Carbon-13 Magnetic Resonance. XVI.[1] Chemical Shifts in Acepleiadiene and Acepleiadylene

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Abstract: Carbon-13 data are presented for the hydrocarbons acepleiadiene and acepleiadylene. The chemical-shift ranges of the two compounds are consistent with their being classified as nonalternant. These ranges also reflect the marked differences in reactivities of the two compounds. The large upfield shifts observed for the intraannular carbon atoms in acepleiadylene are shown to be compatible with Platt's formulation of a stable peripheral $4n + 2$ π-electron shell which is delocalized to produce a diamagnetic ring-current effect. The proton spectrum of acepleiadiene has been analyzed and the ordering of the nuclei in the AA'BB' and AB systems in both the "diene" and "dylene" established on the basis of the carbon-13 decoupling experiments.

In earlier papers in this series we have described some of the general characteristics, as evidenced by the carbon-13 chemical shifts, of a selection of alternant[3] and nonalternant[1] hydrocarbons. The chemical-shift ranges displayed by the nonalternant systems (14–22 ppm) are clearly greater than observed in the alternant systems (<10 ppm). However, these shifts are not simply related to π-electron charge and can only be justified in the main by considering both π- and σ-electronic features. To explain some anomalous chemical shifts, in particular for intraannular carbon atoms, possible ring-current contributions have also been discussed.[1,3]

The hydrocarbons acepleiadiene (I, see Figure 1) and acepleiadylene (II, see Figure 2) provide us with further examples in the nonalternant hydrocarbon series. Acepleiadylene (II) is isoelectronic with the alternant hydrocarbon pyrene. Both hydrocarbons contain sixteen π electrons, $4n$ according to the Hückel rule, while their observed properties are more in keeping with the Hückel $4n + 2$ rule which implies aromatic stability. As is well established, however, extensions of the Hückel rule, while remarkably satisfactory for catacondensed polycyclic systems, have not correlated well with the properties of cyclocondensed aromatic hydrocarbons. An alternative treatment based on the free-electron model[4-7] has been proposed. It was suggested that a stable peripheral π-orbital system could be dominant in both catacondensed and cyclocondensed structures and that other unsaturation would act only as a substituent. Platt[7,8] modified this view with the concept that a stable peripheral π-electron "shell" will be separated from inner π electrons by circular nodes and, therefore, the two loci of unsaturation will consist of more or less discrete molecular orbitals. Such a concept affords an explanation of the $4n + 2$ character of the benzenoid cyclocondensed hydrocarbons (*e.g.*, pyrene, coronene, ovalene) and of acepleiadylene, in addition to dicyclopenta[*e.g.*, *kl*]heptalene (azupyrene),[9] the latter of which has no benzenoid rings. In contrast, acepleiadiene (I) (and pleiadiene) is quite reactive and possesses limited resonance stabilization.[10] The periphery of this hydrocarbon contains 13 π electrons, while the total number of π electrons in the systems is 14 ($4n + 2$). Its reactivity perhaps indicates a limited degree of conjugation compared with acepleiadylene, and it was hoped that this electronic feature would be evidenced by the carbon-13 spectra. Further, the proton spectra of acepleiadylene can only be analyzed with some resulting ambiguities,[11] to be discussed. We have used the carbon-13 data in an attempt to resolve these ambiguities.

Experimental Section

Carbon-13 spectra were obtained using a Varian AFS-60 analog frequency sweep spectrometer in the manner described previously.[1] Due to the limited solubility of acepleiadiene (I) and acepleiadylene (II) (18 mol % in carbon disulfide and *ca.* 5 mol % in carbon disulfide:dioxane for I and II, respectively), it was necessary to accumulate some part of the spectra on a Varian C-1024 time-averaging device. Proton spectra were determined using a Varian A56/60 spectrometer.

Results

The pmr spectrum of acepleiadylene (II) has been analyzed,[11] though not explicitly due to the uncertainties in the ordering of the nuclei in the AA'BB' and AB systems associated with the protons H-5,6,7,8 and H-3,4 or H-9,10, respectively. Schaefer and Schneider[12] have attempted to determine this order on the basis of the calculated π electron densities. The results obtained by the latter workers were used in making the initial carbon-13 assignments but have subsequently

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[1] Previous paper in this series: A. J. Jones, T. D. Alger, D. M. Grant, and W. M. Litchman, *J. Amer. Chem. Soc.*, 92, 2386 (1970).

