Synthesis and Study of Pseudo-Aromatic Compounds. III. The Correlation of Nuclear Magnetic Resonance Solvent Shifts with π-Electronic Delocalization Energies in Aromatic Compounds

DOMENICK J. BERTELLI AND CARLO GOLINO

The Department of Chemistry, University of California at Santa Barbara, Santa Barbara, California

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The shift of the proton absorptions of solvents in n.m.r. spectra due to aromatic solutes are shown to give correlations with accepted criteria for π-electron delocalization and π-electron delocalization energies for benzenoid aromatic compounds.

Displacements of proton absorption positions in n.m.r spectra due to solvent–solute interactions are well known. These shifts may be accounted for by bulk susceptibility differences between the solvent and solute, but are more commonly due to a combination of bulk susceptibility effects and specific solvent–solute interaction (*i.e.*, hydrogen bonding, etc.).[1] An additional magnetic effect due to the induction of localized fields in the π-electrons of aromatic molecules, by the applied field, is also well known.[2] This effect is based upon the fact that the induced ring current[3] in the π-electrons of aromatic molecules will generate a field which will reinforce the applied field in certain regions and oppose the applied field in other regions. Since statistically there is more volume above and below the plane of the solute molecule than around the periphery which a solvent molecule can occupy, the net effect is that the solvent receives an over-all magnetic shielding by the solute and a stronger applied field is necessary for resonance to occur in the solvent.

Elvidge and Jackman[4] have suggested that an aromatic compound can be defined as a compound which will sustain an induced ring current. These authors have further assumed that the magnitude of the ring current should be directly proportional to the aromaticity of a molecule and thus be a means of assessment of aromaticity. Since the above-mentioned solvent shielding effect should be limited to molecules which sustain a ring current, this shielding effect might also serve as a criterion for the presence of π-electron delocalization. It is the purpose of this work to establish the extent to which a correlation between solvent shifts, due to aromatic solutes, and π-electron delocalization energies exists and the general applicability of such a relationship.

An expression has been derived relating the proton resonance position of a given molecule to the bulk susceptibility of the medium in which the molecule is situated.[5] This expression has been used to derive a second formula useful for the determination of magnetic susceptibilities using two concentric solutions.[6] The formula has the form

$$\chi = \frac{3\Delta f}{2\pi f m} + \chi_0 \qquad (1)$$

where χ is the magnetic susceptibility being determined, χ_0 is the magnetic susceptibility of a reference compound, Δf is the difference in the resonance position of the reference molecule in the isolated state and under the effect of the added compound, f is the frequency of the n.m.r. spectrometer, and m is the weight of the compound being studied in 1 ml. of solution. The above formula (1) was derived for isotropic molecules. Since aromatic or polyolefinic molecules are anisotropic, formula 1 cannot have a quantitative relationship toward them. However, it appears that by taking a simple empirical approach, a formula similar to eq. 1 might be useful. Since it has been demonstrated that aromatic solutes cause an over-all shift in the resonance position of solvents in excess of simple magnetic susceptibility effects,[2] there should be a relation between the solvent shifts and ring current magnitudes. Therefore, a formula (eq. 2) that expresses the solvent shift

$$\frac{\Delta f}{fm} = Q \qquad (2)$$

where Q is some function dependent on the anisotropy and magnetic susceptibility, might be qualitatively useful. Although eq. 2 is due to a combination of effects for organic molecules, it should be possible to dissect out specific variables by holding the other factors constant. Thus, by considering a series of molecules which are essentially compositionally identical as far as their atomic contribution to their magnetic susceptibility, one should be able to separate out contributions from other specific magnetic effects.

The fact that cyclooctatetraene is a nonplanar molecule which exhibits no aromatic behavior is firmly established.[7,8] Therefore the magnitude of (2) derived from solvent–shift data for cyclooctatetraene will not contain any contribution from π-electron delocalization and thus possess no contribution from ring current. By comparison, benzene should contribute the same per-atom susceptibility effect as cyclooctatetraene, but additionally a ring current effect, due to the presence of π-electron delocalization, will also contribute to the magnitude of (2). Thus, it should be possible, by subtraction of the magnitude of (2) for cyclooctatetraene from the same quantity calculated for benzene, to determine the contribution from π-electron delocalization to the magnitude of (2) for benzene. This assumption

$$\text{shielding constant} = \left(\frac{\Delta f \text{ molecule}}{fm} - \frac{\Delta f \text{ cyclooctatetraene}}{fm}\right) 10^6$$

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(1) A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960).

