Fig. 1.—Temperature dependence of τ for various mixtures of BF_3, $(CH_3)_2O$, and $(C_2H_5)_2O$. Solid portion of lines indicates range over which data were taken. Compositions of mixtures are listed in Table I.

The activation energy for exchange of BF_3 varied from 11 kcal. in those mixtures which contained a significant excess of uncomplexed ether to 16.1 kcal. for mixtures in which the ether was completely complexed. (Mixture F, which exhibited a slightly lower ΔE, was overheated during a malfunction of the equipment and, as a result, contained several per cent of the mixed ether $C_2H_5OCH_3$.) The data thus indicated the existence of two modes of exchange. The prevailing mechanism when little free ether was present was associated with a higher activation energy and a much slower rate of exchange (large τ) than was the process which predominated when an appreciable quantity of free ether was present. In the presence of uncomplexed ether, the exchange mechanism undoubtedly involved the transfer of a BF_3 molecule from the complexed ether to the free ether; thus

$$(C_2H_5)_2O \cdot BF_3 + (CH_3)_2O \rightleftarrows (C_2H_5)_2O + (CH_3)_2O \cdot BF_3$$
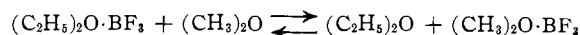
This exchange appears to proceed by the way of a displacement mechanism since the activation energy of exchange is somewhat less than the heats of formation of the BF_3–ether complexes.[3] Such an exchange should require less rearrangement of the solution, and hence be characterized by a smaller activation energy than the exchange of BF_3 between two species of complex

$$(C_2H_5)_2O \cdot {}^*BF_3 + (CH_3)_2O \cdot BF_3 \rightleftarrows$$
$$(C_2H_5)_2O \cdot BF_3 + (CH_3)_2O \cdot {}^*BF_3$$
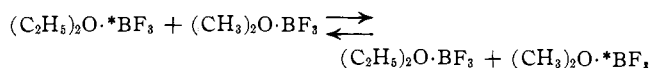
Accordingly, the completely complexed mixture displays a greater activation energy and a slower rate of exchange than the other mixtures.

It is of interest to compare the results of this study with the ^{19}F data of Diehl[4] for the system BF_3–CH_3OH–C_2H_5OH. His values of $\tau \times 10^5$ at $0°$, estimated from a graph in his paper, were 87 at BF_3/Σ alcohol = 0.8 and 1000 at BF_3/Σ alcohol = 0.4. The activation energies for the corresponding systems were reported, respectively, as 7.3 ± 1 kcal.; and "about the same within greater limits of error." The rate of exchange in the alcohol system increased rapidly with BF_3 content for mixtures of BF_3/alcohol > 0.5. The effect of changing the BF_3 content thus was opposite in direction to that observed in the present study.

This divergent behavior of the alcohol system appears to result from a hydrogen bonding effect which has no counterpart in the ether system. Thus, for BF_3/alcohol ratios less than 0.5, dialcohol complexes of BF_3 are formed in which two alcohol molecules are associated through hydrogen bonding. With increasing BF_3/alcohol ratios, progressively smaller mole fractions of the more stable BF_3–dicomplex are to be found in the system, qualitatively accounting for the increase in exchange rate.

(3) D. E. McLaughlin and M. Tamres, J. Am. Chem. Soc., 82, 5618 (1960).

(4) P. Diehl, Helv. Phys. Acta, 31, 685 (1958).

Long-Range Coupling in the Nuclear Magnetic Resonance Spectra of Acenaphthene Derivatives[1]

BY MICHAEL J. S. DEWAR AND ROBERT C. FAHEY[2]

Partial analysis of the proton n.m.r. spectrum of 1-bromoacenaphthene and complete analyses for 5,6-dichloroacenaphthene, acenaphthene, and acenaphthylene are reported. Long-range couplings ($|J_{18}| = 1.5$, $J_{17} = 0$, $|J_{16}| = 0.5$ c.p.s.) are found in acenaphthene but not in acenaphthylene. The results are compared with π-electron coupling constants calculated from equations derived by McConnell.