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[8] J. R. Platt, *ibid.*, 22, 1448 (1954).

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[11] W. A. Schneider, H. J. Bernstein, and J. A. Pople, *J. Amer. Chem. Soc.*, 80, 3497 (1958).

[12] T. Schaefer and W. G. Schneider, *Can. J. Chem.*, 41, 966 (1963).

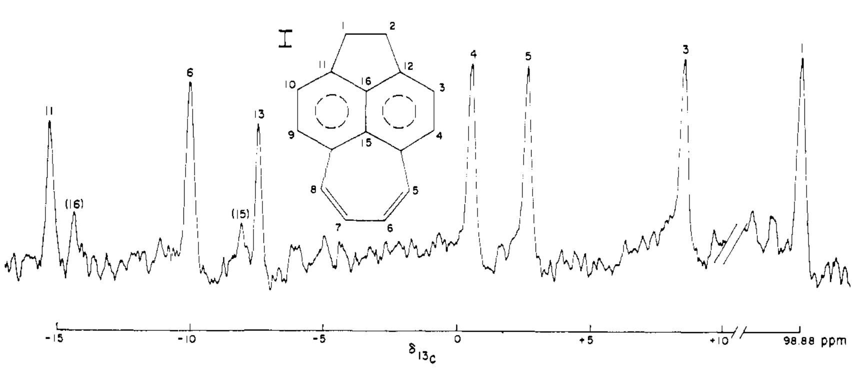

Figure 1. The proton-decoupled carbon-13 magnetic resonance spectrum of acepleiadiene (I).

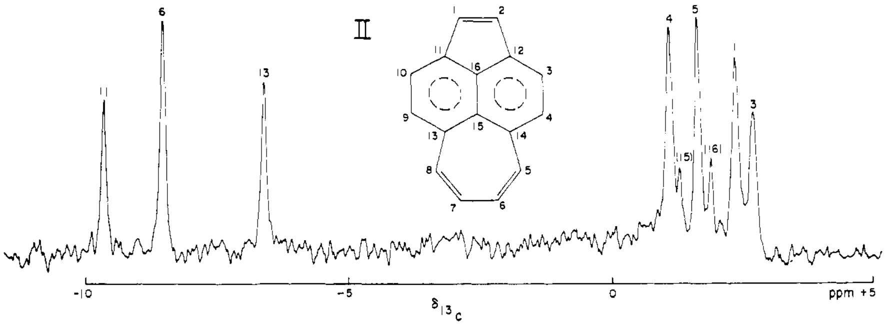

Figure 2. The proton-decoupled carbon-13 magnetic resonance spectrum of acepleidylene (II).

been modified to comply with the requirements set by the carbon-13 data for both acepleiadylene and acepleiadiene. The earlier[12] and modified proton assignments are given in Table I. The pmr spectrum of acepleiadiene (I) was determined in the present work and exhibited the characteristics of a mixed AA'BB' and AB spectrum. However, the lower field doublet of the AB spectrum is further split by long-range coupling (*ca.* 1.5 Hz) with H-1,2. Homonuclear decoupling, irradiating at H-1,2, resulted in sharpening of this doublet. In keeping with the allylic coupling observed between H-1,2 and H-3,8 in acenaphthene,[13] this doublet is assigned to the protons H-3,10 in acepleiadiene. The ordering of the AA'BB' protons H-5,8 and H-6,7 cannot be determined directly from the proton spectrum.

Table I. Chemical Shifts in Acepleiadiene, Acepleiadylene, and 5H-Dibenzo[*a*,*d*]cycloheptatrienone

Compd	position	δ_H,[a] in ppm[c]	δ_H,[b] in ppm[c]	$\delta_{^{13}C}$ in ppm[c]	^{13}C shift range[d]
I	1,2	+4.20	+4.20	+98.88	
	3,10	+0.64	+0.64	+ 8.47	23.82
	4,9	+1.01	+1.01	+ 0.56	
	5,8	(+1.54	+2.22	+ 2.59	
	6,7	+2.22)	+1.54	− 9.91	
	11,12			−15.35	
	13,14			− 7.33	
	15			(− 8.02	
	16			−14.35)	
II	1,2	−0.50	−0.50	+ 2.36	12.36
	3,10	(−0.96	−0.96	+ 2.70	
	4,9	−0.58)	−0.58	+ 1.11	
	5,8	(−0.42	+0.48	+ 1.66	
	6,7	+0.48)	+0.42	− 8.50	
	11,12			− 9.66	
	13,14			− 6.33	
	15			(+ 1.31	
	16			+ 1.90)	
V	1,2	+0.30		− 3.03	
	3,10	−1.07		− 1.78	
	4,9	(−0.27		{− 3.26	
	5,8	−0.27		− 2.42	
	6,7	−0.27)		− 0.18}	
	11,12			− 6.45	
	13,14			−10.27	
	15			−63.01	

