalternant systems is less than that for alternant systems. A plot of π charge *vs.* observed chemical shifts in these systems provides the relatively poor correlation shown in Figure 7. The theoretical line drawn through these points represents the 160 ppm per electron contribution derived by Spiesecke and Schneider.[4] As commonly observed, the greatest discrepancies between theory and experiment occur at the quaternary carbon atom sites. These discrepancies are, however, not substantially improved when total charge is considered (Figure 8), although it should be noted they do not differ substantially between the alternant and nonalternant hydrocarbons considered. Some improvement in the correlation is realized when mobile bond-order terms are incorporated in the calculation of carbon-13 shifts along with π- and σ-charge densities according to the procedure described by Alger, Grant, and Paul[15] using the approximate eq 1

$$\delta_{^{13}C} = 100\Delta Q\pi + 67\Delta Q\sigma - 76\Delta P \qquad (1)$$

These latter results are shown in Figure 9 and clearly the greatest deviations from the perfect agreement line are once again for some quaternary carbon atoms. It

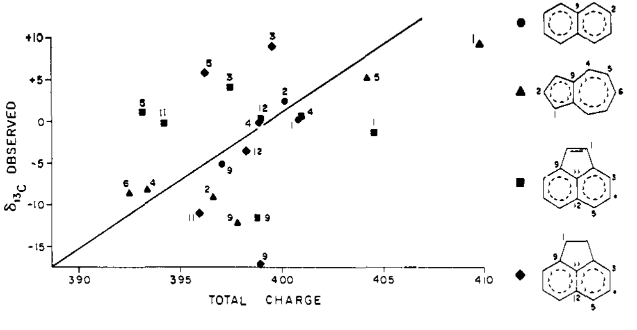

Figure 8. Observed carbon-13 chemical shifts for naphthalene, azulene, acenaphthylene, and acenaphthene are plotted against total electronic charge densities derived using the CNDO/2 method.

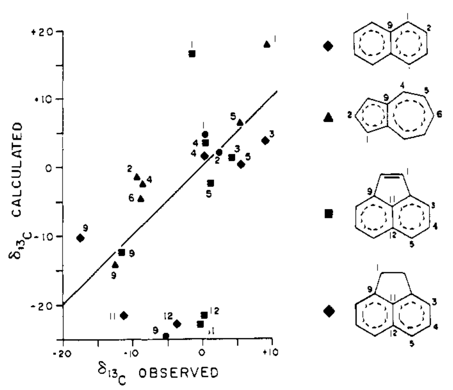

Figure 9. Theoretical carbon-13 shifts predicted from the relationship $\delta_{^{13}C} = 100\Delta Q\pi + 67\Delta Q\sigma - 76\Delta P$ are plotted against the experimental values for naphthalene, azulene, acenaphthylene, and acenaphthene.

is considered significant that the free valences for these carbon atoms also show the greatest positive deviations from the benzene reference value. This observation suggests that the neglect of overlap implicit in the CNDO/2 calculation should be considered. In discussing the electronic characteristics of the alternant hydrocarbons Alger, Grant, and Paul[15] pointed out that wave functions in which overlap was neglected give inordinately high mobile bond orders with a concomitant reduction in the free valences for quaternary carbon atoms. In the nonalternant systems this same variation in calculated bond orders also appears, but in these cases the discrepancies between wave functions with and without overlap is probably modified considerably by the unusual spin-pairing features incorporated in this particular class of compounds. However, in order to compensate for the neglect of overlap, the CNDO/2 bond orders were summed for each carbon atom and reduced by the factors 1.39 and 1.48 for ring and quaternary carbon atoms, respectively, in the manner described by Alger, Grant, and Paul.[15] Table II contains the CNDO/2 parameters for the compounds considered in Figure 9 along with the modified total bond-order terms. Incorporation of these modified terms in eq 1 provided the improved correlation shown in Figure 10. It is of interest to note that the modification apparently overcompensates slightly for the quaternary carbon atoms C-9 and C-5 in azulene and acenaphthylene, respectively. This phenomenon probably follows directly from the reduced mobile bond orders found about these atoms compared with those about C-9 in naphthalene or C-11 and C-12 in acenaphthene. The reduced bond orders imply unfavorable spin pairing for bond formation about C-9 and C-5 in these compounds and consequently correlate well with the known aromatic ($4n + 2$) stability of azulene[29] and (1,2-double bond) reactivity of acenaphthylene.[30] From the general result we are led to conclude that the carbon-13 shifts in the nonalternant hydrocarbons reflect at least in a crude manner the important electronic features of these systems. Furthermore, the approximate wave functions presently available do indeed specify to a fair degree the nature of these electronic structural features. The improvement in correlation noted in Figures 7–10 and in particular that noted between Figures 9 and 10 does stress the hazards of neglecting overlap in calculations of the type which emphasize the importance of either bond orders or related free valences.

