Induced Paramagnetic Ring Currents

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Abstract: The quantum-mechanical theory of induced ring currents in conjugated monocyclic polyenes is shown to predict paramagnetic circulations for molecules with $4n$ π electrons as well as diamagnetic circulations for $4n+2$ systems. However, the paramagnetic currents will be partly quenched by alternation of bond lengths and molecular nonplanarity. Under these circumstances, the usual diamagnetic rules for corresponding proton nmr chemical shifts have to be reversed for $4n$ systems, those outside the ring being displaced to high field and those inside to low field. Experimental data on a number of annulenes and dehydroannulenes are examined for verification of these effects.

The concept of interatomic ring currents induced by external magnetic fields has been used to interpret a number of properties of unsaturated cyclic molecules. Originally it was introduced to account for the high diamagnetism and associated anisotropy of benzenoid aromatic hydrocarbons. A semiclassical theory by Pauling[2a] was followed by a quantum-mechanical treatment due to London[2b] which was fairly successful in correlating the experimental data. Subsequently, the ring current theory has been used to account for various nmr chemical shifts, the effect of a diamagnetic ring current being to cause considerable downfield shifts (deshielding) in the molecular plane outside the ring and even larger upfield shifts (shielding) inside.[3,4]

One important feature about ring currents that is often unappreciated is that they are not necessarily diamagnetic. Berthier, Mayot, and Pullman[5] showed that application of the London theory to some hydrocarbons, notably pentalene and heptalene, led to a *positive* contribution to the magnetic susceptibility or a paramagnetic ring current. Under these circumstances, the usual diamagnetic nmr rules have to be reversed; protons outside the ring should have increased shielding and those inside decreased shielding. In this paper, we shall discuss the theory of ring currents and chemical shifts for monocyclic conjugated polyenes and then examine available data for evidence of such currents of either sign.

Theory of Ring Currents

In his original paper, London[2b] developed a quantum-mechanical theory of ring currents for a cyclic planar molecule with all carbon atoms equivalent. Using an independent-electron model for the π electrons of the type developed by Hückel, he considered the consequences of introducing a magnetic field H perpendicular to the plane of the ring. For a hydrocarbon with alternating bond lengths, the theory is characterized by two resonance integrals β_1 and β_2. London then showed that the energies ϵ_j of occupied molecular orbitals for C_MH_M (M even) are then approximately

$$\epsilon_j = -\{\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos[(4\pi/M)(j + eHS/hc)]\}^{1/2} \quad (1.1)$$

where S is the area of the ring. If β_1 corresponds to the long C–C bonds so that $|\beta_1| < |\beta_2|$, then the values of j corresponding to occupied molecular orbitals in the neutral hydrocarbon depend on whether M is of the form $4n+2$ or $4n$. If $M = 4n+2$, as in benzene, for example, j takes values $0, \pm 1, \pm 2, \ldots, \pm n$. If $M = 4n$, however, the values are $0, \pm 1, \ldots, \pm(n-1), +n$, and the energy of the highest occupied molecular orbital is $(\beta_1 - \beta_2)$ in the absence of an applied magnetic field. In this latter case, there will be an unoccupied molecular orbital with energy $-(\beta_1 - \beta_2)$ and degeneracy will occur for zero alternation (Figure 1).

The magnetic susceptibility due to the ring current is obtained by differentiating the total energy twice with respect to H

$$\chi = 2[\partial^2/\partial H^2 \sum_j^{\text{occ}} \epsilon_j]_{H=0} \quad (1.2)$$

If the bonds are alternating in length, one of the types will be longer than in a nonalternating system such as benzene and the other will be shorter. If β_0 is the β value for benzene, we may reasonably write

$$\beta_1 = \lambda^{1/2}\beta_0; \quad \beta_2 = \lambda^{-1/2}\beta_0 \quad (\lambda \leq 1) \quad (1.3)$$

so that λ is the ratio of the β integrals and its deviation from unity is a measure of the degree of alternation. Substitution of (1.1) in (1.2) gives

$$\chi = \beta_0(\pi e S/hc)^2 f_M(\lambda) \quad (1.4)$$

where $f_M(\lambda)$ is a reduced susceptibility

$$f_M(\lambda) = (32\lambda^{1/2}/M^2)\sum_j^{\text{occ}} [1 + 2\lambda \cos(4\pi j/M) + \lambda^2]^{-3/2} \times [\lambda + (1+\lambda^2)\cos(4\pi j/M) + \lambda \cos^2(4\pi j/M)] \quad (1.5)$$

