benzene and 72% chlorobenzene from 1-chloro-2-iodobenzene.

Relative reactivities of several oligohalobenzenes were estimated from competition experiments at room temperature on the assumption of a second-order rate law; such mild conditions were necessary in order that some of each reactant be unconsumed at the end of the experiment. Reactivities relative to unity for 1-bromo-2,6-dichlorobenzene were as follows (the halogen removed is in *italics*): *4-bromo*-3,5-dichlorotoluene, 0.2; *1-bromo*-2,6-dichlorobenzene, (1.0); *1-iodo*-2,4-dibromobenzene, 1.4; 1,*2*,3-tribromobenzene, 4.6; *1-bromo*-2,4,6-trichlorobenzene, 33; *1*,4-dibromo-2,6-dichlorobenzene, 34; 1,*2*,3,5-tetrabromobenzene, 80; and *1-iodo*-2,4,6-trichlorobenzene, 900. All these compounds were so much more reactive than 1,2,4-tribromobenzene that no estimate of the relative reactivity of the latter could be made from competition experiments.

Dehalogenation is also effected by t-BuO$^-$K$^+$ in 50:50 mixtures of t-BuOH with certain other dipolar, "aprotic" solvents, but there is a wide variation in reactivity depending on the cosolvent employed. In a series of experiments, 1 equiv of 1-bromo-2,6-dichlorobenzene was exposed to ~0.75 equiv of t-BuO$^-$K$^+$ in constant total solvent volume for 22 hr at room temperature. Bromide ion yields, based on aryl bromide, with the several cosolvents were: DMSO, 74%; N-methylpyrrolidone, 22%; N,N-dimethylacetamide, 10%; sulfolane, 4%; dimethylformamide, 0.1%; and hexamethylphosphoramide, 0.08%. Dehalogenation fails to occur in t-BuOH alone (without cosolvent). With diphenyl sulfoxide cosolvent, 1,2,4-tribromobenzene was unaffected by excess t-BuO$^-$K$^+$ in 6.8 hr at 100°.

Because of concurrent studies on deiodination reactions involving aryl radical intermediates,[2,3] we sought to detect radicals in the dehalogenation of 1-bromo- and 1-iodo-2,6-dichlorobenzenes and 1,2,4-tribromobenzene in benzene-rich systems, such as t-BuO$^-$K$^+$ in 25% t-BuOH–25% DMSO–50% benzene. Dehalogenation occurred as usual, but no biphenyl derivatives were formed. On the other hand, the diazonium fluoroborate from 2,6-dichloroaniline gave, under the same conditions, a substantial amount of 2,6-dichlorobiphenyl.

Although these results discouraged consideration of a radical mechanism, the possibility that the aryl halides somehow accepted an electron, expelled a halide ion, and thereby formed an aryl radical, as in the radical-induced deiodination of aryl iodides in alkaline methanol,[3] was nevertheless examined. In 2 *M* methanolic sodium methoxide with 1-phenyl-2-benzenesulfonhydrazide, 1-chloro-2-bromo-4-iodobenzene lost only iodine, forming *o*-bromochlorobenzene, but with t-BuO$^-$K$^+$ in 50% t-BuOH–50% DMSO the same halide afforded mainly bromide ion (55%) and *p*-chloroiodobenzene (37%), though 39% iodide ion and 22% *o*-bromochlorobenzene were also formed. Thus the reactivity pattern observed in the t-BuOH–DMSO system is not that characteristic of the electron-transfer mode of dehalogenation.