Table II. CNDO/2 Parameters for Naphthalene, Azulene, Acenaphthylene, and Acenaphthene

Compd	Position	$Q\pi$	$Q\sigma$	Sum of bond orders Uncorrected	Sum of bond orders Corrected[a]
Naphthalene	1	1.007	3.000	1.285	0.924
	2	1.001	3.010	1.323	0.952
	9	0.985	2.985	1.622	1.096
Azulene	1	1.162	2.935	1.261	0.908
	2	0.958	3.008	1.310	0.944
	4	0.861	3.073	1.255	0.904
	5	1.049	2.992	1.305	0.940
	6	0.881	3.044	1.282	0.924
	9	1.009	2.969	1.551	1.049
Acenaphthylene	1	1.020	3.024	1.169	0.835
	3	0.970	3.003	1.286	0.927
	4	1.006	3.002	1.304	0.939
	5	0.989	2.942	1.303	0.938
	9	1.017	2.971	1.498	1.011
	11	1.014	2.928	1.595	1.080
	12	0.982	3.007	1.609	1.089
Acenaphthene	3	1.018	2.977	1.293	0.930
	4	0.984	3.004	1.303	0.937
	5	1.019	2.933	1.306	0.940
	9	0.997	2.992	1.463	0.989
	11	1.011	2.948	1.592	1.076
	12	0.969	3.013	1.608	1.086

[a] Compensated for overlap: ring carbon atom factor 1.39, quaternary carbon atom factor 1.48 (ref 15).

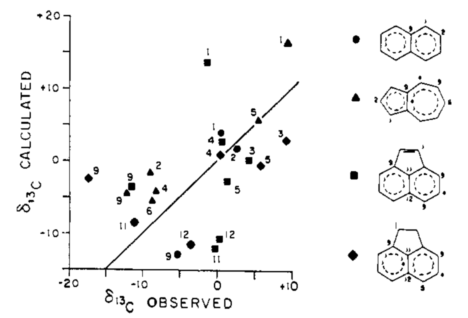

Figure 10. Theoretical carbon-13 shifts predicted from the relationship $\delta_{^{13}C} = 100\Delta Q\pi + 67\Delta Q\sigma - 76\Delta P$ and modified for overlap are plotted against the experimental values for naphthalene, azulene, acenaphthylene, and acenaphthene.

Some of the scatter observed in Figure 10 can be anticipated on the basis of a number of rather crude approximations made in the derivation of eq 1,[15] and in the basic formulation of any wave mechanical treatment of the relatively large molecules considered in this study. The utilization of the so-called average energy (ΔE) approximation used to reduce the second-order perturbation expression for the carbon-13 chemical shift undoubtedly constitutes one of the more serious simplifications underlying eq 1. It is significant therefore that such close agreement between both alternant[15] and nonalternant hydrocarbons should be achieved with only one value for ΔE, though the CNDO/2 electronic energy levels do vary only slightly between the two classes of compounds, as shown in Figure 11. The similarity of the present correlation to that derived for the heterocycles[8–11] is also remarkable. Equation 1,

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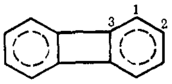
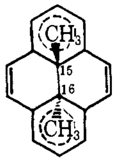
(29) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, p 297.

(30) D. C. Morrison, *J. Org. Chem.*, **25**, 1665 (1960).

however, fails to discuss shielding terms arising from localized anisotropic or interatomic electron currents induced by the magnetic field. Only in isolated cases[15,16,31] has it been considered necessary to discuss so-called ring-current effects which are in general less important than charge polarization and bond-order terms. The somewhat large positive shift of C-11, and to a lesser extent C-12 in acenaphthylene, compared with the corresponding shifts in acenaphthene may suggest the presence of a peripheral ring current in this compound. These effects are discussed qualitatively in the following section.

B. Ring-Current Effects. It has been assumed to date that zero contributions to carbon-13 shifts will arise from the ring-current effects at locations directly perpendicular to the path of the current flow. Such an assumption does not seem unreasonable since the magnetic effects induced by diamagnetic ring currents change from diamagnetism to paramagnetism immediately upon crossing from locations inside the ring to locations outside the ring (or *vice versa* for paramagnetic ring current effects).[32] However, ring-current induced magnetic effects are neither zero nor negligible for carbon atoms which are inside or outside the annulus of the ring current. For example, it has been tentatively suggested that these arguments indicate that the ring current in biphenylene forms an annulus whose radius from the center of the four-membered ring bisects the bond between the quaternary and C-1 carbon atoms.[16]