The induced current per unit magnetic field is

$$I = c\chi/S = (\pi^2 e^2 \beta_0/h^2 c) S f_M(\lambda) \quad (1.6)$$

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[1] Belfer Graduate School of Science, Yeshiva University, New York, N. Y.

[2] (a) L. Pauling, *J. Chem. Phys.*, **4**, 673 (1936); (b) F. London, *J. Phys. Radium*, **8**, 397 (1937).

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

[4] L. M. Jackman, F. Sondheimer, Y. Amiel, D. A. Ben-Efraim, Y. Gaori, R. Wolovsky, and A. A. Bothner-By, *J. Am. Chem. Soc.*, **84**, 4307 (1962).

[5] G. Berthier, M. Mayot, and B. Pullman, *J. Phys. Radium*, **12**, 717 (1951); see also L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, Inc., New York, N. Y., pp 194–210, and ref 29, p 205.

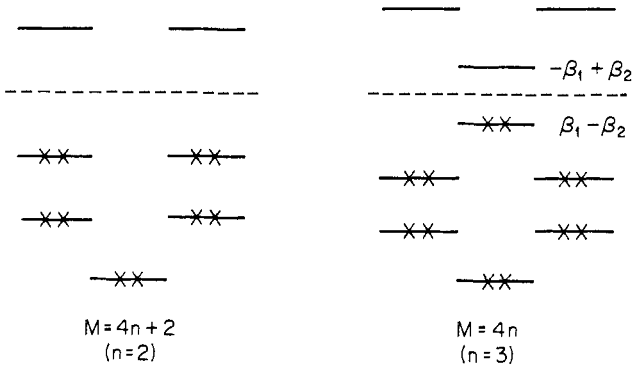

Figure 1. π-Type molecular orbitals for cyclic polyenes, C_MH_M.

and if the molecule has the form of a regular planar polygon, this becomes

$$I = (\pi^2 e^2 \beta_0 R_{CC}{}^2/4h^2c)M \cot(\pi/M) f_M(\lambda) = AM \cot(\pi/M) f_M(\lambda) \quad (1.7)$$

where R_{CC} is the CC bond length. The variable part of I is plotted in Figure 2 for certain values of M.

The following points about these results are noteworthy.

(1) For all degrees of bond alternation, the theory always predicts a *negative* contribution to the susceptibility (diamagnetic ring current) if $M = 4n + 2$ and a *positive* contribution (paramagnetic ring current) if $M = 4n$.

(2) For all sizes of rings, the magnitude of the calculated ring current is partially quenched if bond alternation occurs. The larger the ring, the more effective is the quenching due to a given amount of alternation.

(3) For rings with $M = 4n$, infinite paramagnetism (*i.e.*, a first-order change in energy with magnetic field) is predicted in the absence of alternation ($\lambda = 0$). This is because the highest occupied and lowest unoccupied molecular orbitals become degenerate if $\beta_1 = \beta_2$ (Figure 1). However, this is not likely to occur since, even in the absence of a magnetic field, the molecule will tend to alternate its bond lengths so that the degeneracy is removed and the molecular orbital with $j = +n$ will have a lower energy. Such alternation is well known for cyclooctatetraene (where the molecule is nonplanar) and is predicted by more detailed calculations for cyclobutadiene.[6]

(4) For rings with $M = 4n + 2$, diamagnetism is predicted, but there is no *a priori* reason to expect significant alternation for small rings. Longuet-Higgins and Salem[7] have given reasons for expecting alternation for sufficiently large rings, but for $(4n + 2)$-type molecules, these factors probably do not operate until about $M = 30$. In the absence of alternation, eq 1.4 predicts an increase of diamagnetic current with $M(= 4n + 2)$.