The following mechanism is compatible with these observations.

$$t\text{-BuO}^- + \text{CH}_3\text{SOCH}_3 \rightleftharpoons t\text{-BuOH} + \text{CH}_3\text{SOCH}_2\text{:}^- \qquad (1)$$

$$\text{CH}_3\text{SOCH}_2\text{:}^- + \text{ArX} \longrightarrow \text{Ar:}^- + \text{CH}_3\text{SOCH}_2\text{X} \qquad (2)$$

$$\text{Ar:}^- + t\text{-BuOH} \longrightarrow \text{ArH} + t\text{-BuO}^- \qquad (3)$$

$$\text{base} + \text{CH}_3\text{SOCH}_2\text{X} \longrightarrow \text{X}^- + \text{?} \qquad (4)$$

Step 1 is amply precedented.[4] Step 2 is a nucleophilic displacement *on halogen*, forming an aryl anion and a halomethyl methyl sulfoxide. Nucleophilic displacements on halogen are implicated in the base-catalyzed isomerization and disproportionation of oligohalobenzenes[5] and in the scrambling of 1,2,4-triiodobenzene.[6] Step 3 is straightforward. Little is known about the chemistry of halomethyl sulfoxides, but step 4 seems likely to occur. Both SN2 and α-elimination reactions are conceivable, but no organic products from the proposed step 4 have been detected.

The proposed mechanism accounts for the beneficial effect of *o*-halogen substituents (they stabilize phenyl anions[7]), the dehalogenation susceptibility order I > Br > Cl, the absence of radical intermediates, and the dependence of reactivity on cosolvent identity. The reactive cosolvents are "semiprotic" in the sense that they can yield protons to strong bases to form carbanions which may react analogously to the dimsyl anion in step 2, but truly aprotic solvents such as diphenyl sulfoxide, dimethylformamide, and hexamethylphosphoramide are ineffective (We have some evidence that the very slow reactions in the latter two solvents are of a different character.)

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(2) J. F. Bunnett and C. C. Wamser, *J. Am. Chem. Soc.*, **88**, 5534 (1966).

(3) J. F. Bunnett and C. C. Wamser, *ibid.*, **89** 6712 (1967).

(4) G. A. Russell and S. A. Stevens, *J. Org. Chem.*, **31**, 248 (1966); J. I. Brauman and N. J. Nelson, *J. Am. Chem. Soc.*, **88**, 2332 (1966).

(5) C. E. Moyer, Jr., and J. F. Bunnett, *ibid.*, **85**, 1891 (1963).

(6) J. F. Bunnett and D. J. McLennan, unpublished work.

(7) G. E. Hall, R. Piccolini, and J. D. Roberts, *ibid.*, **77**, 4540 (1955); J. F. Bunnett, *J. Chem. Educ.*, **38**, 278 (1961).

Diamagnetic Susceptibility Exaltation as a Criterion of Aromaticity

Sir:

We wish to report the development of an experimental criterion of aromatic character based on the diamagnetic susceptibility exaltation of a compound, a criterion which responds uniquely to the presence of appreciable *cyclic* π-electron delocalization in molecules.

The molar susceptibility, χ_M, of a compound in a fluid system is the average of three orthogonal components: $\chi_M = \frac{1}{3}(\chi_x + \chi_y + \chi_z)$.[1,2] For benzenoid aromatics it is known[1] that $\chi_x \approx \chi_y < \chi_z$ (if z is taken normal to the molecular plane); benzenoid aromatics thus exhibit enhanced diamagnetic anisotropy, *i.e.*, $\Delta\chi \gg 0$, where $\Delta\chi = \chi_z - \frac{1}{2}(\chi_x + \chi_y)$. The great magnitude of the anisotropy has been attributed[3,4] to

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(1) P. W. Selwood, "Magnetochemistry," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1956, pp 110–122.

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

the presence of appreciable cyclic delocalization of π electrons ("ring currents") in these molecules,[5] and observation of this anisotropy has been used commonly[6] as a test for aromatic character.

The direct measurement of anisotropy is difficult at best and can be accomplished only with crystalline substances. This has prompted several attempts to construct a workable system for estimating anisotropies from the more easily accessible χ_M data,[7,8] but none has proved wholly successful. In fact, it is unnecessary to determine the anisotropy in order to discover if the electronic characteristics causing it are present, for cyclic delocalization manifests itself not only by the presence of a large perpendicular anisotropy but also by an increase in the average susceptibility over that expected for a nondelocalized structure.[4,9] The magnitude of this *exaltation* in χ_M may be used as a criterion of aromatic character.