Introduction

In the course of other work,[3] n.m.r. analysis was used to establish the stereochemistry of the products obtained in the polar addition of deuterium bromide to acenaphthylene. The products of addition, cis-1-bromoacenaphthene-2-d_1 (I) and trans-1-bromoacenaphthene-2-d_1 (II), were identified on the basis that the coupling J_{12} would be largest for the cis isomer. Analysis of the ABX portion of the n.m.r. spectrum of 1-bromoacenaphthene (III) is reported here and is consistent with this assignment. In the course of these studies we found that the C_1 and C_2 proton lines in these and other acenaphthene derivatives were split by long-range coupling with the aromatic protons.
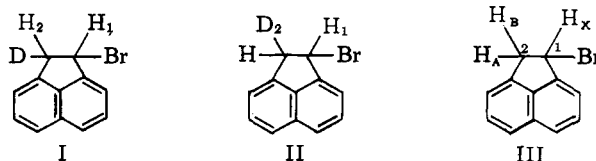
In the past few years long-range coupling has been a subject of special interest.[4] Although considerable attention has been focused on olefins, acetylenes, and five-membered heterocyclic rings, relatively little is known about the details of long-range coupling in benzene derivatives. It has been shown that the splitting of the formyl proton resonance line in 2,4-disubstituted benzaldehydes is due to a coupling with a ring proton in either the 3- or 5-position rather than the nearest 6-position.[5] Hoffman[6]

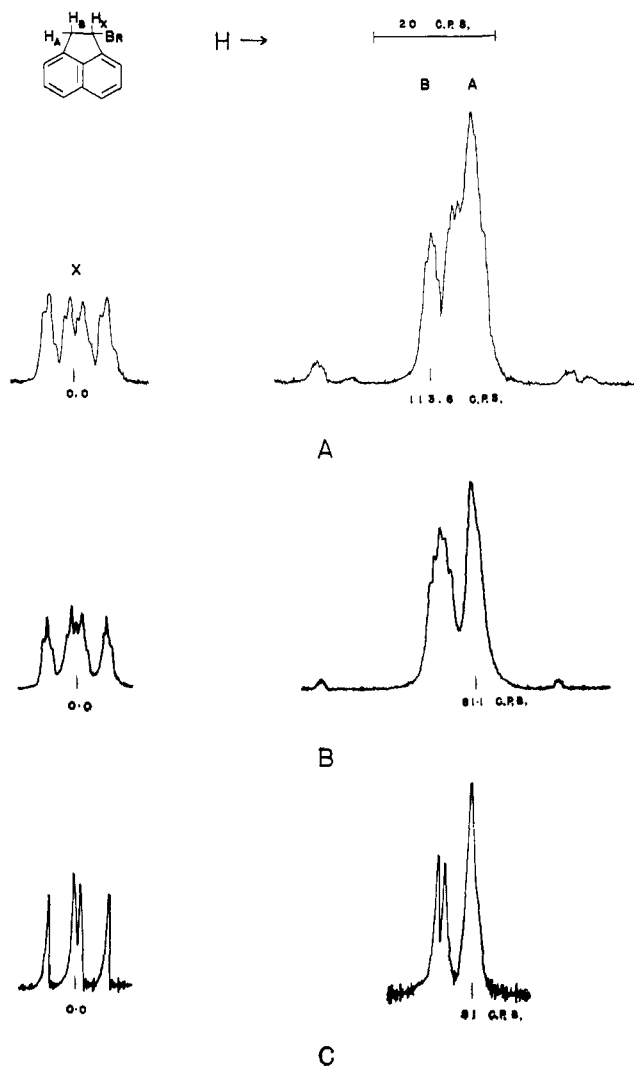(4) See E. O. Bishop, Ann. Reports, 58, 55 (1961).