(5) If the rings are nonplanar and buckled, as they frequently will be for larger M, the magnitude of the ring currents will be further reduced because of less effective overlap of 2pπ atomic orbitals. At the same time, the area S should be replaced by a projected area on the plane perpendicular to the applied magnetic field and may also be somewhat smaller.

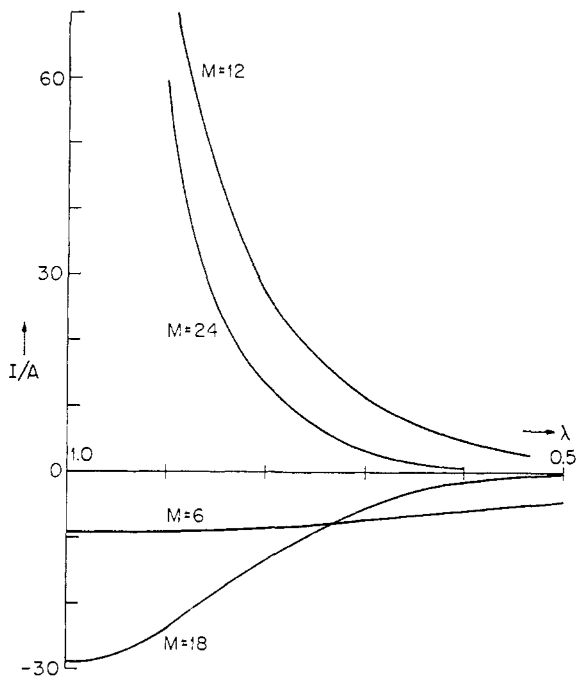

Figure 2. Ring currents per unit magnetic field *vs.* the alternation parameter λ.

(6) Theoretical chemical shifts may be obtained from the ring current per unit applied field by multiplication by a spatial factor depending on the location of the proton and the shape of the carbon skeleton. Such a model gives reasonable results for benzene.[8] For larger rings, we shall not attempt detailed calculations in view of uncertainties about the geometry and degree of alternation. However, it is always true that protons on the outside of a diamagnetic $(4n + 2$ type) ring will experience a downfield shift and those on the inside a somewhat larger upfield shift. Opposite rules apply to paramagnetic ($4n$ type) rings. For planar undistorted regular polygonal $(4n + 2)$-type molecules, the chemical shifts are predicted to increase with the size of ring, but, as noted previously, alternation and other distortions will be more effective in quenching the current for large rings so it is difficult to predict whether such changes will be observed experimentally.

In summary, therefore, the London-type theory based on eq 1.4 and 1.5 predicts a paramagnetic ring current for $4n$ cyclic systems and a diamagnetic current for $4n + 2$ systems. However, the magnitude of the paramagnetic currents are likely to be severely limited by an alternation of bond lengths which is probably an intrinsic property of the $4n$ systems. Effects of paramagnetic ring currents are most likely to be detected in nmr chemical shift data, which we shall now consider.

Evidence for Paramagnetic Ring Currents

A review of the literature on the syntheses and properties of annulenes, mainly due to the Sondheimer group,[9] indicates that there is already evidence that $4n$ π-electron conjugated monocyclic hydrocarbons exhibit a ring current effect and that it is opposite in

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[6] M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 3255 (1965).

[7] H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* (London), **A251**, 172 (1959); **A257**, 445 (1960).

[8] C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

[9] F. Sondheimer, *Pure Appl. Chem.*, **7**, 363 (1963), and subsequent papers.

Table I. Nmr Chemical Shifts of Some Annulenes and Dehydroannulenes (τ Scale)

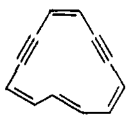
	Annulenes		Dehydroannulenes							
			Mono		Bis		Tri		Tetra	
Ring size	In	Out	In	Out	In	Out	In	Out	In	Out
6		2.73								
8[a]		4.31								
10										
12[a]					−0.9 (av ?)	4.97 5.47 5.82		5.55		
14	4.4 (av)[b] 10.0[c]	2.4[c]	10.7	1.2– 2.7	15.5	0.45 1.57				
16[a]	3.27 (av ?)				2.25 (av ?)	4.35 4.93				
18	4.55 (av)[d] 13.0[c]	0.72[c]					8.26	1.8– 3.1		
20[a]										
22									1.8 (av ?)	3.6– 5.0
24[a]	3.16 (av ?)									