(2) A. A. Bothner-By and R. E. Glick, *ibid.*, **26**, 1651 (1957), and references cited therein.

(3) J. A. Pople, *ibid.*, **24**, 1111 (1956); J. A. Pople, W. G. Schneider, and H. J. Bernstein, *Proc. Roy. Soc.* (London), **A236**, 515 (1956); J. A. Pople, *Mol. Phys.*, **1**, 175 (1958); R. McWeeny, *ibid.*, **1**, 311 (1958).

(4) J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 859 (1961).

(5) W. C. Dickinson, *Phys. Rev.*, **81**, 717 (1951).

(6) D. P. Evans, *J. Chem. Soc.*, 2003 (1959)

(7) W. B. Pearson, G. C. Pimental, and K. S. Pitzer, *J. Am. Chem. Soc.*, **74**, 3437 (1952).

(8) R. C. Pink and A. R. Ubbelohde, *Trans. Faraday Soc.*, **44**, 708 (1948).

should be generally applicable to any conjugated polyene.

It has been shown that, for solutions of aromatic solutes in chloroform and acetonitrile, the ring current shift due to the aromatic solutes is much greater in magnitude than for nonpolar solvents.[9,10] These larger solvent shifts have been attributed to specific interactions between the aromatic solute and the solvent molecules which hold the solvent in a position above and below the plane of the aromatic molecule. For this reason it would be expected that Q must also be a function of the intermolecular attraction of the solute and solvent molecules.

Clearly any relationship between magnitudes derived from (2) and aromaticity must be empirical, and based on a consistency of Q over a range of structural variations. However, by minimizing these structural variations it appeared that useful data might be obtained from this treatment and indicated a preliminary investigation would be worthwhile.

Since the ring current, diamagnetic susceptibility exaltation, and diamagnetic anisotropy are all functions of the delocalization of the π-electrons, a means of measuring ring current magnitudes must also measure a quantity directly proportional to the diamagnetic susceptibility exaltation and diamagnetic anisotropy. Diamagnetic anisotropies have been measured for several nonbenzenoid aromatic hydrocarbons.[11] This data has been used to infer the extent of π-electron delocalization in the molecules studied. Also the authors have assumed a relationship between the diamagnetic anisotropy and resonance energies of nonbenzenoid aromatic hydrocarbons, although there appears to be no simple theoretical relationship between these two physical properties.[11] For this reason it appeared worthwhile to compare the shielding constants derived from solvent effects with empirical resonance energies.

A means of determining magnetic properties of π-electron delocalized systems by a simple process not requiring specialized instrumentation, which might be compared with theoretical calculations, appears highly useful. The fact that magnetic data involves only one state and does not involve a reaction, and thus the comparison of the relative stability of two states, is a distinct advantage in many cases. This latter point has been the basis for using diamagnetic susceptibility exaltations as a criterion for aromaticity and has been emphasized previously.[11,12] The present method should essentially measure a quantity directly proportional to the diamagnetic susceptibility exaltation, but suffers from the disadvantage that a single molecule, cyclooctatetraene, is used as a reference. Whether this latter point introduces a more severe limitation than the use of Pascal sums to estimate the diamagnetic susceptibility reference cannot be ascertained at this point.

To test the validity of these assumptions, a series of aromatic compounds have been studied to determine the adherence of the observed shielding constants derived from n.m.r. solvent shifts to established criterion for π-electron delocalization (Figure 1).[13] Also a comparison is made with the diamagnetic susceptibility exaltation perpendicular to the molecular plane, the molecular diamagnetic anisotropy,[14,15] and molar susceptibility exaltations[8,11,16] obtained from classical methods (Figures 2 and 3).