The exaltation,[8a] Λ, of a compound is the difference between the susceptibility exhibited by a compound and that predicted for the identical but not cyclically delocalized structural counterpart: $\Lambda = \chi_M - \chi_M'$. We postulate that all compounds which possess cyclically delocalizable electrons will exhibit $\Lambda \gg 0$, while virtually all other compounds will exhibit $\Lambda \sim 0$. To test this postulate the exaltations of an extensive series of cyclic alkenes, cyclic polyenes, and aromatic compounds have been calculated using the best system for estimating average susceptibilities currently available, that of Haberditzl[10] (suitably extended where necessary[11]).

It is seen from inspection of Table I that the postulate is verified, at least for neutral carbocyclic systems; *all* the aromatic compounds exhibit large, positive values of Λ ($> \sim 12$), while *no* nonaromatic compounds except cyclopentadienes and cycloheptatrienes exhibit exaltations larger than the combined uncertainties in χ_M and χ_M'.[12]

Table I. Exaltations of Cyclic Hydrocarbons[a]

Compound	χ_M	χ_M'	Λ
Monocyclic Hydrocarbons			
Cyclopentane	59.2^{b}	56.8	2.4
Cyclopentene	49.5^{k}	47.0	2.5
Cyclopentadiene	$44.5^{b,k}$	38.0	6.5
5,5-Dimethylcyclopentadiene	67.5^{k}	62.7	4.8
Cyclohexane	68.1^{b}	68.1	0.0
Cyclohexene	57.5^{b}	58.3	−0.8
1,3-Cyclohexadiene	48.6^{b}	49.3	−0.7
1,4-Cyclohexadiene	48.7^{b}	48.5	0.2
Benzene	54.8^{b}	41.1	13.7
Cycloheptane	78.9^{k}	79.5	−0.6
Cycloheptene	69.3^{k}	69.7	−0.4
1,3-Cycloheptadiene	61.0^{k}	60.7	0.3
1,4-Cycloheptadiene	61.0^{k}	59.9	1.1
1,3,5-Cycloheptatriene	59.8^{k}	51.7	8.1
3,7,7-Trimethyl-1,3,5-cycloheptatriene	95.6^{k}	88.5	7.1
Toluene	66.1^{b}	53.3	12.8
Cyclooctane	91.4^{b}	90.8	0.6
Cyclooctene	80.5^{k}	81.0	−0.5
1,3-Cyclooctadiene	72.8^{k}	72.0	0.8
1,5-Cyclooctadiene	71.5^{k}	71.2	0.3
1,3,5-Cyclooctatriene	65.1^{k}	64.0	1.1
Cyclooctatetraene	$53.9^{i,k}$	54.8	−0.9
Styrene	68.2^{b}	55.6	12.6
Multicyclic Alternant and Nonalternant Aromatic Compounds			
Biphenyl	103.3^{c}	78.2	25.1
Fluorene	110.5^{c}	84.8	25.7
Indene	$80.5^{b,k}$	61.4	19.1
Triphenylmethane	165.6^{b}	125.2	40.4
Naphthalene	91.9^{b}	61.4	30.5
Azulene	91.0^{f}	61.4	29.6
Anthracene	130.3^{h}	81.7	48.6
Phenanthrene	127.9^{b}	81.7	46.2
Tetracene	168.0^{h}	102.0	66.0
Pyrene	154.9^{e}	97.6	57.3
Acepleiadylene	155.0^{k}	97.6	57.4
Perylene	171.0^{d}	121.0	50.0
Coronene	243.3^{h}	140.4	102.9
Pseudo-Aromatic Compounds			
Pentafulvene	43.0^{j}	41.9	1.1
Heptafulvalene	94 ± 3^{k}	92.0	2 ± 3
Cyclooctatetraene	$53.9^{i,k}$	54.8	−0.9
Heptalene	72 ± 7^{k}	78.2	-6 ± 7
9,9-Dimethyldibenzopentafulvene	105.1^{g}	88.8	16.3
9,10-Dimethyldibenzopentalene	132.4^{g}	117.7	14.7
[16]Annulene	105 ± 2^{k}	109.6	-4.6 ± 2