[a] 4*n* π-electron systems. [b] Room temperature. [c] −60°. [d] 110°.

kind from that displayed by $4n + 2$ systems. The nmr chemical shifts of the $4n + 2$ cyclic polyenes are well explained on the basis of a diamagnetic ring current.[3,4] Those hydrogens in the molecular plane, outside the ring, experience a decreased shielding (a downfield shift by *ca.* 2–4 ppm) and those inside the ring, an increased shielding (an upfield shift by *ca.* 6–11 ppm). These dramatic changes in chemical shift cannot be readily explained on any other basis of which we are aware. We now suggest that the ring current theory holds for 4*n* systems as well.

Table I summarizes most of the nmr chemical shift data available for conjugated monocyclic polyunsaturated systems. The annulene nomenclature is used: monodehydro systems contain one triple bond; bisdehydro, two, etc. Correlations can be seen for the 4*n* and the $4n + 2$ systems from the chemical shifts of the inner and outer hydrogens which are consistent with the expectations of the ring current theory discussed above.

Three of the entries in Table I, bisdehydro[12]- (I), bisdehydro[16]- (II), and tetradehydro[24]annulenes (III), we believe provide the best evidence for a paramagnetic ring current at present. Another 4*n* π-electron system, which has recently been synthesized[10] and has precipitated our generalization of the paramagnetic ring current hypothesis for 4*n* systems, is cyclododecatrienetriyne (IV).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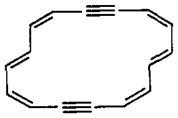
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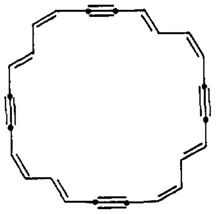
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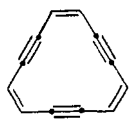
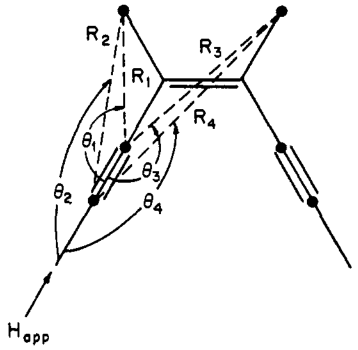

IV

The nmr spectrum of IV (in CCl_4) exhibits an absorption due to the six equivalent hydrogens at τ 5.55. This chemical shift is *ca.* 1.2 ppm to high field relative to that of most olefinic hydrogens. An effect that could cause such a shielding that we examined first is the local anisotropy of the triple bonds. The magnitude of this effect can be calculated by assuming that the upfield shift of an olefinic hydrogen in IV is produced by magnetic dipoles located at the positions of the carbon atoms of two flanking triple bonds (the third triple bond is too distant to have an effect) and by the generalized equation

$$\Delta\sigma = \Delta\chi\left[\frac{1}{3R_1^{\,3}}(1 - 3\cos^2\theta_1) + \frac{1}{3R_2^{\,3}}(1 - 3\cos^2\theta_2) + \ldots \frac{1}{3R_n^{\,3}}(1 - 3\cos^2\theta_n)\right] \qquad (2)$$

where R_1, R_2, . . ., R_n are the distances from the hydrogen in question and the carbons of the triple bonds.[11,12] (See the representation below denoted as A.)



A

Two such calculations (using 1.54, 1.34, and 1.21 A for the bond distances) were made: in one a value of -11.8×10^{-6} cm^3/mole was chosen for the magnetic anisotropy, $\Delta\chi$, of the triple bond as being the most reasonable one from among those that range from −1.6 to -19.4×10^{-6} cm^3/mole cited in the literature;[13] in the other the largest reasonable value, -19.4×10^{-6} cm^3/mole[14] for $\Delta\chi$ was used. The first value gives a predicted upfield shift of 0.75 ppm, the latter value, an

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[10] K. G. Untch and D. C. Wysocki, *J. Am. Chem. Soc.*, **88**, 2608 (1966).