Fig. 1.—N.m.r. spectrum of 1-bromoacenaphthene (aromatic proton resonance not shown): A, at 60 Mc./sec.; B, at 40 Mc./sec.; C, at 40 Mc./sec. with spin decoupling of the aromatic proton resonance.
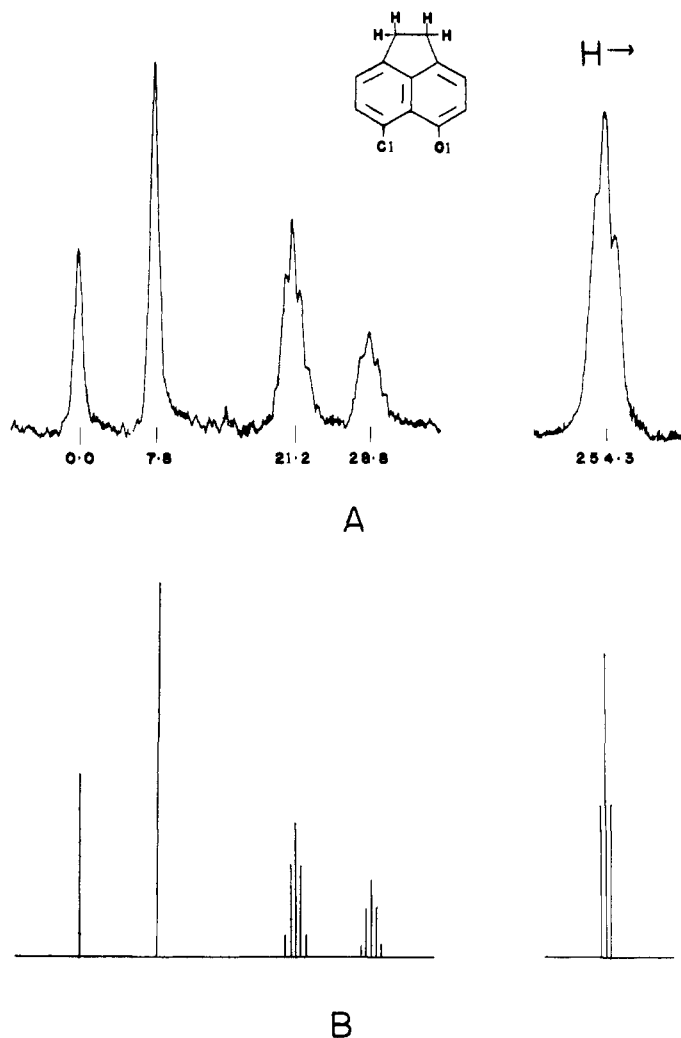

Fig. 2.—N.m.r. spectrum of 5,6-dichloroacenaphthene; the resonance line at 254.3 c.p.s. is shown at reduced gain: A, observed at 60 Mc./sec.; B, theoretical spectrum calculated from the parameters given in the text.

has observed splitting of the methyl resonance in a variety of toluene derivatives, but the ring protons responsible for the splittings were not identified. Long-range coupling between the 3- and 7-positions of indene ($|J| = 0.7$ c.p.s.) and of benzofuran ($|J| = 0.9$ c.p.s.) have been found as well as a coupling of undetermined magnitude between the 1- and 7-positions of indene.[7]

In view of these observations it was of some interest to establish the origin and magnitude of the long-range coupling observed in derivatives of acenaphthene.

Results

1-Bromoacenaphthene (III).—The n.m.r. spectrum of 1-bromoacenaphthene was measured at 60 Mc. (Fig. 1A) and at 40 Mc. (Fig. 1B). All lines appear as narrow multiplets due to long-range coupling with the aromatic protons. Four of the six lines comprising the X resonance pattern appear at low field (0.0 c.p.s.). The outer two lines were too weak to detect. The intensity pattern found is that expected if J_{AX} and J_{BX} are of the same sign.[8] The strong center lines of the AB pattern

(5) D. G. de Kowalewski and V. J. Kowalewski, *J. Chem. Phys.*, **37**, 1009 (1962).

(6) R. A. Hoffman, *Mol. Phys.*, **1**, 326 (1958).

(7) J. A. Elvidge and R. G. Foster, *J. Chem. Soc.*, 590 (1963).

(8) J. D. Roberts, "An Introduction to the Analysis of Spin–Spin Splitting in High-resolution Nuclear Magnetic Resonance Spectra," W. A. Benjamin, Inc., New York, N. Y., 1961, p. 84.

tern overlap in both the 40-Mc. and the 60-Mc. spectra. Two of the weak outer lines are detected at 40 Mc. and all four appear in the 60-Mc. spectrum.

The spectrum of III was also measured at 40 Mc. employing spin decoupling techniques[9] to remove the effects of long-range coupling (Fig. 1C). The X and AB resonances were observed using decoupling frequencies of 71 and 142 c.p.s., respectively. All lines appear considerably narrowed and the decoupled AB pattern shows that, at 40 Mc., two of the four strong AB lines occur at almost exactly the same field (81 c.p.s.). Owing to the high noise level, none of the weak lines was observed under decoupling conditions.