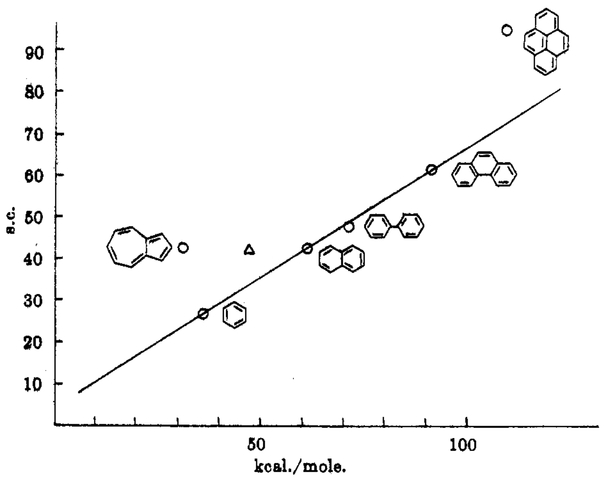

Figure 1.—Empirical resonance energy; Δ, azulene corrected for strain energy.

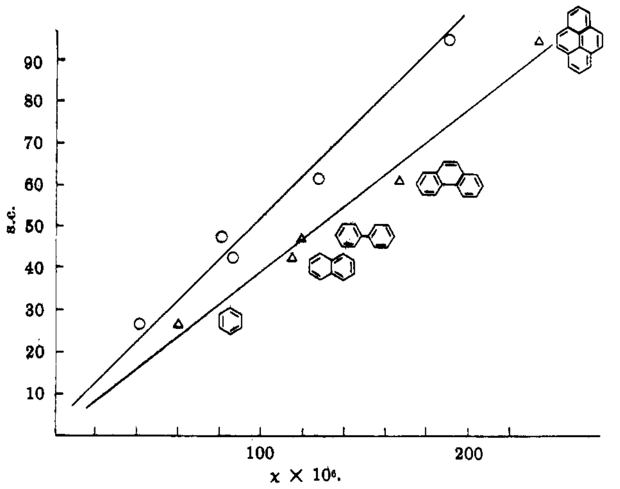

Figure 2.—○, diamagnetic susceptibility exaltation perpendicular to the molecular plane; Δ, molecular diamagnetic anisotropy.

Experimental

All n.m.r. measurements were on a Varian A-60 60-Mc. instrument. Most of the compounds used were commercial chemicals which were recrystallized to literature melting points where necessary. The benzene used was reagent grade and not purified further. The cyclooctatetraene and cyclohexadiene were commercial samples and purified by vapor phase chromatography before use. The n.m.r. spectra of these compounds indicated that there were no detectable aromatic compounds present. The cycloheptatriene used was an experimental sample given to us by the Shell Development Company and was also purified by

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(9) A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, **34**, 1064 (1961).

(10) W. G. Schneider, *J. Phys. Chem.*, **66**, 2653 (1962).

(11) E. D. Bergmann, J. Hoarau, A. Pacault, A. Pullman, and B. Pullman, *J. Chim. Phys.*, **49**, 474 (1952).

(12) D. P. Craig, "Non-Benzenoid Aromatic Compounds," D. Ginsberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, pp. 24–29.

(13) (a) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 98; (b) A. Streitwieser, Jr., "Molecular Orbital Calculations for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 244, and references cited therein.

(14) J. Hoarau, N. Lumbroso, and A. Pecault, *Compt. rend.*, **242**, 1702 (1956).

(15) K. Lonsdale, *Proc. Roy. Soc.* (London), **A159**, 149 (1937); K. Lonsdale and K. S. Krishnan, *ibid.*, **A156**, 597 (1936).

(16) H. Akamatsu and Y. Matsunaga, *Bull. Chem. Soc. Japan*, **26**, 364 (1953).

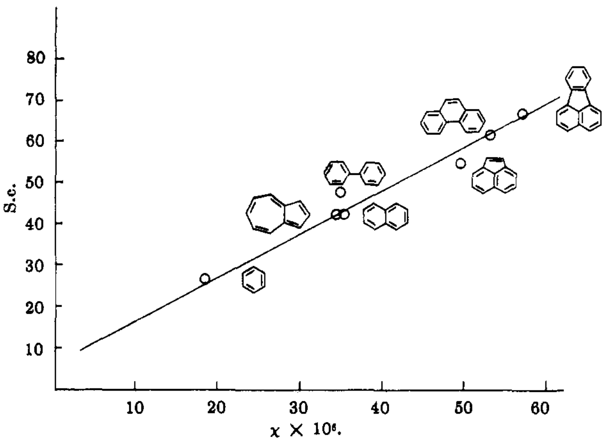

Figure 3.--Molar diamagnetic susceptibility exaltation.

