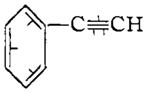
which accounts for the considerable charge q_4 which we found in sections 5 and 6.

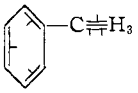
The foregoing discussion has been entirely in terms of VB theory. Our computations made in the framework of LCAO MO theory correspond of course to a somewhat different weighting of resonance structures, together with some additional ones. Nevertheless there is a sufficient degree of coincidence between the two theories so that our discussion of VB resonance structures has valid qualitative significance for the understanding of the distinctions between strong and ordinary conjugation and between strong and ordinary hyperconjugation.

Two further examples of VB resonance structures in conjugation and hyperconjugation may be instructive. For allene, π_x and π_y bonds are equally important. The principal resonance structure is $H_2\underset{\shortmid\shortmid}{=}C\overset{\shortmid}{=}C\underset{\shortmid\shortmid}{=}C\overset{\shortmid}{=}H_2$. The only π-type resonance here is (first-order) hyperconjugation involving excited structures $H_2\underset{\shortmid\shortmid}{=}\overset{\circ}{C}—C\overset{\shortmid}{\underset{\shortmid\shortmid}{\equiv}}C—\overset{\circ}{H}_2$ and $\underset{\circ}{H}_2—C\overset{\shortmid}{\underset{\shortmid\shortmid}{\equiv}}\underset{\circ}{C}\overset{\shortmid}{=}H_2$. In ethylene twisted until the two CH_2 planes are perpendicular, the principal resonance structure is $H_2\overset{\shortmid}{=}\underset{\circ}{C}—\overset{\circ}{C}\underset{\shortmid\shortmid}{=}H_2$. Here there is strong hyperconjugation with each of the two structures $\overset{\circ}{H}_2—\underset{\circ}{C}\overset{\shortmid}{=}C\underset{\shortmid\shortmid}{=}\underset{\circ}{H}_2$ and $H_2\overset{\shortmid}{=}C\underset{\shortmid\shortmid}{=}\overset{\circ}{C}—\underset{\circ}{H}_2$ (also, less important, with $\overset{\circ}{H}_2—C\overset{\shortmid}{\underset{\shortmid\shortmid}{\equiv}}C—\underset{\circ}{H}_2$).

To illustrate further the new bond symbols introduced here, one might use (for one of the principal resonance structures in each case) the following symbols to make clearer the structures of phenylacetylene and of toluene from the point of view of conjugation or hyperconjugation



and



As another example, the VB formulation of CO_2 involves resonance between two equivalent structures $O\overset{\shortmid}{=}C\underset{\shortmid\shortmid}{=}O$ and $O\underset{\shortmid\shortmid}{=}C\overset{\shortmid}{=}O$.

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The Proton Magnetic Resonance Spectra of Azulene and Acepleiadylene

BY W. G. SCHNEIDER, H. J. BERNSTEIN AND J. A. POPLE[1]

RECEIVED DECEMBER 23, 1957

The proton resonance spectra of the non-alternant hydrocarbons, azulene and acepleiadylene, have been measured under conditions of high resolution. A satisfactory assignment of the spectra to individual protons in the molecules was possible and proton chemical shifts and spin coupling constants were evaluated. The chemical shifts are much larger in the non-alternant hydrocarbons, compared to the corresponding shifts in alternant hydrocarbons. The observed spin coupling constants between adjacent protons, increase with the size of the carbon ring, being of the order of 3.5, 7 and 12 c./sec. for the 5, 6 and 7-membered rings. The "ring current" model, which gave a fairly satisfactory interpretation of the proton shifts in the spectra of alternant hydrocarbons, is inadequate for the non-alternant hydrocarbons. This failure of the model is attributed to the highly asymmetric nature of the electron charge distribution in the non-alternant molecules. Surprisingly large shifts of the proton resonances were observed on dilution in various solvents. These dilution shifts were anomalous; the protons on the 7-membered carbon ring gave rise to a much larger dilution shift than the 5-membered carbon ring on the same molecule. This behavior is discussed in terms of an intermolecular interaction characteristic of these hydrocarbons.

The relative chemical shifts of protons bonded to different carbon atoms in polynuclear aromatic hydrocarbons are of some interest. Previous work[2] had shown that the proton chemical shifts of alternant aromatic hydrocarbons can be satisfactorily accounted for in terms of the "ring current" model.[3] An earlier proton resonance spectrum of the non-alternant hydrocarbon azulene, which was measured under conditions of moderate resolution,[2] did not permit a complete assignment of the spectrum. Moreover, the range of chemical shifts indicated by the spectrum did not appear to be reproduced by the spectrum calculated by the ring current model. The proton spectra of the non-alternant hydrocarbons, azulene and acepleiadylene, which are isomeric with naphthalene and pyrene, respectively, have now been measured under conditions of higher resolution. A complete assignment of the spectra has been made on the basis of which individual chemical shifts and spin-coupling constants could be evaluated.