Analysis of the spectra at both 40 and 60 Mc. gave, within experimental error, the same values for the nuclear parameters. The results found are given below and include the value for the shift of the X resonance relative to TMS as an internal standard. The signs of J_{AX} and J_{BX} are the same (assumed positive)

$J_{AX} = 2.7$ c.p.s.	$\delta_{TMS} - \delta_X = 5.65$ p.p.m.
$J_{BX} = 6.8$	$\delta_A - \delta_X = 2.03$
$|J_{AB}| = 18.8$	$\delta_B - \delta_X = 1.89$

but the sign of J_{AB} is undetermined. The proton whose chemical shift is to highest field is assigned as the A proton (*cis* to bromine). This assignment is based on the assumption that the C–Br bond exerts an effect in III

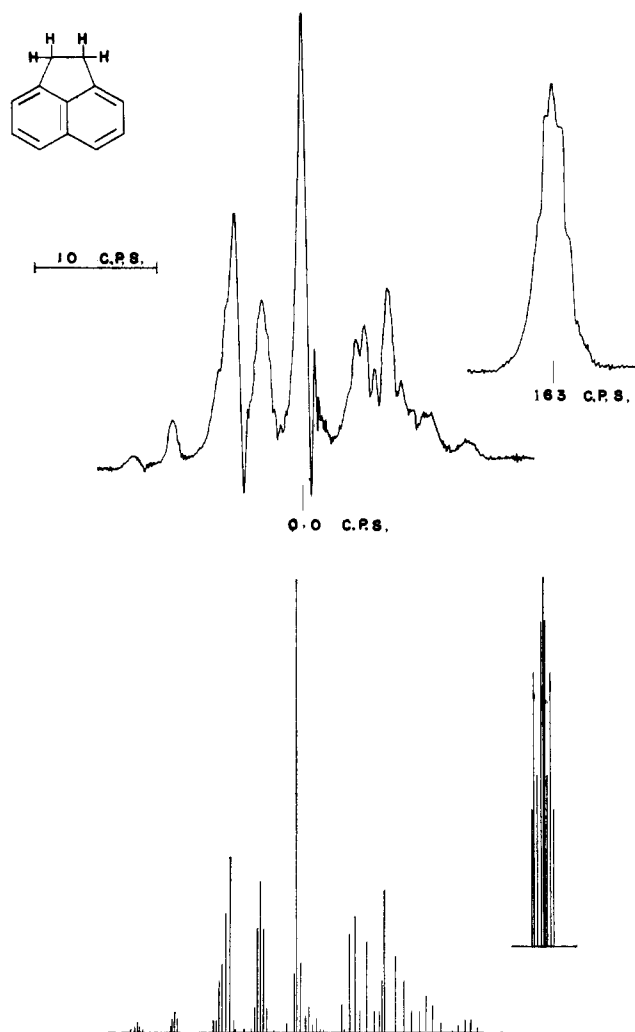(9) R. Freeman, *Mol. Phys.*, **3**, 435 (1960).

Fig. 3.—N.m.r. spectrum (40 Mc.) of acenaphthene. Resonance at 163 c.p.s. is shown at reduced gain. Theoretical spectrum was calculated including long-range coupling.

similar to its effect in vinyl bromide where it has been found that the proton *cis* to bromine is the most shielded.[10] From this assignment it follows that J_{BX} is the *cis* coupling and J_{AX} the *trans* coupling. This is in agreement with our previous designation for the deuterio compounds I and II based on chemical evidence. Further, it accords with the theoretical[11] and experimental[4] variation of vicinal coupling constants as a function of dihedral angle.

Analysis of the aromatic proton resonance pattern could, in principle, give information about the origin of the long-range couplings. However, in this case the resonance pattern is far too complex to permit interpretation and related compounds with some symmetry were chosen for further study.

5,6-Dichloroacenaphthene (IV).—A simple and direct analysis of the 60-Mc. n.m.r. spectrum of 5,6-dichloroacenaphthene (Fig. 2A) is possible. The aromatic lines (0–29 c.p.s.) constitute an AB pattern in which the high field pair appear as narrow quintuplets. The five-membered ring protons gave a narrow triplet at 254.3 c.p.s. The C_8–H resonance[12] in acenaphthene appears at higher field than the C_7–H resonance (see below). In chlorobenzene the *ortho* proton resonance is

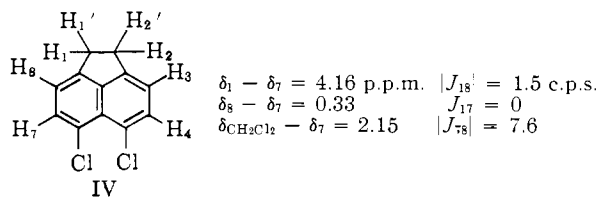(10) C. N. Banwell and N. Sheppard, *Mol. Phys.*, **3**, 351 (1960).