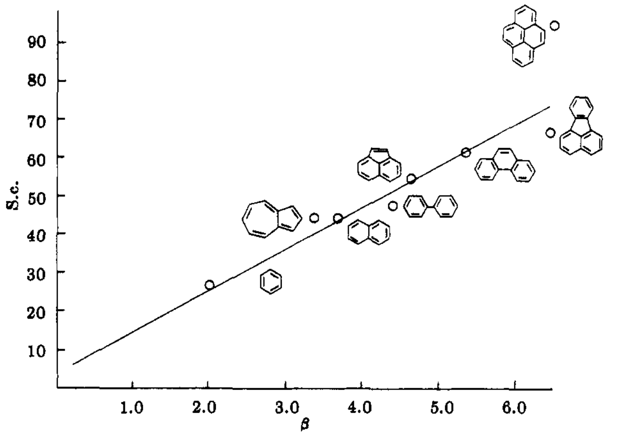

Figure 4.—Hückel MO delocalization energies.

vapor phase chromatography. The n.m.r. spectrum of this purified sample showed no detectable toluene. The dicycloheptatrienyl[17] and heptafulvalene[18] were prepared by published procedures. The techniques used employed concentric n.m.r. cells similar to those described in the literature,[19] and thus the differences in the resonance frequency of the samples in each tube were determined simultaneously.

The solvents used were dimethyl sulfoxide and cyclohexane. The dimethyl sulfoxide was purified by two distillations at 1 mm., the second one directly onto Linde type 4A Molecular Sieves. The cyclohexane was used without further purification. The data derived from the dimethyl sulfoxide solutions proved to be more reliable because of the substantially larger frequency shifts observed for the same concentrations.

The n.m.r. cell was made up of a standard thin-wall, 5-mm.-o.d. n.m.r. cell purchased from Varian Associates into which was inserted a second tube made from a piece of 3-mm.-o.d. glass tubing, sealed at one end. The pure solvent was placed in the outer tube and the solution, in the inner tube. The solutions were made up to 5–6% solute. It was found necessary to clean and dry both tubes before each determination, and runs were made on three to five separate solutions for each compound. The frequency shifts between the inner and outer tubes varied from *ca.* 1.5 to 3.5 c.p.s. depending upon the solvent used and are reproducable to ±0.1 c.p.s.

Because the resolution of the n.m.r. was highly critical to the instrument settings, it was found most convenient to prepare a standard consisting of a sealed inner tube containing benzene–dimethyl sulfoxide which was contained in a second sealed tube containing dimethyl sulfoxide. The instrument was then adjusted to give a specific Δf value for this standard before any sample was determined. For this reason the present data cannot be reproduced independently, but the slope of the lines (Figures 1–4) are reproducable. Therefore, in order for this method to be used independently, it is necessary only to determine the shielding constant for any compound in Table I and adjust new data by the appropriate determined ratio. It was also found necessary to allow the samples to remain in the instrument probe for *ca.* 30 min. before taking data to allow for temperature equilibration. All samples were run at 38–40°.

Results and Discussion

The data derived from cyclohexane (Table I) is of little value because the small difference between the data from eq. 2 for cyclooctatetraene and the individual aromatic compounds caused too large an experimental error in the molar shielding constant. This data does indicate that for the molecules studied eq. 2 gives a reasonable correlation for both polar and nonpolar solvents. The greater scatter in the data of Table I for cyclohexane is due to the larger experimental error introduced by the smaller differences in frequency between pure solvent and the solutions for this system.