Experimental

The proton magnetic resonance spectra were measured with a Varian V-4300 NMR spectrometer operating at a fixed frequency of 40 Mc./sec. and equipped with a Varian Field Stabilizer. The frequency separation of the signals in the spectra was measured by the side-band technique in the usual manner.

A sample of purified azulene and 1- and 2-methylazulene were kindly provided by Dr. E. Heilbronner. The spectra of the methylazulenes provided a useful confirmation of the proton assignment. Another sample of azulene was obtained from K. and K. Laboratories, Long Island, N. Y. The sample of acepleiadylene was provided by Professor V. Boekelheide. It had been purified by chromatographic methods and recrystallization and had a sharp melting point at 160–161°.

The spectrum of azulene was measured, above its melting point, at 125° and that of acepleiadylene at 175°. Heating of the samples was accomplished by means of an apparatus previously described[2] which had been modified to permit simultaneous spinning of the sample by the stream of hot nitrogen gas used to heat the sample. The samples were contained in a 5 mm. o.d. glass tube together with a sealed

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[1] Visiting Research Associate, National Research Council, Summer 1957.

[2] H. J. Bernstein, W. G. Schneider and J. A. Pople, *Proc. Roy. Soc. (London)*, **A236**, 515 (1956).

[3] J. A. Pople, *J. Chem. Phys.*, **24**, 1111 (1956).

glass capillary containing decalin which served as an external reference compound for the frequency measurements.

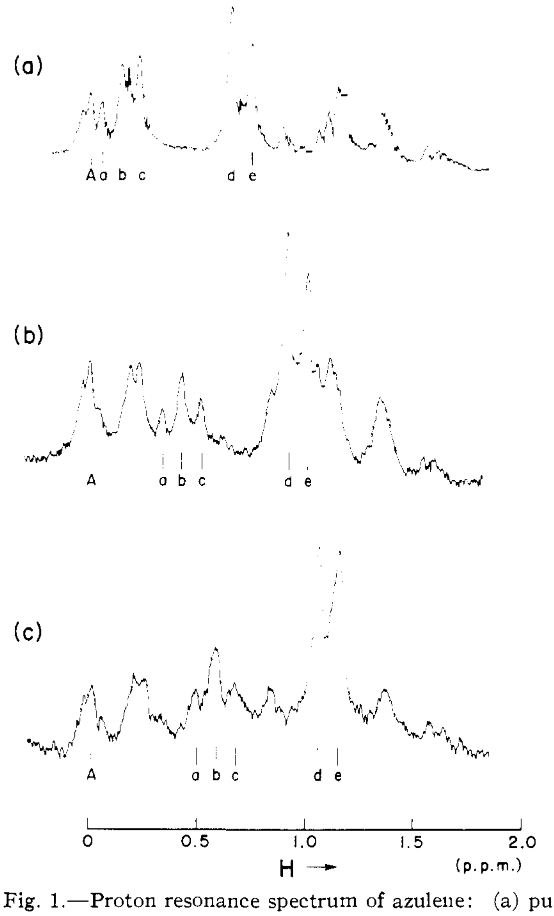

Fig. 1.—Proton resonance spectrum of azulene: (a) pure azulene (at 125°); (b) 20 mole % solution in dioxane; (c) 3 mole % solution.

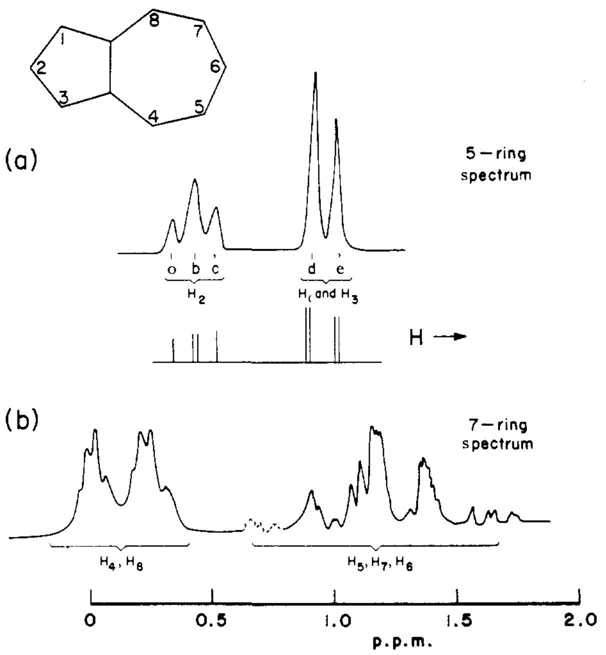

Fig. 2.—Proton resonance spectra of the 5- and 7-membered ring protons.