(11) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(12) Throughout this paper it will be understood that reference to a given proton or proton set is taken to include those other protons which are equivalent by symmetry. Thus the C_8–H resonance is also the C_3–H resonance, $\delta_8 - \delta_7 = \delta_3 - \delta_4$ and $J_{78} = J_{34}$.

only slightly shifted to lower field from the *meta* proton resonance[13] so that it is reasonable to expect that the presence of chlorine in the 5- and 6-positions of acenaphthene does not greatly alter the shifts of the C_8 and C_7 protons. Thus, the C_8 proton is assigned the higher field chemical shift and the long-range coupling must then be ascribed to the 8-position.

It might have been naïvely expected that, for long-range coupling of C_8–H with the two C_1 protons, the C_8–H lines would appear as triplets. However, owing to the strong coupling between the C_1 and C_2 protons, the C_8–H resonance lines appear as quintuplets with a 1:4:6:4:1 intensity distribution even though $J_{28} = 0$. The line separation is the average of J_{18} and J_{28} so that, with $J_{28} = 0$, it is equal to $^1/_2 J_{18}$. Similarly, the C_1 and C_2 proton lines appear as triplets with a spacing of $^1/_2 J_{18}$. This "apparent" coupling between protons for which the formal coupling constant is zero has been termed "virtual long-range coupling" and has been discussed at length by Musher and Corey.[14]

The chemical shifts and coupling constants found are given below and were used to calculate the theoretical spectrum shown in Fig. 2B (see Experimental for details). The chemical shift of the C_7 proton relative to the solvent (methylene chloride) is also shown.

$$\delta_1 - \delta_7 = 4.16 \text{ p.p.m.} \quad |J_{18}| = 1.5 \text{ c.p.s.}$$
$$\delta_8 - \delta_7 = 0.33 \quad\quad J_{17} = 0$$
$$\delta_{CH_2Cl_2} - \delta_7 = 2.15 \quad |J_{78}| = 7.6$$

Acenaphthene (V).—The n.m.r. spectrum of acenaphthene (V) measured at 40 Mc. is shown in Fig. 3. The C_1–H resonance at high field appears as a narrow multiplet and the aromatic region shows considerable fine structure. When the aromatic region was observed while decoupling the high field (C_1–H) resonance the simplified spectrum of Fig. 4 was observed. The decoupled spectrum could be analyzed as an ABC type since there is no significant coupling between the protons of different rings. An iterative computer program written by J. D. Swalen was used in this analysis. Further details are given in the Experimental section. This ABC analysis gave the chemical shifts and the values for J_{67}, J_{68}, and J_{78} shown below.

The C_7 proton is readily assigned since it is the only one with two large couplings to two other protons. The C_6 and C_8 protons are assigned the lowest and highest chemical shifts in the aromatic region since α-naphthyl positions are deshielded by the paramagnetic anisotropy of the neighboring aromatic ring to a greater extent than are β-naphthyl positions.[15] These assignments are in agreement with those of MacLean and Mackor[16] for 1,8- and 1,5-dimethylnaphthalene where the aromatic protons are expected to have chemical shifts similar to those in acenaphthene.

Comparison of Fig. 3 and 4 shows that there is no appreciable long-range coupling to the 7-position since the lines assigned to transitions of this proton are equally sharp with and without decoupling of the C_1–H resonance. There is a small coupling to the C_6 proton and a larger coupling with the C_8 proton. The theoretical spectrum of Fig. 3 accords well with the observed spectrum and was calculated using the param-

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

(14) J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1962).

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

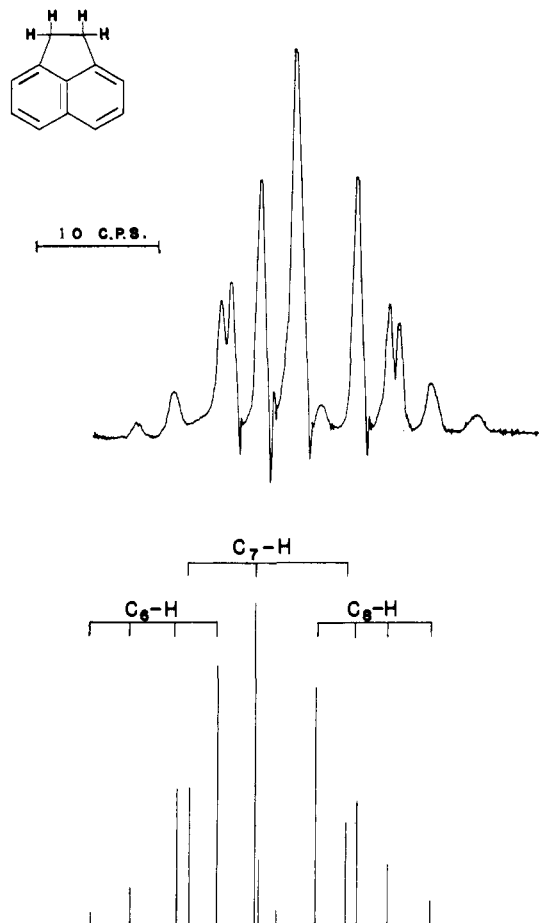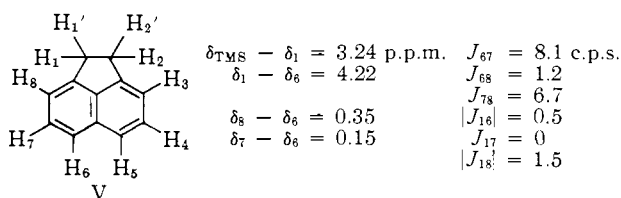(16) C. MacLean and E. L. Mackor, *Mol. Phys.*, **3**, 223 (1960).