TABLE I

	Dimethyl sulfoxide solvent			Cyclohexane solvent,
Compd.	$\frac{\Delta f}{mf}$	s.c.[a]/g.	*M* s.c.	$\frac{\Delta f}{mf}$
Benzene	0.94	0.34	26.5	0.65
Biphenyl	0.93	0.33	47.8	0.57
Naphthalene	0.93	0.33	42.2	0.61
Azulene	0.93	0.33	42.2	
Acenaphthalene	0.96	0.36	54.6	
Phenathrene	0.95	0.35	61.6	0.62
Pyrene	1.07	0.47	94.9	
Fluoranthene	0.93	0.33	66.6	
Cyclooctatetraene	0.60			0.46

[a] s.c. = shielding constant.

The higher values in Table I derived from dimethyl sulfoxide solutions indicate that this solvent interacts in a similar manner to acetonitrile with aromatic solutes.[9,10] From Table I it is evident that most aromatic molecules give essentially the same shielding constant (s.c.) per gram, and from Figure 1 that the molar shielding constant gives a correlation with empirical resonance energies, from the limited data available.[20] From Figure 4 it can be seen that a correlation exists between the molar shielding constant and the delocalization energies derived from Hückels MO calculations.[21] Finally, from Figures 2 and 3 it can be seen that the shielding constant also gives a correlation with experimental diamagnetic susceptibility data.[11,14,15] Therefore, the present method appears useful as a simple method for gaining useful information concerning the π-electronic interactions of conjugated polyenes, and that the assumptions made in the introduction are not too severe approximations.

The fact that the lines in the figures tend not to pass through the origin indicates that the shielding constants are too high. Thus cyclooctatetraene does not correct for all of the contribution to the shielding constant in excess of the ring current. This is most likely a reflection of the ability of aromatic π-electron systems to

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[17] W. Von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **76**, 3203 (1954).

[18] J. R. Mayer, Ph.D. Dissertation, Yale University, 1955.

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

[20] R. B. Turner, "Theoretical Organic Chemistry (The Kekule Symposium)," Butterworths Scientific Publications, London, 1959, p. 67; see also ref. 13.

[21] B. Pullman and A. Pullman, "Les Theories Electroniques de la Chimique Organique," Masson and Cie., Paris, 1952, p. 226; A. Pullman, B. Pullman, E. D. Bergmann, G. Berthier, E. Fischer, Y. Hirshberg, and J. Pontis, *J. Chim. Phys.*, **48**, 359 (1951).

coordinate better than the π-electrons of polyolefins with the solvent.

The fact that pyrene deviates considerably from the line given by the other benzenoid aromatics studied (Figure 1) appears worth further consideration.[22] It has been suggested that it might be valid to consider the bridging bonds of polycyclic polyenes as perturbations of basic monocyclic systems.[23,24] That is that certain polycyclic polyenes, for example pyrene, might show some characteristics attributable to the monocyclic system containing the same number of π-electrons as are in the periphery of the polycyclic system. For this reason, it might be expected that pyrene should show some properties associated with a monocyclic system possessing 14 π-electrons. Since the magnetic susceptibility of an aromatic molecule will be directly related to the square of the radius of the ring system, magnetic susceptibility measurements have been used to detect this type of contribution. Lonsdale has calculated the effective radii of the orbitals of benzene, naphthalene, and pyrene.[15] The effective radii increases *ca.* 9% from benzene to naphthalene, indicating a small contribution from monocyclic character in naphthalene, while the increase from benzene to pyrene is *ca.* 23%.

The present method is apparently incapable of detecting the small effect present in naphthalene while sufficiently sensitive to detect the larger contribution in pyrene. Assuming that this interpretation is correct, the fact that the shielding constant of pyrene is only 40% larger than the remaining benzenoid molecules listed in Table I would indicate that the ground state of pyrene exhibits a relatively small contribution from a monocyclic peripheral model as anticipated.[25]

It is interesting to note that fluoranthene, which is isomeric with pyrene, shows a normal per-gram shielding constant and thus appears to possess no character associated with a 14-membered monocyclic ring system. The fact that fluoranthene falls off the line in Figure 4 indicates that its delocalization energy would be more closely approximated by the sum of the individual delocalization energies of benzene and naphthalene. These latter data indicate that there may be little π-electronic interaction in the ground state between the benzene and naphthalene systems in fluoranthene.[11,21]