Calculations of the ring-current contribution to carbon-13 shifts are difficult and to the authors' knowledge have not been performed. However, estimates of the magnitude of the effect may be derived from experimental data. From proton nmr studies Boekelheide and coworkers[33] have shown that the high-field shift of the intraannular methyl groups in *trans*-15,16-dimethyldihydropyrene may be attributed to a ring-current contribution of the order of 5–7 ppm. This value was derived by comparison with the methyl resonance in the corresponding metacyclophane. As a consequence the high-field carbon-13 shifts (+3.6 ppm)[15] of the quaternary carbon atoms C-15,16 in pyrene were interpreted in terms of a peripheral ring-current contribution of similar magnitude. In this compound such an estimate may be on the conservative side, since the *normal* position for a quaternary carbon atom is at −5 to −10 ppm relative to benzene. These considerations would provide a ring-current contribution to carbon-13 shifts estimated at nearer 10 ppm in pyrene. In the 4*n* hydrocarbon, biphenylene, the effect is opposite in direction[16] (paramagnetic)[32] but the magnitude is approximately the same as in pyrene for both C-1 and the quaternary carbon atom, C-3. The estimated magnitude of the ring-current contribution in these systems therefore corresponds to approximately one-third of the total carbon-13 chemical-shift range for hydrocarbons containing conjugated double bonds.

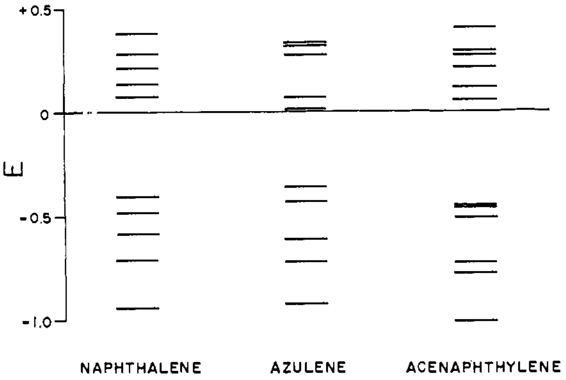


Figure 11. Electronic energy levels for naphthalene, azulene, and acenaphthylene derived using the CNDO/SCF method.

The nonalternant hydrocarbons described herein offer several possibilities for observation of anomalous carbon-13 chemical-shifts for intraannular carbon atoms. For example, C-11 in acenaphthylene, C-15 in fluoranthene, and C-12 and C-13,14 in benzo(ghi)-fluoranthene might be expected to be intraannular relative to $4n + 2$ (diamagnetic) peripheral ring currents. However, interpretation of the observed data in these cases is perhaps not as clear-cut as in the pyrene and biphenylene studies. Comparing the carbon-13 shifts in acenaphthene with those in acenaphthylene it is apparent that the major changes occur at C-11 (+10.97 ppm, upfield shift), C-9,10 (+5.87 ppm, upfield shift) and C-3,8 (−4.85 ppm, downfield shift) on formation of the 1,2 double bond. The large upfield shift at C-11 could perhaps be attributed to the effect of a peripheral ring current. However, the chemical shift at C-12 in acenaphthylene is essentially similar to that at C-11 and tends to preclude the suggestion of a peripheral current. Further, formation of the 1,2 double bond results in an upfield shift of +3.67 ppm at C-12 and +5.87 ppm at C-9,10. It seems likely, therefore, that these upfield shifts are more readily attributed to effects of charge migration. Qualitative evidence for charge migration (π or total) is indeed reflected in the theoretical parameters shown in Figure 6 at C-11, C-12, and C-9,10 in these compounds. These data suggest that acenaphthylene be regarded as a naphthalene unit weakly coupled with a strongly localized double bond. By analogy one might expect fluoranthene be best regarded as a naphthalene unit weakly coupled with an essentially unperturbed benzene ring. Consequently, the ring currents in acenaphthylene and fluoranthene presumably should be regarded as essentially naphthalene-like. The need to invoke arguments for ring-current contributions to the carbon-13 shifts in these molecules does not, at the present time, appear to be valid. In dismissing the ring-current argument in these cases, however, a note of caution must be added: attempts to calculate the electronic spectra of these systems based on the weakly coupled naphthalene model did not show even qualitative agreement.[34]

(31) J. J. Burke and P. C. Lauterbur, *J. Amer. Chem. Soc.*, **86**, 1870 (1964); G. E. Maciel and G. B. Savitsky, *J. Phys. Chem.*, **69**, 3925 (1965); P. H. Weiner and E. R. Malinowski, *ibid.*, **71**, 2791 (1967).

(32) J. A. Pople and K. G. Untch, *J. Amer. Chem. Soc.*, **88**, 4811 (1966); H. C. Longuet-Higgins, Special Publication No. 21, The Chemical Society, London, 1967, p 109; see also ref 18.