Further measurements were carried out at room temperature on solutions of azulene in dioxane, cyclohexane and chloroform and a 3.8 mole % solution of acepleiadylene in dioxane. In each case a sealed capillary containing a reference liquid was introduced into the sample tube. For the solutions of azulene in dioxane, water was used as a reference; for azulene in cyclohexane and chloroform, dioxane was used; and for acepleiadylene in dioxane, cyclohexane was used.

In order that all measurements could be referred to a common reference, the water–dioxane, decalin–dioxane and cyclohexane–dioxane signal separations (with dioxane in a sealed capillary) were determined in separate experiments. To reduce all the measurements to a comparable basis with dioxane as external reference, bulk susceptibility corrections were applied to each measurement. The volume susceptibilities of azulene and acepleiadylene were assumed to be equal to naphthalene and pyrene, respectively.[2] The change in chemical shift in azulene and acepleiadylene due to change in bulk susceptibility with temperature was assumed equal to the change in bulk susceptibility of the reference decalin over the same temperature range. The volume susceptibility of the solutions was computed on the assumption of additivity of the volume susceptibility of the components according to their respective volume fractions.

Results and Discussion

(a) **Azulene.**—Figure 1 shows reproductions of the proton resonance spectra of (a) pure azulene (at 125°), (b) a 20 mole % solution of azulene in dioxane and (c) a 3 mole % solution in dioxane. The direction of increasing applied magnetic field is from left to right and the separation of the lines in the spectra in p.p.m. relative to the lowest field signal, A, is indicated by the scale at the bottom of the figure. The three spectra appear strikingly different from each other. On dilution of azulene in dioxane the set of five lines labelled a, b, c, d, e shift to higher field relative to the remaining lines in the spectrum. Moreover the frequency separation of the lines of this set, which evidently form a related group, are only slightly altered in the three spectra. The mutual separation of the remaining lines in the spectrum likewise vary only slightly in the three spectra. Thus we have two distinct sets of signals, the two sets being displaced relative to each other on dilution with dioxane. This observation was a valuable aid in arriving at an assignment of the spectrum.

The formula of azulene, together with the numbering of the carbon atoms to which the protons are attached, is shown in Fig. 2. The 5-membered carbon ring has three protons, two of which are equivalent, H_1 and H_3, whereas the 7-membered ring has two such sets, H_4 and H_8, and H_5 and H_7. On subtracting off the set of five lines a, b, c, d, e from the azulene spectra shown in Fig. 1 the two separate spectra shown in Fig. 2 can be constructed. This procedure is, of course, rather inaccurate and the relative intensities of the lines in each of the two spectra are subject to considerable error. Nevertheless the spectrum of Fig. 2a is readily identified as an AB_2 spectrum,[4,5] and this can reasonably be assigned to the three protons of the 5-membered ring. According to reference 4 the spectrum should consist of eight lines with the

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(4) H. J. Bernstein, J. A. Pople and W. G. Schneider, *Can. J. Chem.*, **35**, 65 (1957).

(5) The notation employed here is that of reference 4. The letters A, B, . . . , refer to two sets of nuclei giving rise to a chemical shift, $\gamma H_0(\sigma_A - \sigma_B)$, which is of the same order of magnitude as the spin-coupling constant, J. The notation AB_2 indicates that the spectrum arises from three nuclei, two of which are equivalent.

relative spacings shown at the bottom of Fig. 2a. When the ratio of $J/\eta H_0 \Delta\sigma$ is between 0.1 and 0.2, three of the observed signals (b, d and e) are closely spaced doublets and are not resolved, giving rise to only five signals with the approximate relative intensities observed. Analysis of the spectrum of pure azulene (using Table V of reference 4) gives a value of 0.60 ± 0.01 p.p.m. for the chemical shift and 3.8 ± 0.5 c./sec. for the spin–spin coupling constant. Analysis of the spectra of the 20 mole % and 3 mole % solutions in dioxane give 0.53 ± 0.01 p.p.m. and 3.5 ± 0.5 c./sec., and 0.51 ± 0.01 p.p.m. and 3.5 ± 0.5 c./sec., respectively. There has been a small but significant change in the chemical shift on dilution but within experimental error the spin–spin coupling constant is unaltered. The relative intensities calculated[4] for the a, b, c, d and e lines of the spectrum for the 20 mole % solution of azulene in dioxane are 0.8, 2.0, 1.2, 4.3 and 3.7, respectively, which compare favorably with those observed in Fig. 1b. The signals a, b, c which occur at lower field are assigned to the proton H_2 of the 5-membered ring and signals d, e which together have twice the intensity of a, b and c are assigned to H_1 and H_3.