[a] All values of χ_M, χ_M', and Λ are given in units of -10^{-6} cm^3/mole. The values of χ_M' are not corrected for "ring-current diamagnetism."[10] [b] G. W. Smith, "A Compilation of Diamagnetic Susceptibilities," General Motors Corp. Research Report, GMR-317, Detroit, Mich., 1960. [c] G. W. Smith, "Supplement to GMR-317," General Motors Corp. Research Report, GMR-396, Detroit, Mich., 1963. [d] H. Shiba and G. Hazato, *Bull. Chem. Soc. Japan*, **22**, 92 (1949). [e] K. Krishnan and S. Bannerjee, *Phil. Trans. Roy. Soc. London, Ser. A*, **234**, 265 (1935). [f] W. Klemm, *Chem. Ber.*, **90**, 1051 (1957). [g] E. D. Bergmann, J. Hoarau, A. Pacault, B. Pullman, and A. Pullman, *J. Chim. Phys.*, **49**, 472 (1952). [h] H. Akamutu and Y. Matsunaga, *Bull. Chem. Soc. Japan*, **26**, 364 (1953); **29**, 800 (1956). [i] S. Shida and S. Fujii, *ibid.*, **24**, 173 (1951). [j] J. Thiec and J. Wiemann, *Bull. Soc. Chim. France*, 177 (1956). [k] This work. Volume magnetic susceptibility determinations were made on neat liquids or in CH_2Br_2, CCl_4, or benzene solutions by the methods of D. C. Douglass and A. Fratiello, *J. Chem. Phys.*, **37**, 3161 (1963), and K. Frei and H. J. Bernstein, *ibid.*, **37**, 1891 (1962). Densities were determined using Lipkin bi-capillary pycnometers (Ace Glass Co.). All compounds and solvents were purified and degassed before use.

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(3) L. Pauling, *J. Chem. Phys.*, **4**. 673 (1936); F. London, *J. Phys. Radium*, **8**, 397 (1937).

(4) D. P. Craig, "Aromaticity," D. Ginsburg, Ed., "Non-Benzenoid Aromatic Compounds," Interscience Publishers, Inc., New York, N. Y., 1959, pp 1–42.

(5) Whether this anisotropy results solely from ring current (see R. J. Abraham and W. W. Thomas, *J. Chem. Soc., Phys. Org. Sect.*, 127 (1966)), partially from ring current and partially from circulation of localized electrons (J. A. Pople, *J. Chem. Phys.*, **41**. 2559 (1964)), or exclusively from localized electrons (J. I. Musher, *ibid.*, **43**, 4081 (1965)) is a subject of controversy which we are investigating.

(6) *E.g.*, H. Watanabe, K. Ito, and M. Kubo, *J. Am. Chem. Soc.*, **82**, 3294 (1960); Y. Matsunaga, *Bull. Chem. Soc. Japan*, **30**, 227 (1957); L. Mulay and S. M. E. Fox, *J. Am. Chem. Soc.*, **84**, 1308 (1962); N. A. Bailey, M. Gerloch, and R. Mason, *Mol. Phys.*, **5**, 327 (1966).

(7) H. Shiba and G. Hazato, *Bull. Chem. Soc. Japan*, **22**, 92 (1949).

(8) (a) A. Pacault, *Bull. Soc. Chim. France*, D40 (1949); (b) B. Pullman and A. Pullman, "Les Theories Electroniques de la Chimie Organique," Masson & Cie, Paris, 1952, pp 529–533, 541–550.

(9) Cyclic delocalization augments the magnitude of χ_z without affecting the magnitude of the other components; χ_M is thus increased by one-third the augmentation in χ_z.