(33) V. Boekelheide and J. B. Phillips, *Proc. Nat. Acad. Sci. U. S.*, **51**, 550 (1964); *J. Amer. Chem. Soc.*, **89**, 1695 (1967); R. J. Molyneux, E. Sturm, and V. Boekelheide, *ibid.*, **89**, 1704 (1967); V. Boekelheide and T. Miyasaka, *ibid.*, **89**, 1709 (1967).

In the case of the carbon-13 shifts in benzo(ghi)-fluoranthene, it might be speculated that ring-current effects do become more important. This is suggested by the narrowing of the chemical shift range (14.12 ppm) compared with the other nonalternant ($4n + 2$) systems and probably reflects the higher degree of conjugation which is possible in this compound. Further, the separation between the singly intense quaternary carbon atom peaks (6.56 ppm), compared with 0.28 ppm in acenaphthylene and 2.22 ppm in fluoranthene, indicates additional contributions to the shielding term for the higher field peak (+1.68 ppm) of this pair. Similarly, of the three double intense peaks assigned to the remaining quaternary carbon atoms, the line at +0.43 ppm is at considerably higher field than the remaining two (−5.16 and −9.25 ppm). The chemical shifts of these higher field lines (+0.43 and +1.68 ppm) are indeed commensurate with a peripheral $4n + 2$ π-electron ring-current flow, which would require that the intraannular carbon atoms C-12 and C-13,14 resonate at these higher fields. The ambiguities in the carbon-13 assignments for benzo[*ghi*]fluoranthene must remain until studies of suitably substituted derivatives can be made.

C. Steric Effects. A relatively large downfield shift at C-3,8 (−4.85 ppm) was noted earlier in forming the 1,2 double bond in acenaphthylene compared to acenaphthene. Examination of a model indicates that in the planar unsaturated compound the protons H-1,2 are closer to H-3,8 than are the corresponding methylene protons in the saturated system. If this effect has a steric origin, it appears to be in the wrong direction. However, it is possible that the interaction of H-3,8 with H-1,2 in the saturated derivative may be enhanced due to the number of protons involved. It might also be anticipated that this effect would be reflected at C-11 in these compounds if its origin is indeed steric. To help clarify this point we have obtained the carbon-13 data for 1,8-dimethylnaphthalene (Table I). The shift at C-2,7 in this compound (−1.32 or +0.12 ppm) is considerably lower than in either acenaphthene (C-3,8) or acenaphthylene, while the shift at C-9 (corresponding to C-11) is directly comparable to that in naphthalene.[15] It is also noteworthy that the methyl shift in 1,8-dimethylnaphthalene (+102.54 ppm) is 7.32 ppm to lower field than in 1-methylnaphthalene[35] in sharp contrast to the higher field shift (1.77 ppm) noted between toluene and *o*-xylene.[21] These results would tend to suggest that the shifts in acenaphthene and acenaphthylene cannot be accounted for using steric arguments. The theoretical parameters (Figure 6) indicate that charge migration must once again be considered dominant.

Steric effects similar to those observed for the carbon atoms C-4,5 in phenanthrene,[1] however, must be considered to contribute to the high-field shifts of C-5,6 (+4.87 ppm) in benzo[*ghi*]fluoranthene and C-1,6 (+5.61) and C-7,10 (+7.84) in fluoranthene. van der Waal interaction between the corresponding protons in these systems is considered relatively large.[26,27]

Conclusions

The primary aim of the present study was to differentiate between the electronic features which distinguish the alternant from the nonalternant hydrocarbons. The results clearly show that the carbon-13 chemical-shift ranges provide a marked distinction between the simple compounds studied in the two categories. The carbon-13 shift range for unsubstituted $4n + 2$ benzenoid-alternant hydrocarbons is usually less than 10 ppm, whereas for the nonalternant systems described this range varies between 14 and 22 ppm. These ranges are nevertheless narrow compared with those observed in simple aliphatic systems,[19] emphasizing that the electronic environment of the carbon atoms in conjugated systems is remarkably similar. It is emphasized, however, that the carbon-13 chemical shifts are not simply related to the π-electron charge as has been suggested by Lynch[36] for a variety of compounds. Considerations of both π- and σ-electronic variations are necessary to account for the general electronic features in the majority of alternant[15] and nonalternant hydrocarbons. Perhaps what is even more remarkable is the close similarity in the correlation of carbon-13 shifts in alternant, nonalternant, and heterocyclic molecules provided by the simple wave mechanical treatments.

Acknowledgments. This work was supported by the National Institutes of Health, Grant No. GM-08521-08.

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(34) E. Heilbronner, J. P. Weber, J. Michl, and R. Zahradnik, *Theor. Chim. Acta*, **6**, 141 (1961).

(35) A. J. Jones, unpublished results.

(36) B. M. Lynch, *Chem. Commun.*, 1337 (1968), and references therein.