Azulene is an additional example of a molecule which might exhibit observable characteristics of its monocyclic homolog. Experimentally it has been shown that the molar diamagnetic susceptibility and anisotropy of azulene[26,14] is approximately equal to that of naphthalene, which leads to the conclusion that azulene should possess the same π-electronic delocalization energy as naphthalene. This latter conclusion is in marked disagreement with the resonance energy of azulene derived from heat of hydrogenation data.[20] However, again the high magnetic susceptibility exaltation may be due to the r^2 term in the magnetic susceptibility and be attributable to azulene possessing more extensive characteristics of a monocyclic 10 π-electron system than naphthalene. Therefore, the large shielding constant found for azulene would have been predictable from the known magnetic susceptibility data, and may be attributable again to the ground state assuming some character of the related monocyclic analog.

This method was also applied to heptafulvalene,[18] dicycloheptatrienyl,[17] and cycloheptatriene using dimethyl sulfoxide solvent (Table II). From the data it is quite evident that these molecules exhibit solvent shielding abilities of approximately the same magnitude as cyclooctatetraene. From our initial discussion it would seem impossible for any conjugated polyene to exhibit a magnitude derived from eq. 2 lower than that of cyclooctatetraene. However, an additional factor not dealt with in our original discussion will account for this fact. Since cyclooctatetraene, cycloheptatriene, and 1,3-cyclohexadiene have molar diamagnetic susceptibilities approximately equal to that of dimethyl sulfoxide,[27] they should not cause a shift toward higher field for the solvent hydrogen atoms if bulk susceptibility were the only important factor. Although each hydrocarbon molecule will contribute the same per-atom susceptibility, the molecular area will also be important because the method depends on the statistical number of solvent molecules that the solute can shield regardless of π-electron delocalization. Thus, although both cycloheptatriene[27] and cyclooctatetraene have approximately the same diamagnetic susceptibility per molecule, the larger area of cyclooctatetraene will enable it, statistically, to shield more solvent molecules. Therefore the ratio of solvent area to solute area should be important. The data for cyclohexane shows that, for example, benzene will shift the resonance position of cyclohexane approximately 70% as much as dimethyl sulfoxide. Although this difference will be due to some sort of solvent–solute interaction,[28] as demonstrated for the benzene–acetonitrile systems,[9,10] it will depend to some extent on the relative area of benzene *vs.* cyclohexane and benzene *vs.* dimethyl sulfoxide. If the effect were due entirely to solvent–solute interaction, it would be hard to explain the successive increase in shielding efficiency in the series cyclohexadiene, cycloheptatriene, and cyclooctatetraene. Since all three of these molecules are essentially olefinic, they should all show approximately the same ability to coordinate with the solvent. The sensing mechanism for measuring the

Table II

Compd.	$\frac{\Delta f}{mf}$
Cycloheptatriene	0.51
Dicycloheptatrienyl	0.42
Heptafulvalene	0.40
Cyclooctatetraene	0.60
1,3-Cyclohexadiene	0.48
Cyclohexane	0.20

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[22] Since pyrene fits well into the correlations of Figure 2, it is apparent that this effect is also observed for classical magnetic measurements and is not characteristic of the present method.

[23] J. R. Platt, *J. Chem. Phys.*, **22**, 1448 (1954).

[24] M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3345 (1952); M. J. S. Dewar and R. Pettit, *J. Chem. Soc.*, 1617 (1954); D. Peters, *ibid.*, 1023 (1958).

[25] See ref. 13b, p. 288.

[26] W. Klemm, *Ber.*, **90**, 1051 (1957). The values range from equal to that of naphthalene to azulene having *ca.* a 10% greater diamagnetic susceptibility, but the difference is not important in the present discussion.

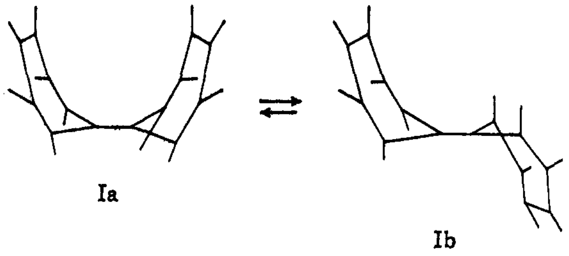
[27] Assuming the diamagnetic susceptibility calculated from Pascal tables is reasonably correct.