(10) W. Haberditzl, *Sitzber. Deut. Akad. Wiss., Berlin, Kl. Chem. Geol. Biol.*, No. 2 (1964); *Angew. Chem. Intern. Ed. Engl.*, **5**, 288 (1966). For example, using terminology and increments of Haberditzl, χ_M' of 1,3,5-cycloheptatriene would be estimated (units, -10^{-6} cc/mole): $6C_2^*\text{–}H = 6(3.2) = 19.2$; $2C_2\text{–}H = 2(3.8) = 7.6$; $2C\text{–}C^* = 2(2.6) = 5.2$; $5C^*\text{–}C^* = 5(2.4) = 12.0$; $3C\pi C = 3(2.2) = 6.6$; 7Ⓒ (inner electron cores) $= 7(0.15) = 1.05$; total $\chi_M' = 51.65$. The exaltation would be: $\Lambda = \chi_M - \chi_M' = 59.8 - 51.7 = 8.1$.

(11) χ_M' values of benzo-annelated aromatics (naphthalene, anthracene, phenanthrene, and tetracene) were evaluated by use of an average annelation increment, $\Lambda = 20.3$, derived from their principal susceptibilities and estimated "σ anisotropies" (*cf.* B. P. Dailey, *J. Chem. Phys.*, **41**, 2304 (1964)), *e.g.*, $\chi_M'(\text{naphthalene}) = \chi_M'(\text{benzene}) + 20.3 = 61.4$.

(12) The uncertainty in χ_M is commonly about 1%, while that in χ_M' is at least that large under the most favorable circumstances. Thus no significance can be attached to values of $|\Lambda| \sim 1$. Furthermore, "constitutive corrections" have been found necessary for small-ring and other strained systems (*e.g.*, $\Lambda \sim 2.5$ for the cyclopentane systems); these, as well as the area dependency of Λ, will be discussed in subsequent publications.

Cyclopentadiene and cycloheptatriene provide an especially interesting test of the postulate. Cyclic delocalization *via* hyperconjugative π–σ interaction has been predicted for cyclopentadiene.[13] The exaltation observed supports this prediction although the smaller exaltation exhibited by 5,5-dimethylcyclopentadiene would imply that cyclic hyperconjugative delocalization may be less effective in the *gem*-dimethyl case. Cyclic delocalization through overlap of the indented 1–6 π-orbital lobes of the buckled ring has been invoked[14] to rationalize the structure and enhanced resonance energy of the cycloheptatriene system, a rationalization strongly supported by the sizeable exaltation exhibited by this system. Among the monocyclic hydrocarbons observed, cyclopentadiene and cycloheptatriene alone might reasonably have been expected to exhibit exaltation; they alone do so.

It is especially significant that the pseudo-aromatic compounds cyclooctatetraene, pentafulvene, heptalene, dibenzopentalene, and [16]annulene exhibit *small* exaltations which place them among the nonaromatic compounds. The above results confirm the absence of diamagnetic ring current in these systems and, consequently, their nonaromatic nature.

Observation of appreciable *negative* exaltations for [16]annulene and heptalene is consistent with the theory of induced *paramagnetic* ring currents.[15] However, the exaltations of pseudo-aromatic compounds establish that these 4*n* π-electron systems do not exhibit the strongly paramagnetic behavior predicted for bond-equivalent systems[8b] but demonstrate the quenching of orbital paramagnetism which accompanies bond alternation.[16,17] Magnetic susceptibility is clearly a sensitive indicator of the bond alternation in such systems.[17]

Experimental details and discussion of this work as well as investigations of additional carbocyclic and heterocyclic organic and inorganic systems will be presented in subsequent publications.

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(13) R. S. Mulliken, *J. Chem. Phys.*, 7, 339 (1939); C. A. Coulson, "Valence," 2nd ed, Oxford University Press, London, 1961, p 312; G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp 672–675.

(14) R. E. Davis and A. Tulinsky, *Tetrahedron Letters*, 839 (1962); M. Trätteberg, *J. Am. Chem. Soc.*, **86**, 4265 (1964).

(15) See J. A. Pople and K. G. Untch, *ibid.*, **88**, 4811 (1966); H. C. Longuet-Higgins, Chemical Society International Symposium on Aromaticity, Sheffield, England, July 6–8, 1966; Special Publication No. 21, The Chemical Society, London, 1967, pp 109–111; F. Baer, H. Kuhn, and W. Regel, *Z. Naturforsch.*, **22a**, 103 (1967).