[a] Proton assignments in II.[12] [b] Proton assignments made on basis of ^{13}C spectral comparisons. [c] Parts per million relative to benzene, parentheses indicate uncertainties in assignment. [d] Excluding C-1,2 in acepleiadiene.

Carbon-13 spectra were determined using selective proton decoupling techniques.[1] This method enables unequivocable assignment of the signals due to the carbon atoms C-1,2, C-3,10, and C-4,9 in acepleiadiene and C-1,2 in acepleiadylene. In addition the distinction between the carbon-13 signals associated with the AA'BB' and AB systems in both compounds was readily made. Quaternary carbon atoms were distinguished by the absence of large induced proton splittings in the coupled spectra. Further, the 1:2 intensity ratio of the signals arising from the quaternary carbon atoms C-15 and C-16, in both compounds, compared with all others enabled their assignment. The carbon-13 spectra of acepleiadiene and acepleiadylene are shown in Figures 1 and 2, respectively. Chemical shifts are given in Table I. Remaining uncertainties in the assignments for the carbon atom pairs C-5,8:C-6,7, C-11,12:C-13,14, and C-15:C-16 in acepleiadiene and similarly in acepleiadylene, though with the addition of the pair C-3,10:C-4,9 are resolvable by comparing the shifts in the two compounds with those

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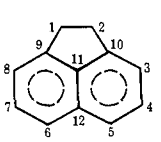
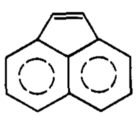
(13) M. J. S. Dewar and R. C. Fahey, *J. Amer. Chem. Soc.*, **85**, 2704 (1963).

observed in acenaphthene (III) and acenaphthylene (IV).[4]



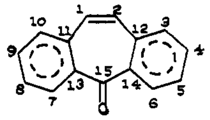
III



IV

In the spectrum of acepleiadiene the lowest field double-intensity quaternary carbon atom signal occurs at −15.35 ppm while in acepleiadylene a corresponding line occurs at −9.66 ppm. These shift values do not differ substantially from those at the 9,10 positions in acenaphthene (−17.37 ppm) and acenaphthylene (−11.50 ppm), but perhaps more striking the differences, −5.69 ppm compared to −5.87 ppm, are remarkably similar and suggest that these lines be assigned to the analogous carbon positions C-11,12. As a consequence the lines at −7.33 ppm and −6.33 ppm must be assigned to C-13,14 in the diene (I) and dylene (II), respectively. The similarity of these latter values is a further indication of the correctness of this assignment, only minor differences in electronic structure between the two compounds occurring at this position. A similar analogy between the differences in chemical shifts at C-3,8 in acenaphthene and acenaphthylene (−4.85 ppm) and C-3,10 in acepleiadiene and acepleiadylene (−5.77 ppm) favors assignment of the higher field line (+2.70 ppm) of the pair associated with the AB system to this position in acepleiadylene (II). It will be recalled that assignment of the corresponding carbon atoms in acepleiadiene (+8.47 ppm) was obtained unequivocably by selective proton decoupling.

The carbon-13 resonances associated with the AA′BB′ systems in both compounds were determined by selective decoupling but the ordering of these nuclei is obtained less rigorously. From a model it seems probable that the protons H-4,9 and H-5,8 in acepleiadiene and acepleiadylene will sterically interact through interference of the van der Waals radii of these nuclei. Such an interaction is analogous to, but not likely to be as pronounced as, the well-established van der Waals interaction in angular polycyclic hydrocarbons, which exhibit low-field proton chemical shifts for the interacting protons[14] and high-field carbon-13 chemical shifts for the corresponding directly bonded carbon atoms.[3,15] In addition, the adjacent quaternary carbon atom resonances in, for example, phenanthrene[3] and triphenylene[15] reflect this in a smaller magnitude upfield shift. It is therefore suggested that the higher field carbon-13 signal of the pair associated with C-5,8 and C-6,9 be assigned to C-5,8 in both acepleiadiene (+2.59 ppm) and acepleiadylene (+1.66 ppm). It is interesting to note that the shift of the quaternary carbon atoms C-13,14 (+7.33 and −6.33 ppm) in these compounds corresponds well with that observed at the junction of the six and seven-membered rings in 5H-dibenzo[*a*,*d*]-cycloheptatrienone (V), the carbon-13 shifts of which are also presented in Table I.