This assignment of the five-membered ring signals was confirmed by an examination of the spectra of 1-methylazulene and of 2-methylazulene. In the spectrum of the latter the a, b, c signals were absent, while in the 1-methyl compound they appeared as a doublet and the d, e signals were reduced in intensity by one-half. The assignment is also consistent with that of the tri-substituted compound, *s*-guaiazulene, previously reported.[4]

The spectrum shown in Fig. 2b is accordingly assigned to the protons of the 7-membered carbon ring. There are two well separated band systems, preliminary intensity considerations suggesting that the low field part corresponds to two of the five protons. At this point the analysis of *s*-guaiazulene[4] is again useful. This compound has a signal from position 4 at lowest field so the low field part of Fig. 2b is assigned to protons 4 and 8. The 7-ring spectrum is of type AB_2X_2, that is, one single nucleus, one pair with a small chemical shift relative to that of the first nucleus, and another pair with a large chemical shift. It has, in fact, many features in common with the proton spectrum of pyridine which has recently been analyzed.[6] The amount of detail available was rather less than for pyridine, so no attempt was made to estimate spin-coupling constants between non-nearest neighbors. Also, any coupling between protons in different rings was neglected. This seems reasonable on account of the simple form of the 5-ring spectrum. A similar result was found for naphthalene.[7] It was found that the main features were reproduced using

$$\eta H_0(\sigma_6 - \sigma_4) = 0.92 \text{ p.p.m.}$$
$$\eta H_0(\sigma_5 - \sigma_4) = 1.33 \text{ p.p.m.}$$

for the chemical shifts relative to proton 4, and

$$J_{45} = J_{56} = 10.0 \text{ c./sec.}$$

for the spin-coupling constants.

It is to be noted that the assignment noted here differs in several respects from that given previously[2] on the basis of a spectrum of lower resolution. In particular the protons H_4 and H_8 were incorrectly assigned; these are now found to give rise to the extreme low field signals.

As mentioned above, the position of the two sets of signals relative to one another depends on the concentration of azulene. For purposes of interpretation, we consider the relative chemical shifts in a dilute solution (3 mole %). The displacement of the center of signal 2 from the center of signal 4,8 is then

$$\eta H_0(\sigma_2 - \sigma_4) = 0.45 \text{ p.p.m.}$$

The complete set of relative chemical shifts is illustrated in Fig. 3a.

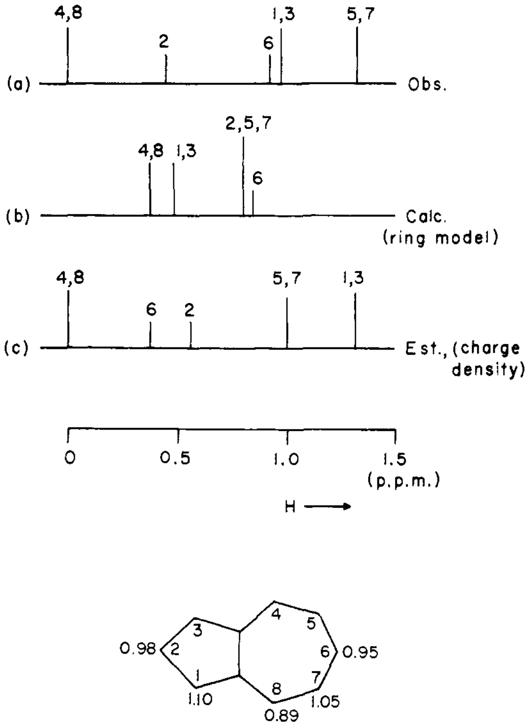

Fig. 3.—Diagram showing the comparison of observed and calculated relative chemical shifts: (a) observed spectrum; (b) calculated by the ring-current model; (c) estimated from the charge density diagram shown in (d).

Turning to the theoretical interpretation of the chemical shifts, there are two effects which might be expected to contribute.