Fig. 4.—Spin decoupled n.m.r. spectrum of acenaphthene at 40 Mc./sec. Observed spectrum is a composite of spectra obtained with a decoupling frequency of 170 c.p.s. (optimum for decoupling the low field lines) and 158 c.p.s. (optimum for the high field lines). The theoretical spectrum was calculated from the parameters given in the text.

eters given below (see Experimental for further detail).

$\delta_{TMS} - \delta_1 = 3.24$ p.p.m. $J_{67} = 8.1$ c.p.s.
$\delta_1 - \delta_6 = 4.22$ $J_{68} = 1.2$
                        $J_{78} = 6.7$
$\delta_8 - \delta_6 = 0.35$ $|J_{16}| = 0.5$
$\delta_7 - \delta_6 = 0.15$ $J_{17} = 0$
                        $|J_{18}| = 1.5$

V

Acenaphthylene (VI).—The 60-Mc. spectrum of acenaphthylene (Fig. 5A) shows a single sharp peak at 22.1 c.p.s. for the C_1–H resonance; thus there is no significant long-range coupling to the 1-position. The remaining lines of the spectrum are readily analyzed as an ABC spin system. Two line assignments (corresponding to different relative signs for the *ortho* and *meta* coupling constants) were found to be consistent with the line frequencies and gave reasonable values for the nuclear parameters. The calculated line intensities with all couplings positive (Fig. 5B) are in excellent agreement with the observed intensities, whereas the calculated intensities for the assignment with J_{35} negative (Fig. 5C) clearly differ from the observed intensities. The analysis with all J's positive is assigned as correct. Spectra were measured in carbon tetrachloride, methylene chloride, and acetone solutions at both 60 and 40 Mc. All six spectra obtained were analyzed independently. The coupling
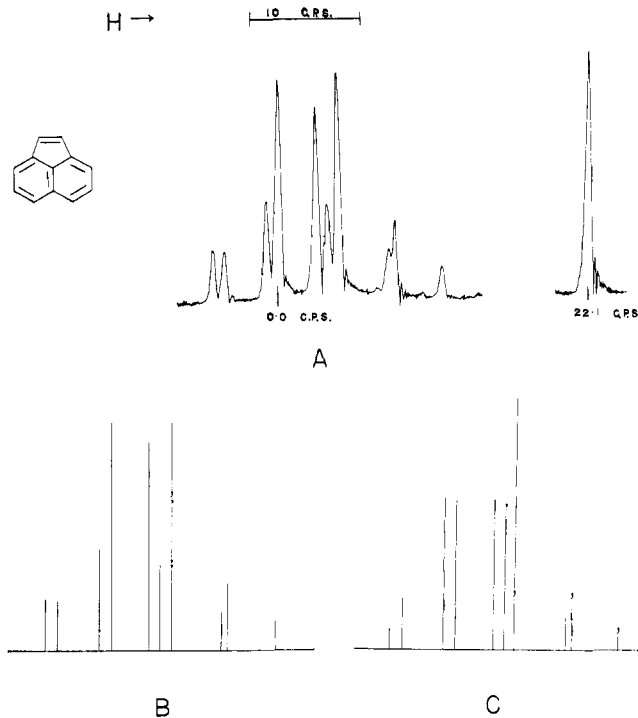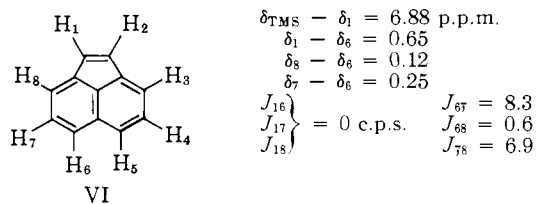

Fig. 5.—N.m.r. spectrum of acenaphthylene at 60 Mc./sec.: A, observed; B, calculated with all J's positive; C, Calculated with $J_{67} > J_{78} > 0$ and $J_{68} < 0$.

constants found were the same in all cases within experimental error. The chemical shifts showed small changes with solvent. The following results found for carbon tetrachloride as solvent are typical.