[11] J. A. Pople, *Discussions Faraday Soc.*, **34**, 7 (1962).

[12] A. A. Bothner-By and J. A. Pople, *Ann. Rev. Phys. Chem.*, **16**, 43 (1965).

[13] S. Castellano and J. Lorenc, *J. Phys. Chem.*, **69**, 3552 (1965).

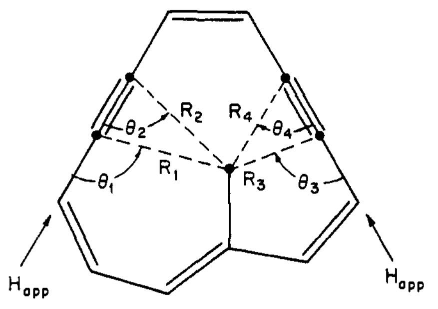
[14] J. A. Pople, *J. Chem. Phys.*, **37**, 53 (1962).

upfield shift of 1.24 ppm. Taking the chemical shift of the olefinic hydrogens in cyclohexene as a standard, τ 4.4, then the calculated chemical shifts of the hydrogens of IV, using the above two values for $\Delta\chi$, are τ 5.15 and 5.64, respectively. Though these predicted chemical shifts for the hydrogens of IV are in good agreement with that observed, we believe that the observed value of τ 5.55 is best explained by a paramagnetic ring current, since the corresponding hydrogens in vinylacetylene[15] and 1,10-deca-*cis*,*cis*-2,8-diene-4,6-diyne-diol[16] show chemical shifts at τ 4.3. These two models should show the local anisotropy effect as well, but it appears to be small or cancelled by some other effect.

The trienetriyne IV is not the most suitable system for an investigation of a paramagnetic ring current effect because it lacks intraannular hydrogens. The magnitude of the ring current effect is much less on the outer hydrogens than the inner ones for the $4n + 2$ systems, and the magnitude of this effect for the $4n$ systems should be of the same order. What is needed for examination is a $4n$ π-electron monocyclic system containing intraannular hydrogens. Three such molecules that are considered here have been prepared and were listed above, I, II, and III. The nmr chemical shifts assigned to the inner hydrogens are : I, τ -0.9; II, τ 2.25; and III, τ 1.80. These values are quite low for olefinic hydrogens and they provide evidence for a paramagnetic ring current in $4n$ systems.

A close examination of I is revealing. From the nmr spectrum[9] it is seen that the two *trans* hydrogens are magnetically equivalent and therefore averaging. The molecule must be rapidly interconverting between equivalent conformers *via* rotation of the *trans* double bond. Two possible conformations are likely, one with the *trans* double bond perpendicular to the molecular plane, the other, in the plane. The latter conformer is a planar molecule and can benefit from any delocalization energy that a 12 π-electron system may possess. Despite the higher strain energy evident from Dreiding molecular models for the planar conformer, we predict this planar arrangement is preferred and that at room temperature the nmr spectrum is an averaged one, with the *trans* hydrogens spending half the time inside the ring and the other half outside. According to this interpretation, the observed value of τ -0.9 is an average of two chemical shifts, one at *ca.* τ 5.5 (using IV as a model) and the other at *ca.* τ -6.4. Variable temperature nmr studies on I should easily test our prediction.