(1) The aromatic ring currents induced in the molecule will produce different secondary magnetic fields at different protons and will lead to a separation of signals. A simple calculation based on this effect gave a satisfactory interpretation of the proton spectra of a number of alternant aromatic hydrocarbons.[2]

(2) The local charge density will vary from one carbon atom to another leading to different effective shieldings. Any effect of this sort will be more marked in non-alternants since, according to molec-

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[6] W. G. Schneider, J. A. Pople and H. J. Bernstein, *Can. J. Chem.*, **35**, 1487 (1957).

[7] J. A. Pople, W. G. Schneider and H. J. Bernstein, *ibid.*, **35**, 1060 (1957).

ular orbital theory, the charge density is nearly uniform in alternant molecules.

The chemical shifts due to the ring current effect can be estimated by a calculation similar to that employed for the alternant hydrocarbons.[2] According to this method, the shift to low field of the signal due to a proton at distance R from an aromatic ring of radius a is proportional to a^2/R^3. Assuming that the current induced in each ring is the same as that in benzene and sufficient to explain the chemical shift of 1.9 p.p.m. between benzene, and ethylene, we can obtain the shifts in azulene from the geometrical dimensions. In this calculation, the pentagon and heptagon have been taken as regular figures with side 1.40 Å. and the length of all C–H bonds as 1.10 Å. This leads to the set of chemical shifts illustrated in Fig. 3b. This is drawn to the same scale as the experimental figure above. It is clear that the ring model does not give a quantitative explanation of the spread of the spectrum. The total spread predicted is only 0.5 p.p.m. whereas that observed is 1.3 p.p.m. Further, the ordering is incorrect, the principal inconsistency being that the 1,3 signals are predicted to lie on the low field side of the 2 signal while the opposite is observed. A more detailed quantum-mechanical theory of the ring current[8] indicates that a slightly larger current flows in the 5-ring, but this does not affect the results substantially.

The effect of the non-uniformity of charge distribution is difficult to estimate quantitatively, but we may at least try to correlate the order of the signals, by supposing that the signal is displaced by an amount proportional to the π-electron charge density on the neighboring carbon atom predicted by self-consistent molecular orbital theory. These charge densities have recently been calculated by Pariser[9] and are shown in Fig. 3d. The set of chemical shifts predicted in this way is illustrated in Fig. 3c. No significance is to be attached to the scale here. It is interesting to note that the 4,8 signals are predicted to lie at lowest field. This correlation with charge density also gives the signals 1, 2 and 3 in the correct order. It appears, then, that if these two effects are superposed, we obtain a set of positions quite close to those observed except for the relative order of 2 and 6.

We now return to the question of the relative displacement of some signals in the spectrum of azulene on dilution with dioxane, which was mentioned above. Dilution shifts of this kind can usually be attributed to association effects. On the basis of the assignment made, it is clear that the proton signals of the 5- and 7-membered rings are displaced relative to each other. In order to obtain the absolute shifts of both sets of signals, it is necessary to refer all signals to a common reference. The proton signal of dioxane was used as an *external* reference for this purpose. The results are shown in Table I. Since it had been established that the separation of signals within the 5-ring spectrum and within the 7-ring spectrum change but slightly, it was only necessary to measure the position of one signal in each to determine the shifts as a function of concentration. For this purpose signal A (see Fig. 1) was chosen for the 7-ring spectrum and signal b for the 5-ring spectrum.

TABLE I

EFFECT OF DILUTION IN DIOXANE ON THE CHEMICAL SHIFTS (IN P.P.M.) OF THE 5- AND 7-MEMBERED RINGS OF AZULENE

	Concn. of azulene (mole %) 100	20	3	Dilution shift (p.p.m.)
5-Ring spectrum[a] (signal b)	−3.52	−4.23	−4.33	0.81
7-Ring spectrum[a] (signal A)	−3.67	−4.65	−4.90	1.23

[a] Chemical shifts are given in p.p.m. relative to an external dioxane reference. Negative sign denotes that the signal appears on the low field side of the reference signal. Appropriate corrections have been made for differences in bulk susceptibility. Signal b and signal A, respectively, are indicated in Fig. 1.

From Table I it may be seen that both the 5-ring and the 7-ring spectrum shift to lower field on dilution with dioxane. (The proton signal of dioxane appears on the high field side of the azulene spectrum.) Dilution to 3 mole % of azulene shifts the 7-ring spectrum by 1.23 p.p.m., whereas the corresponding shift for the 5-ring spectrum is 0.81 p.p.m. Thus as shown in Table I, in pure azulene, the separation between the A and b signals is 0.15 p.p.m., and in a 3% dioxane solution it is 0.57 p.p.m. Dilution in cyclohexane and chloroform shows similar results.