$\delta_{TMS} - \delta_1 = 6.88$ p.p.m.
$\delta_1 - \delta_6 = 0.65$
$\delta_8 - \delta_6 = 0.12$
$\delta_7 - \delta_6 = 0.25$
J_{16}
J_{17} $= 0$ c.p.s. $J_{67} = 8.3$
J_{18} $J_{68} = 0.6$
                    $J_{78} = 6.9$

VI

Discussion

The long-range coupling found here for acenaphthene is undoubtedly a π-electron transmitted coupling. McConnell[17] has treated π-electron coupling in aromatic molecules using molecular orbital theory and has derived eq. 1 for the π-contribution to the coupling between aromatic protons.

$$J_{NN'} = (\beta Q)^2 p^2_{NN'}/h\Delta E \qquad (1)$$

Here, ΔE is the average electronic excitation energy (taken as 4 e.v.[17]), $p_{NN'}$ is the bond order between carbon atoms N and N', and Q is the effective isotropic hyperfine splitting constant for the fragment H–C· (about -25 gauss). Equation 1 may be applied to calculate long-range couplings of the type present in acenaphthene if one Q term is replaced by the hyperfine constant for the fragment H–C–C·. The hyperfine splitting found for radicals with rapidly rotating methyl groups is near 25 gauss. The equal magnitude and opposite signs for these two kinds of hyperfine splittings has been demonstrated both theoretically[18] and experimentally.[19]

The 25-gauss value found in radicals with freely rotating methyl groups will not be accurate for structures with fixed geometry. The hyperfine constant varies

(17) H. M. McConnell, *J. Mol. Spectry.*, **1**, 11 (1957).
(18) A. C. McLachlan, *Mol. Phys.*, **1**, 233 (1958).
(19) A. Forman, J. N. Murrell, and L. E. Orgel, *J. Chem. Phys.*, **31**, 1129 (1960).

approximately as $\cos^2 \varphi$, where φ is the angle between the H–C–C· plane and the axis of the π-orbital.[18,20] Thus, Q is roughly given by $-50 \cos^2 \varphi$ gauss.[20] In acenaphthene, φ is estimated at $25°$ so that Q takes the value 41 gauss. As a first approximation we have assumed that the $p_{NN'}$ for acenaphthene are equal to those for the corresponding positions in naphthalene. The long-range couplings calculated using eq. 1 are compared with the observed values in Table I.

TABLE I

LONG-RANGE COUPLING IN ACENAPHTHENE

	$p_{NN'}q$	$J_{NN'}$, c.p.s.	$|J_{exptl}|$, c.p.s.
J_{16}	-0.362	-0.3	0.5
J_{17}	$.000$	0	0
J_{18}	$.725$	-1.1	1.5

The calculated values agreed remarkably well with the observed values considering the approximations involved in these calculations. Further, the theory accounts for the absence of long-range coupling in acenaphthylene; for the bond orders, p_{1N} (N = 6, 7, 8), are all less than 0.1,[21] leading to calculated π-electron couplings of appreciably less than 0.1 c.p.s.

It is somewhat disconcerting to note that more refined valence bond calculations by McConnell[22] predict a π-contribution to the *meta* proton coupling in naphthalene of the same magnitude as the *para* coupling but negative in sign. Extension to acenaphthene leads to an expected long-range coupling to the 4-position of 0.5 c.p.s. A coupling of this size was not found. It would thus appear that the less sophisticated MO calculations are in somewhat better agreement with experiment.

Experimental

Materials.—Acenaphthylene (98/100%) and acenaphthene (99/100%) were purchased from Rutgerswerke-Aktiengesellshaft, Castrop-Rauxel 2, Germany. 1-Bromoacenaphthene was prepared by addition of hydrogen bromide to acenaphthylene.[3] 5,6-Dichloroacenaphthene was synthesized by a procedure similar to that given in the literature.[23] Reagent or spectroscopic grade solvents were used.