V

The assignment of the signals due to C-15 and C-16 in acepleiadiene and acepleiadylene cannot be absolute, and while the discussion of their ordering in the latter would seem to be academic this is not the case in the former. The tentative assignment for these positions in acepleiadiene given in Table I is based on the ordering of the shifts for the corresponding positions in acenaphthene. Further justification for this assignment is derived from the arguments pertaining to ring-current effects presented in the following section.

Having assigned the majority of carbon-13 resonances in acepleiadiene and acepleiadylene, it is possible to reconsider the proton chemical shifts by simply relating the frequencies employed to decouple the appropriate carbon resonances. Thus, C-6,7 was decoupled at higher frequency than C-5,8 indicating that the lower field portion of the AA′BB′ multiplet in the proton spectra of both compounds be assigned to H-6,7. Interpretation of the ordering of the nuclei in the AB portion of the proton spectrum of acepleiadylene was assisted by the long-range coupling observed in the pmr spectrum of the saturated derivative and by the selective decoupling experiments. In this case the ordering derived by Schaefer and Schneider[12] was confirmed.

Discussion

Attention is drawn to two major features in the carbon-13 shift data presented in Table I: (a) the chemical-shift range in acepleiadiene (excluding the aliphatic carbons C-1,2) is almost twice the magnitude of that observed in acepleiadylene and (b) the upfield shifts of the carbon atoms C-15 and C-16 (+10–16 ppm) in acepleiadylene relative to acepleiadiene. In terms of carbon-13 chemical-shift ranges it is clear that both of these systems fall into the general category for nonalternant hydrocarbons. The ranges previously observed for this class of compounds being from 14 to 22 ppm,[4] whereas in unsubstituted alternant hydrocarbons the range is usually <10 ppm.[3] It should also be noted that the Hückel 4*n* hydrocarbon biphenylene, which is also alternant, exhibits a carbon-13 shift range of 34 ppm.[15] These chemical-shift ranges have been attributed to either uneven charge distribution (modified by bond order and/or average energy terms) or to electron delocalization effects. In general it is apparent that the more uneven the charge distribution the greater the chemical-shift range. If the shift at one carbon position differs markedly from another then to some degree the chemical-shift range will reflect the reactivity of a molecular system. However, reactivity or stability cannot, in general, be associated with the carbon-13 chemical-shift range. Perhaps this is not surprising since carbon-13 shifts are measured for molecules in the ground state, while reactivity refers to the transition state in an ensuing chemical reaction. Nevertheless, between compounds which possess similar basic structures there does appear to be a qualitative relationship between shift range and reactivity. For

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(14) *E.g.*, N. Jonathan, S. Gordon, and B. P. Dailey, *J. Chem. Phys.*, **36**, 2443 (1962); J. D. Memory, G. W. Parker, and J. C. Halsey, *ibid.*, **45**, 3567 (1966).

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

example, the reactivity of phenanthrene relative to triphenylene is apparently reflected in the carbon-13 shift ranges 9.5 ppm[3] and 6.5 ppm,[15] respectively, while in the present compounds, acepleiadiene (24 ppm) is more reactive than acepleiadylene (12 ppm). The evidence available at the present time, however, precludes extension of these arguments into a general rule concerning reactivity and carbon-13 shift ranges.[16]