In general, all aromatic molecules show a shift of the proton signals to low field on dilution. Such shifts have been observed previously in benzene on dilution in hexane by Zimmerman and Foster,[10] and in toluene, mesitylene, chlorobenzene and benzonitrile on dilution with aliphatic solvents by Bothner-By and Glick.[11] Dilution shifts of this kind can be accounted for satisfactorily in terms of the ring-current model for aromatic hydrocarbons. Because of the mobile π-electrons, a large diamagnetic current is induced in the plane of the ring by a magnetic field perpendicular to the molecule. This ring current gives rise to a small secondary magnetic field which is such as to reinforce the primary field at points outside the ring but in its plane. In the direction at right angles to the molecular plane, on the other hand, the two fields are opposed. In a concentrated solution of aromatic molecules, the protons of a given molecule will find themselves close to the ring current of neighboring molecules, the position of closest approach being on top of or below the molecular plane. This, then, leads to a shift to high field with increasing concentration, or a shift to low field on dilution.

Polynuclear aromatic hydrocarbons may be expected to show even larger dilution shifts of the proton signals because of their larger "ring" diamagnetism. This was confirmed by a direct measurement of the dilution shift of naphthalene in dioxane which was found to be approximately

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(8) J. A. Pople, unpublished results.

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

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

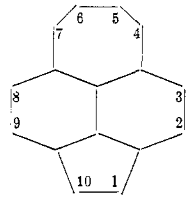
(11) A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.*, **26**, 1651 (1957).

0.9 p.p.m., to be compared with 0.6 p.p.m. for benzene.[11] The dilution shift of the 7-ring spectrum in azulene (Table I) is 1.23 p.p.m.[12]

The effect of different dilution shifts for the 5- and 7-membered rings is more difficult to interpret. A possible explanation for which there is some supporting evidence is the following: Because of the different size of the two rings, the effective secondary magnetic fields resulting from current circulations in them will be different. Since the 7-membered ring encloses a larger area, it will give rise to a larger magnetic dipole and protons in its neighborhood will have a larger shift to high field. Thus, in order to explain the required result (larger shift for protons on the 7-ring), we have to postulate a preferred mutual orientation in which the 5-ring of one molecule interacts with the 5-ring of another, or the 7-ring of one molecule with the 7-ring of another, or both. In the latter orientation the planes of the two molecules may be expected to be very roughly at right angles to each other, on the average the long molecular axes tending to be parallel. But in such orientations the electric dipole[13] directions of neighboring molecules would be parallel, which represents a rather unfavorable configuration for maximum dipole interaction. This, however, is the configuration found in the crystal structure of azulene, where the molecules are lined up with their long axes parallel as in naphthalene and with like rings closest.[15]

(b) **Acepleiadylene.**—Proton resonance spectra of acepleiadylene are shown in Fig. 4. Figure 4(I) is that for a 3.8 mole % solution in dioxane while Fig. 4(II) is that for the pure hydrocarbon measured at 175°. A dilution displacement of some of the signals relative to others is again apparent. The two spectra of Fig. 4 are placed above each other so that the first signal in each are aligned. Signal separations are indicated approximately on the p.p.m. scale and the direction is such that shifts to higher applied magnetic fields are from left to right.

The formula of acepleiadylene is



The protons may be divided into those attached to 5-, 6- and 7-membered rings, respectively. If spin-coupling between protons attached to different rings is negligible, the two 5-ring protons 1 and 10 will give rise to a single sharp signal. This is immediately identified as line e in the observed spectra. The 6-ring protons 2, 3, 8 and 9 are equivalent in pairs so they will give two superposed AB spectra. This consists of a characteristic set of four symmetrical lines, the inner pair being more intense than the outer. This group is readily identified as the two pairs c and d. The magnitude of the chemical shift between 2 and 3 (or between 9 and 8) is 0.60 ± 0.03 p.p.m. for the pure liquid and 0.4 ± 0.03 p.p.m. for the dilute solution. It is not possible to determine which protons give the signal at higher field. The spin coupling constant $J_{23} = J_{89}$ is found to be 7.5 ± 1 c./sec.