The ring current explanation for the observed chemical shifts of the inner hydrogens of the three annulenes, I, II, and III, is strengthened by testing the alternative hypothesis that the downfield shift is due to the local diamagnetic anisotropy of the triple bonds. Carrying out appropriate calculations using eq 2 with the "frozen" molecule in a conformation with the maximum anisotropy effect and using the largest value for $\Delta\chi$ (-19.4×10^{-6} cm^3/mole), we may obtain upper limits for the local anisotropy contribution to the chemical shifts. For compound I, the angle and distance parameters were measured from a *planar* Dreiding molecule model (R_1 = 2.16 A, R_2 = 2.28 A, R_3 = 2.36 A, R_4 = 2.16 A, θ_1 = 80°, θ_2 = 110°, θ_3 = 116°, θ_4 = 86°; see diagram B). This calculation leads to a downfield shift of 1.48 ppm. For compounds II and III, the necessary parameters were measured similarly from Dreiding molecular models with carbon atoms 1 through 7 and 1 through 8, respectively, fixed in a plane: (II) R_1 = 1.60 A, R_2 = 1.64 A, θ_1 = 109°, θ_2 = 66° (see structure C); (III) R_1 = 1.60 A, R_2 = 1.64 A, R_3 = 2.29 A, R_4 = 3.43 A, θ_1 = 109°, θ_2 = 66°, θ_3 = 155° 38′ (calcd), θ_4 = 164° 03′ (calcd) (see structure D). These calculations give downfield shifts of 1.51 and 0.57 ppm for II and III, respectively. The predicted chemical shifts, based on local anisotropies of the triple bonds, for these four dehydroannulenes are listed in Table II.



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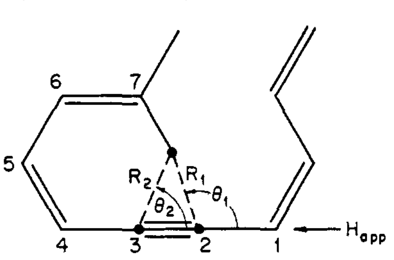
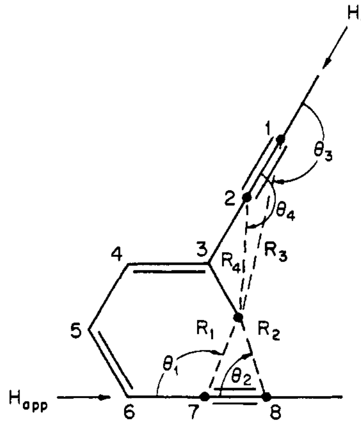


C



D

It is seen that the magnitude of the calculated shift for the inner hydrogen of I is not nearly enough to account even for the observed averaged value, τ -0.9, let alone that expected for the noninterconverting molecule. In the nmr spectrum of II the intensity of the low-field multiplet accounts for all the four *trans* double-bond hydrogens. It is highly probable that this molecule is also interconverting between equivalent conformers *via* rotation of the *trans* double bonds. Under

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(15) R. C. Hirst and D. M. Grant, *J. Am. Chem. Soc.*, **84**, 2009 (1962).
(16) L. D. Colebrook, private communication.

Table II. Predicted Chemical Shifts, τ, Based on Local Anisotropy Effects[a]

	$\Delta\tau$, ppm	τ_{calcd}	τ_{obsd}
Bisdehydro[12]annulene (I)	-1.48	2.92	-0.9
Bisdehydro[16]annulene (II)	-1.51	2.89	2.25
Tetradehydro[24]annulene (III)	-0.57	3.83	1.80
Cyclododecatrienetriyne (IV)	$+1.24$	5.64	5.55

[a] Using -19.4×10^{-6} cm^3/mole for $\Delta\chi$.

this circumstance, the value calculated for the downfield shift, $\Delta\tau$, would be halved and the lack of agreement between the predicted chemical shift and that observed (Table II) would be more pronounced. It is not clear why tetradehydro[24]annulene (III) apparently does not interconvert between equivalent conformers, if indeed the molecule has the structure assigned to it. Dreiding molecular models of II and III indicate that rotation of the *trans* bonds ought to occur with approximately equal facility. However, the nmr spectrum of III shows an absorption at low field, τ 1.80, with an intensity that accounts for only *ca.* half of the *trans* double bond hydrogens.