N.m.r. Procedures.—Solutions were prepared as: 1-bromoacenaphthene, 39% w./v. in $CDCl_3$; 5,6-dichloroacenaphthene, saturated solution in CH_2Cl_2 at $25°$; acenaphthene, 20% w./v. in CCl_4; acenaphthylene, 20% w./v. in acetone, 20% w.v. in CCl_4, 50% w./v. in CH_2Cl_2. Spectra were measured at 60 Mc./sec. on a Varian DP-60 spectrometer and at 40 Mc./sec. on a Varian V-4300-B spectrometer. Calibration of the spectra was accomplished by linearly interpolating between side bands. At least six traces were measured for each sample. Spin decoupling was performed according to the procedure of Freeman.[9] The DP-40 spectrometer used for these studies was adapted for audio field modulation and phase sensitive detection as described by Anderson.[24a] All of the decoupling experiments reported here

were performed with a strong irradiating field ($\gamma H_1/2\pi = 15 \pm 2$ c.p.s.) which was calibrated according to the procedure of Anderson.[24b]

Calculations.—Calculations were carried out on an IBM 7090 computer using an iterative Fortran program written by Swalen.[25] A variety of iterative programs for analysis of n.m.r. spectra are in current use.[10,25–28] The program used here utilizes the spin energy levels obtained from an assignment of the observed transitions. A given assignment may not be unique so that several assignments must usually be tried.[11,29] With acenaphthylene only two assignments gave converged solutions to reasonable values of the coupling constants. Of these, one was eliminated by comparison of observed and calculated intensities. A variety of starting parameters was used for the iterative scheme with each line assignment and convergence to the same final set was always found.

Acenaphthene was a more difficult problem. All line assignments but one could be eliminated on the basis of intensities and unrealistic values for the coupling constants. However, the one acceptable line assignment was found to give satisfactory convergence (within experimental error for the line frequencies) to a variety of different sets of nuclear parameters depending upon the starting parameters chosen to begin the iterative process. Some of these solutions could be eliminated on the basis of line intensities. The choice was finally narrowed to a single solution by comparing the observed 60 Mc. spectrum with the theoretical 60 Mc. spectrum calculated from the parameters obtained from the 40 Mc. analysis.

In order to calculate the spectra of IV and V including long-range coupling, it was necessary to assume values for the coupling constants between the C_1 and C_2 protons. The values used were $J_{11'} = 18.8$, $J_{12} = 2.7$, and $J_{12'} = 6.8$ c.p.s., which correspond with the couplings found for III. These values may not be precisely correct for IV and V, but this is of no great importance since these coupling constants only determine the strength of the coupling (clearly strong coupling) among the C_1 and C_2 protons and even fairly large variations in these parameters do not cause detectable changes in the spectra.

The program used is limited to a maximum of eight spins. A complete treatment of acenaphthene including long-range coupling would be a ten-spin problem so that it was necessary to make approximate calculations in this case. The aromatic proton spectrum was calculated as a seven-spin problem (protons 1, 1', 2, 2', 3, 4, and 5). The C_1 and C_2 proton resonance was calculated as an eight-spin problem neglecting only the protons of positions 4 and 7 which are not involved in long-range coupling. The errors introduced by these approximations are not serious and the differences between this and a completely accurate calculation could probably not even be detected with present resolution. The calculated spectra of Fig. 2 and 3 consisted of many more lines than are actually shown. Calculated lines separated by 0.3 c.p.s. or less were summed and plotted as a single line.

Finally, the values for chemical shifts and coupling constants reported here are thought to be reliable to at least ± 0.01 p.p.m. and ± 0.2 c.p.s., respectively. The errors in the case of acenaphthylene are probably a factor of two lower.

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(21) Calculated from data given in "Dictionary of Values of Molecular Constants," edited by C. A. Coulson and R. Daudel, Vol. 111, Centre de Chemie Theorique de France, Paris.

(22) H. M. McConnell, *J. Chem. Phys.*, **30**, 126 (1959).

(23) M. M. Dashevskii and G. P. Petrenko, *Ukrain. Khim. Zh.*, **21**, 370 (1955).

(24) W. A. Anderson in "NMR and EPR Spectroscopy," Pergamon Press, New York, N. Y., 1960: (a) p. 180, (b) p. 164.

(25) J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962).

(26) A. A. Bothner-By, C. Naar-Colin, and H. Gunther, *J. Am. Chem. Soc.*, **84**, 2748 (1962).

(27) R. A. Hoffman, *J. Chem. Phys.*, **33**, 1256 (1960).

(28) V. J. Kowalewski and D. G. de Kowalewski, *ibid.*, **36**, 266 (1962).

(29) S. Castellano and J. S. Waugh, *ibid.*, **34**, 295 (1961).