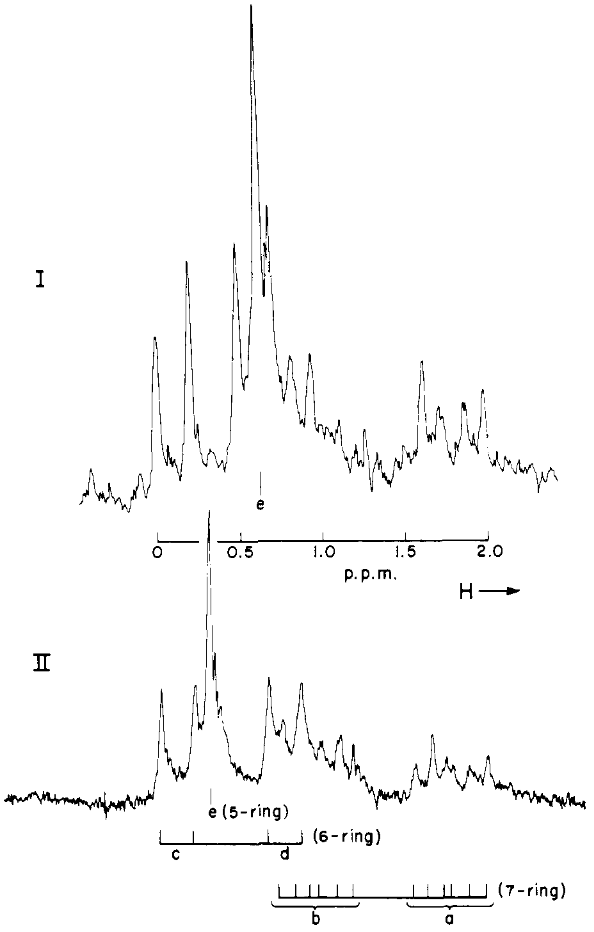


Fig. 4.—Proton resonance spectrum of acepleiadylene: 1, spectrum of a 3.8 mole % solution of acepleiadylene in dioxane; II, pure acepleiadylene (at 175°).

This now leaves only the 7-ring spectrum unaccounted for. The four protons here form two equivalent pairs, but there is now likely to be a coupling constant between the members of one pair (5,6). The spectrum will therefore be of type A_2B_2 and should be similar to that observed in naphthalene.[7] As shown in Fig. 4(II) two groups of about six lines can be distinguished, symmetrical about the mid-point. These can be assigned with some confidence to the 7-membered ring. From the details we can derive fairly good values for the chemical shift and spin coupling constant between neighboring protons.[7] The chemical shift is 0.8 ± 0.05 p.p.m. in the pure liquid and 0.85 ± 0.05 p.p.m. in dilute solution. The spin coupling constants are $J_{45} = J_{67} = 13 \pm 1$ c./sec. and $J_{56} = 13 \pm 3$

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[12] Although the ring model was found not suitable for interpreting the spectrum of azulene itself, it will still have validity for comparing dilution shifts.

[13] The electric dipole moment of azulene is about one debye, the 5-membered ring forming the negative end of the dipole.[14]

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

[15] J. M. Robertson, private communication, 1956.

c./sec. Once again it is not possible to say which of the pairs (4,7) and (5,6) give the signal at highest field.

It has not proved possible to give a detailed discussion of the interpretation of the relative chemical shifts for this molecule. In the first place, a complete assignment has not been made and, secondly, self-consistent charge densities are not available. However, the application of the ring model is again unsuccessful as it predicts too small a spread for the spectrum.

The dilution shifts for the individual signals were found to consist of a displacement to low field by about 1.7 p.p.m. for the 6- and 7-ring spectra, and 1.32 p.p.m. for the 5-ring spectrum. The general situation is therefore very similar to azulene, where the 7-membered ring shifted to low field more than the 5-ring, and a similar type of preferred molecular interaction between neighboring acepleiadylene molecules would have to be assumed. The crystal structure of acepleiadylene is not known.

One point of interest that arises from these two spectra concerns the relative values of the spin-coupling constants between neighboring protons in 5-, 6- and 7-membered aromatic rings. These differ considerably. For the 5-membered ring of azulene the coupling constant is only 3.5 c./sec. Small values are also found in other 5-membered ring molecules such as furan.[16] The values for 6-membered rings in various substituted benzenes[7,17] and naphthalene range around 6–8 c./sec. Finally all the values for 7-membered rings found in the present paper are in the region of 10–13 c./sec.

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(16) Unpublished results.

(17) H. S. Gutowsky, C. H. Holm, A. Saika and G. A. Williams, THIS JOURNAL, **79**, 4596 (1957).