(16) G. Wagniere and M. Gouterman, *Mol. Phys.*, **5**, 621 (1962).

(17) T. Nakajima and S. Kohda, *Bull. Chem. Soc. Japan*, **39**, 805 (1966).

(18) National Science Foundation Fellow, 1962–1966.

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The Structure of Thamnosin. A Novel Dimeric Coumarin System

Sir:

Thamnosin was first isolated from *Thamnosma montana* Torr. and Frem. and formulated as $C_{25}H_{26}O_5$.[1] Reinvestigation of the molecular formula by high-resolution mass spectrometry[2] forced a revision to $C_{30}H_{28}O_6$. Further investigations on this substance as indicated below have led to the structural assignment IV, a novel system not previously encountered in nature.

The presence of the coumarin chromophores (1725, 1610, and 1557 cm^{-1}), as well as trisubstituted and *trans*-disubstituted olefinic linkages (820 and 980 cm^{-1}, respectively), were immediately suggested from the infrared spectrum of thamnosin. The nmr spectrum of the latter[3] indicated the presence of a tertiary methyl group (8.78, probably allylic), a vinyl methyl (8.20), two methoxyl groups (6.29 and 6.27), an olefinic proton (4.75, multiplet), and a complex multiplet in the aromatic region (2.4–3.9, ten protons). An expansion of the latter region revealed the presence of a conjugated *trans*-disubstituted double bond (AB pattern at 3.98 and 3.82, J_{AB} = 16 cps).

Dihydrothamnosin, $C_{30}H_{30}O_6$, mp 226–228°, obtained by catalytic reduction (10% palladium on charcoal) showed a disappearance of the above-mentioned absorption for the disubstituted double bond. The chromophoric change created by the hydrogenation reaction as shown in the uv spectrum ($\lambda_{\max}^{\mathrm{MeOH}}$ 227, 256, 298 (sh), and 333 mμ in thamnosin, $\lambda_{\max}^{\mathrm{MeOH}}$ 224, 246 (sh), 254, 300 (sh), and 330 mμ in dihydrothamnosin) indicated that this olefinic system was linked to an aromatic chromophore, the latter most likely being a coumarin system. In fact, the virtual identity of the absorption maxima in the uv spectrum of the dihydro compound with that of suberosin (7-methoxy-6-isopent-2′-enylcoumarin)[4] dictated the presence of a 6-substituted 7-methoxycoumarin skeleton. Furthermore, the intensity of this absorption, being essentially *twice* that of suberosin, suggested that dihydrothamnosin consisted of two 7-methoxycoumarin moieties ($C_{10} \times 2$) and a C_{10}-alkyl residue linked to the 6 position of these molecules.

The nmr spectrum of dihydrothamnosin again showed sharp singlets for a tertiary methyl group (8.97), a vinyl methyl (8.26), two methoxyl resonances (6.25 and 6.22), an olefinic proton (4.83, multiplet), and a series of signals in the aromatic region (2.4–3.9) which now integrated for eight protons. The significant upfield shift of the tertiary methyl (8.78, thamnosin → 8.97, dihydrothamnosin) suggested that it was situated on a carbon atom adjacent to the reducible double bond.

On the basis of the above evidence it was possible to postulate, as a working hypothesis, the following partial structure (I) for thamnosin.

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(1) D. L. Dreyer, *Tetrahedron*, 22, 2923 (1966).

(2) Mass spectra were determined on an AEI MS9 mass spectrometer. In all instances reported molecular formulas were established by this technique. Satisfactory elemental analyses were also obtained for all compounds.

(3) All nmr spectra were measured in deuteriochloroform (unless otherwise stated) with tetramethylsilane as the internal standard with a Varian HA-100 spectrometer. All signals are reported in τ units. In all instances the nmr data were highly informative due to the excellent separation of the signals which could be achieved with essentially all these compounds.

(4) F. E. King, J. R. Housley, and T. J. King, *J. Chem. Soc.*, 1392 (1954).