If electron-delocalization effects are dominant then ring-current contributions to carbon-13 shifts become important, as noted in the cases of pyrene[3] and biphenylene.[15] The high-field shifts at C-15 and C-16 in acepleiadylene are similar to those noted in the isoelectronic system, pyrene, and are perhaps attributable to the ring-current effect expected in these peripheral $4n + 2$ π-electron systems. Comparison of these shifts with those in acenaphthylene[1] provides further justification for this suggestion. Thus the shifts at C-11 and C-12 in acenaphthylene are upfield (+10.97 and +3.67 ppm, respectively) relative to acenaphthene. The shifts at C-15 and C-16 previously noted in the present compounds are approximately 10–16 ppm upfield. While the 10-ppm shift resembles that at C-11 in acenaphthylene, the 16-ppm shift is far in excess for the remaining position and consequently presents an anomaly similar to that observed in pyrene.[3] We therefore conclude that the shifts at C-15 and C-16 can only be accounted for in terms of a $4n + 2$ peripheral π-electron ring current analogous to that described in pyrene.[3] The evidence presented above for delocalization of the peripheral π-electron system in acepleiadylene, also leads to interesting possibilities concerning the charge distribution in acepleiadiene. The first possibility is that the electron charge may be localized, in particular, on the seven-membered ring. This would help account for the large shift range and enhanced reactivity of the saturated derivative. A second, but less likely possibility, is a reverse ring current (paramagnetic) effect,[17] which could account for the extremely low shift at C-15 (−14.35 ppm) in the diene (I). This suggestion would require that a ring current be set up by delocalization of $4n$ π electrons, where $n = 3$. That is, that the electrons at C-15 and C-16 would not take part in this delocalization. The contrast in the chemical shifts at C-15 and C-16 in the diene and dylene could thus perhaps arise as a consequence of the transition from a paramagnetic to a diamagnetic ring-current effect. Whichever of these suggestions be preferred the diamagnetic effect in acepleiadylene seems well established.

Theoretical charge densities (HMO)[18] in acepleiadylene imply an excess charge in the five-membered ring, while similar values derived from pmr studies[12] have been used to suggest that excess charge tends to be concentrated on the outer perimeter of the molecule with a preference to reside in the seven-membered ring. The carbon-13 shifts tend to agree more readily with the theoretical predictions though the shifts of the intraannular carbon atoms require peripheral delocalization of electrons. The concentration of charge in the five-membered ring is considered to be exhibited in the shifts at C-1,2 (+2.36 ppm) and C-6,7 (−8.50 ppm) which are in the direction of the cyclopentadienyl (+25.7 ppm)[19] and tropylium (−27.6 ppm)[19] ions, respectively, relative to the double-bonded carbon atoms in the uncharged parent compounds, cyclopentadiene (−3.23 and −3.49 ppm)[20] and cycloheptatriene (−2.9, 1.3, and 7.6 ppm).[19] The carbon-13 shift values also suggest that the dipole moment in acepleiadylene is from the five- to the seven-membered ring. However, the Hückel charge densities do not readily correlate the observed shifts at C-15, C-11,12, C-5,8, and C-3,10. The anomaly at C-15 appears to be best explained in terms of the ring-current effect, but at C-11,12, C-5,8, and C-3,10 the charge densities are overestimated (C-11,12) or underestimated (C-5,8 and C-3,10) in the theoretical treatment. The remaining carbon-13 values correlate reasonably well with the 160-ppm shift per electron dependence derived by Spiesecke and Schneider.[19] No calculations on the acepleiadiene system appear to have been reported.

Conclusions

The Platt[7,8] formulation of the stable peripheral π-electron "shell" appears to be justified in providing an explanation of the aromatic stability of acepleiadylene (II). Not only is the highly conjugated nature of II evidenced by the relatively narrow carbon-13 chemical-shift range, but also the high-field shifts of the intraannular quaternary carbon atoms imply a peripheral $4n + 2$ π-electron ring-current flow. In contrast the broader carbon-13 shift range in acepleiadiene (I) is interpreted as a feature of the relative reactivity of this system. The reactivity of I is not reflected in the absolute values of carbon-13 shifts at the reactive sites C-5,8 and C-6,7 (+2.59 and −9.91 ppm) compared with acepleiadylene (+1.66 and −8.50 ppm) but appears to be exhibited in the shift at C-15 (−14.35 in I compared to +1.31 ppm in II).

The compounds studied herein also provide an example in which the better defined carbon-13 parameters enable assignment of the proton-chemical shifts in a complex spectrum. This "reverse" technique will become increasingly important and obviates some of the need for studying chemically substituted derivatives.

Acknowledgments. The National Institutes of Health provided support for this work under Grant No. GM-08521-08.

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(16) Note the obvious exception provided by biphenylene (34 ppm); ref 15.

(17) 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; for a detailed discussion see: A. J. Jones, *Rev. Pure Appl. Chem.*, **18**, 253 (1968).

(18) B. Pullman, A. Pullman, G. Berthier, and J. Pontes, *J. Chim. Phys.*, **49**, 20 (1952).

(19) H. Spiesecke and W. A. Schneider, *Tetrahedron Lett.*, 468 (1961).

(20) A. J. Jones and D. M. Grant, unpublished data.