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A Simple Model for Calculating Magnetic Shielding of Nuclei in Molecules

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A simple formula for the nuclear magnetic shielding constant has been proposed. It has been applied to (a) the hydrogen molecule, (b) polynuclear aromatic hydrocarbons, (c) the "induced-current" model proposed by Pople and (d) effects of distant electrons localized to non-bonded atoms. The results obtained are quite satisfactory.

The general expression for the nuclear magnetic shielding constant σ has been given by Ramsey.[1] However, his expression is rather unpractical even for the simplest molecules and, therefore, a simpler expression[2] is desirable even if it is less rigorous. In the present paper, the simplification of Ramsey's expression is studied and the results are examined by numerical examples.

1. A Simple Expression for Nuclear Magnetic Shielding.—The nuclear magnetic shielding constant σ can be expressed[1] for real wave functions, using a second-order perturbation method, as

$$\begin{aligned}\sigma = (e^2/2mc^2)\left(0\right|\sum_k (x_{\mathrm{k}}^2+y_{\mathrm{k}}^2)/r_{\mathrm{k}}^3\left|0\right) - \\ (e^2/m^2c^2)\sum_n{}' [1/(E_{\mathrm{n}}-E_0)] \times \\ \left[\left(0\right|\sum_k m_{z\mathrm{k}}\left|n\right)\left(n\right|\sum_k m_{z\mathrm{k}}/r^3_{\mathrm{k}}\left|0\right)\right] \quad (1)\end{aligned}$$

where x_k and y_k are the x and y coördinates of an kth electron, respectively, with the z-axis along an external magnetic field and the origin at the nucleus for which the shielding is desired, r_k the distance between the kth electron and the origin, and $\left(0\right|\sum_k m_{zk}\left|n\right)$ the matrix element between the molecular ground state and a molecular electronic state n of the orbital angular moment operator for the kth electron of $m_{zk} = (h/2\pi i)(x_{\mathrm{k}}\partial/\partial y_{\mathrm{k}} - y_{\mathrm{k}}\partial/\partial x_{\mathrm{k}})$.

However, eq. 1 is difficult to apply since the wave functions of excited electronic states of molecules are seldom available. If $E_{\mathrm{n}} - E_0$ is replaced by an average energy ΔE of the excited states, the expression can be reexpressed in a simpler form, involving only ground-state wave functions, as

$$\begin{aligned}\sigma = (e^2/2mc^2)\left(0\right|\sum_k (x_{\mathrm{k}}^2+y_{\mathrm{k}}^2)/r_{\mathrm{k}}^3\left|0\right) - \\ (c^2/m^2c^2\cdot\Delta E)\left(0\right|\sum_k m_{z\mathrm{k}}\cdot m_{z\mathrm{k}}/r_{\mathrm{k}}^3\left|0\right) \quad (2)\end{aligned}$$

where the ground-state wave function is assumed to be real. Even eq. 2 is very difficult to evaluate.

However, the general relations[3]

$$\begin{aligned}(n|\partial/\partial x|0) &= -m(2\pi/h)^2(E_{\mathrm{n}}-E_0)(n|x|0) \\ \text{and} \qquad\qquad\qquad\qquad &\qquad\qquad\qquad\qquad (3) \\ (n|\partial/\partial y|0)] &= -m(2\pi/h)^2(E_{\mathrm{n}}-E_0)(n|y|0)\end{aligned}$$

are found to be useful for simplifying eq. 2. Multiplying the both sides of the first of eq. 3 by

$$[(0|y^2\partial/r^3\partial x|n) - (0|xy\partial/r^3\partial y|n) - (0|x/r^3|n)]$$

and those of the second by

$$[(0|x^2\partial/r^3\partial y|n) - (0|xy\partial/r^3\partial x|n) - (0|y/r^3|n)]$$

and adding side by side, one has, upon summing over all excited states

$$(0|m_z\cdot m_z/r^3|0) = -m\sum_n{}'(E_{\mathrm{n}}-E_0)[\{(0|y^2\partial/r^3\partial x|n) -$$

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

(2) Variational calculations of proton shifts have been reported by Das and Bersohn (*ibid.*, **104**, 849 (1956)) and by McGarvey (*J. Chem. Phys.*, **27**, 68 (1957)). The variational derivation of eq. 5 or 6 (see footnote 3) shows that these equations are of better approximation compared with Das and Bersohn's. McGarvey's treatment may be of better approximation than the present one but seems to be still too complicated to apply on such problems as discussed in b, c and d of the present paper.

(3) H. Eyring, J. Walter and G. Kimball, "Quantum Chemistry" John Wiley and Sons, Inc., New York, N. Y., 1944, p. 111.