The four compounds that have been discussed thus far have all contained triple bonds. We attach no significance to this circumstance. It is simply that of the data available at this time in the literature, these cases seem to exhibit shifts which lie outside the normal range of values for olefinic hydrogens and cannot be readily explained on grounds other than a paramagnetic ring current. Two other annulenes, 16 and 24 (see Table I), we suggest display nmr spectra that may be the results of averaging processes (probably *via* bond rotations and bond isomerizations) which cause the hydrogens to become magnetically equivalent. If so, it could turn out that nmr spectra taken at relatively low temperatures would show distinct absorptions due to inner and outer ring hydrogens similar to the [14]- and [18]annulenes, but with the chemical shifts of the corresponding hydrogens shifted in opposite directions.[17]

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(17) NOTE ADDED IN PROOF. For a recent report concerning bond isomerization and variable temperature nmr spectra of [16]annulene, see G. Schröder and J. F. M. Oth, *Tetrahedron Letters*, 34, 4083 (1966).

Infrared Spectra of Methane-, Fluoro-, and Chlorosulfonic Acids

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Contribution from the Department of Chemistry and The Materials Research Center, Northwestern University, Evanston, Illinois 60201. *Received April 27, 1966*

Abstract: The infrared spectra in the region 4000–400 cm^{-1} of methane-, fluoro-, and chlorosulfonic acids were obtained. A gas-diffusion barrier cell prevented reaction with the cell windows. Superheating of the vapors permitted spectra of the monomers to be clearly identified. Shifts in bands due to breaking up of hydrogen bonding prove to be a powerful means of making or confirming band assignments. The systematic variations in band frequencies due either to the liquid–monomer transition or to the variation of X (F, OH, Cl, CH$_3$) in X–SO$_2$–OH are discussed.

The infrared spectra of fluoro- and chlorosulfonic acids in the solid and liquid states, and also in the gaseous state, at temperatures up to 60° were obtained and examined by Savoie and Giguère.[1] Gerding and Maarsen[2] have reported the infrared spectrum of liquid methanesulfonic acid, but they believed that the spectrum was impure because of the attack by the acid on the rock salt plates. In addition, several workers made Raman studies on the liquid acids.[3–7]

Savoie and Giguère[1] observed that good portions of fluoro- and chlorosulfonic acids remain dimerized in the vapor state even near 60°. In our studies with sulfuric and deuteriosulfuric acids,[8] which gave sufficient vapors only above 170° for making measurements, there was no evidence of association in the vapor.

The reported frequency shifts of some of the bands of the fluoro- and chlorosulfonic acids[1] for the transition from liquid to the monomeric vapor state are not comparable to the shifts observed for sulfuric acid.[8] Some shifts, particularly for the –SO$_2$ stretches of fluoro- and chlorosulfonic acids not only are smaller, but even are of the opposite sign. In this paper we will try to find an explanation for this discrepancy. The results so obtained will be compared with those presently obtained for methanesulfonic acid.

Experimental Section

The apparatus for taking the spectra in the region 400–4000 cm^{-1} is described elsewhere.[8] The cell described there, which will be called cell A in this paper, is suitable only for the study of nearly saturated vapors over liquids or solids. For the purpose of superheating the vapor, the liquid or solid sample was heated in a side arm attached to the center of the cell, and the vapor evolved was superheated in the cell itself. Gas windows also were provided. In cell B the gas windows were just outside the furnace, and in cell C they were near the ends, close to the AgCl windows. During the runs, argon at 1 atm flowed through the gas windows. The power of the superheating technique to aid in assigning bands will be shown particularly by the discussion of the S–F and S–O(H) stretches of fluorosulfonic acid.

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(1) R. Savoie and P. A. Giguère, *Can. J. Chem.*, **42**, 277 (1964).
(2) H. Gerding and J. W. Maarsen, *Rec. Trav. Chim.*, **77**, 374 (1958).
(3) A. Simon and H. Kriegsmann, *Chem. Ber.*, **89**, 2384 (1956).
(4) I. Sandemann, *J. Chem. Soc.*, 1135 (1953).
(5) R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, 40, 644 (1962).
(6) R. Vogel-Högler, *Acta Phys. Austriaca*, **1**, 323 (1948).
(7) A. Simon, H. Kriegsmann, and H. Dutz, *Chem. Ber.*, **89**, 2378 (1956).
(8) S. M. Chackalackal and F. E. Stafford, *J. Am. Chem. Soc.*, **88**, 723 (1966).