[28] This can be verified by the fact that although cyclohexane has a higher diamagnetic susceptibility than either cyclohexadiene, cycloheptatriene, or cyclooctatetraene these latter solutes cause a greater solvent shift, which must be due to a specific solvation effect ordering the solvent in a more favorable position for greater shielding due to the anisotropic effect of the double bonds; see ref. 9 and 10.

effect under study is the protons of the solvent which will be partially shielded by the solute molecule from the applied magnetic field of the spectrometer. For this reason it becomes important, statistically, what per cent of the solvent molecules can be shielded by a given solute molecule. Thus cyclooctatetraene could exhibit a somewhat higher value derived from eq. 2 than cycloheptatriene. Although this same factor will be involved with the aromatic molecules studied, apparently the ratio of the increase in area to the number of molecules per gram is sufficiently constant to cause only the small scatter observed from the data derived from (2) in Table I. This factor probably also accounts for the fused-ring systems giving a line of slightly lower slope than benzene and biphenyl, Figures 2 and 3. Finally this assumption indicates that the shielding constants should be low because cyclooctatetraene is larger than a six-membered ring. However, this negative deviation is over compensated for by the greater ability of aromatic solutes to coordinate with solvent molecules.

Since dicycloheptatrienyl can have several conformations, some of which will have cage-like structure, effectively the area of dicycloheptatrienyl will not be two times that of cycloheptatriene, and a still smaller value derived from (2) for dicycloheptatrienyl can be accounted for. Finally, the fact that heptafulvalene has approximately the same shielding ability as dicycloheptatrienyl indicates that heptafulvalene exhibits no π-electronic delocalization in excess of dicycloheptatrienyl and that, furthermore, the molecular areas are approximately the same. This data indicates that heptafulvalene is nonplanar and polyolefinic in nature. The conclusion is in good agreement with heat of hydrogenation data which indicates that approximately 4–6 kcal. of resonance energy is gained by removal of 1 mole of hydrogen in converting dicycloheptatrienyl to heptafulvalene.[29] This latter discrepancy may well be attributable to the effect of the difference in energy between sp^2 and sp^3 hybridized bonds.[30]

In an attempt to more fully resolve the structure of heptafulvalene, n.m.r. in dimethyl ether was determined at 60 Mc. from 40 to -130°, assuming that the similarity in chemical shift of the protons of heptafulvalene[31] might be due, in part, to a rapid inversion Ia–Ib. However, the spectrum showed little change over the temperature range studied. Thus, the equilibrium Ia–Ib, while almost certainly occurring, is evidently not responsible for the similarity of the chemical shift of the protons in heptafulvalene. In view of this fact it appears consistent that the 2,2′ and 7,7′ protons would shift downfield by conversion of the 1 and 1′ carbon atoms of dicycloheptatrienyl from sp^3 to sp^2 hybridization in going from dicycloheptatrienyl to heptafulvalene. This same process would account for the upfield shift of the 4,4′ and 5,5′ protons by an anisotropic effect due to the transanular double bonds.[32]



The present data indicates that good relationships exist between the shielding constant obtained by n.m.r. solvent shifts and various criteria of π-electron delocalization for benzenoid aromatic compounds. Also the fact that the polyolefins of Table II deviate markedly from the aromatic molecules in their ability to shift the resonance position of the solvent allows a reasonably clear means of distinction between conjugated polyolefins and aromatic hydrocarbons by this method. Work is presently in progress to determine if equally good correlations exist for nonbenzenoid conjugated polycyclic polyenes.

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[29] R. B. Turner, W. R. Meador, W. Von E. Doering, and D. W. Wiley, *J. Am. Chem. Soc.*, **79**, 4127 (1957).

[30] M. J. S. Dewar and H. W. Schmeising, *Tetrahedron*, **5**, 166 (1959).

[31] D. J. Bertelli, C. Golino, and D. L. Dreyer, *J. Am. Chem. Soc.*, **86**, 3329 (1964).

[32] For pertinent n.m.r. data, see ref. 31.