Estimation of Local and Nonlocal Magnetic Susceptibilities and a Comparison of Magnetic and Thermodynamic Criteria of Aromaticity for 2-Methoxypyridine and 1-Methyl-2-pyridone

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Abstract: The Hameka formalism for estimation of local magnetic susceptibilities is extended to include most compounds of carbon, hydrogen, oxygen, and nitrogen. With these parameters the susceptibility of alkanes, alkenes, alcohols, ethers, aldehydes, ketones, acids, esters, anhydrides, carbonates, amines, amides, and imines can be predicted with an accuracy of about 1×10^{-6} cm^3 mol^{-1}. These parameters are used to estimate the magnetic susceptibilities of localized models for potentially aromatic molecules and to evaluate the nonlocal susceptibility for these systems. The effect on the nonlocal susceptibility of formal carbonyl insertion into an aromatic ring is examined. A detailed comparison of magnetic and thermodynamic estimates of aromaticity is presented which shows that 2-methoxypyridine and 1-methyl-2-pyridone differ in aromatic character by about one-fifth of the nonlocal character of benzene.

I. Introduction

The concept of aromatic character has provided a durable basis for the productive interaction of theory and experiment for over 100 years.[1-3] Despite that long period of interest, however, there is still not general agreement on quantitative measures of aromaticity. In part, this stems from the fundamental problem of mutable model choices. Prospective quantitative criteria of aromaticity are established by comparison of an estimated property of a hypothetical molecule to a real property of a real molecule; with the use of different models and/or different properties, different quantitative estimates may result.

Structurally, an aromatic molecule possesses $4n + 2$ electrons in a contiguous π system. Physically such molecules exhibit thermodynamic stability and magnetic properties attributable to electron delocalization relative to a localized model.[4] Although a variety of standards have been proposed,[1,2] most of the suggested quantitative criteria of aromatic character focus on determinations of resonance energies or measurements of magnetic properties. The question of whether the thermodynamic and magnetic measures of aromatic character do, in fact, correlate has been raised in different forms by a number of workers.[1,2,5-11]

The most convenient and popular qualitative test of aromaticity clearly is the presence of nonlocal molecular magnetic susceptibility anisotropy due to the circulation of electrons in a "ring current" as inferred from proton chemical shifts.[12] Difficulties in assessing other contributions to the chemical shift have left quantitative uses of this approach open to question.[1,2,5-11] Two other indirect methods of determining magnetic anisotropies are the measurement of the change in chemical shift upon dilution[13] and determination of the Cotton-Mouton effect,[14] which measures the product of the optical electric polarizability and magnetic susceptibility anisotropies. The dilution measurements are only qualitative because a form must be assumed for the molecular distribution function, and the Cotton-Mouton experiments have a large uncertainty due to the local field correction required for the electric anisotropy and a contribution from a hyperpolarizability term of unknown magnitude. On the other hand, high-resolution Zeeman-microwave spectroscopy[15] and single crystal measurements[16] provide direct measurements of magnetic susceptibility anisotropies. The Zeeman technique is useful for relatively small molecules so that it complements the data obtained from singgle crystal measurements on larger systems.

Although direct measurements of the magnetic susceptibility anisotropy are desirable, there are many molecules of interest for which such measurements would be very difficult. Zeeman techniques cannot be used to study conpounds with no dipole moment, low vapor pressure, little population in low J rotational states, or unduly complicated quadrupole coupling. Molecules which do not form large, pure single crystals cannot be studied as solids. Fortunately, information concerning the nonlocal susceptibility can also be extracted by examining the average, or bulk, susceptibility. The dynamic range of the quantity being examined is then much smaller so greater accuracy is needed; however, recent experimental advances have made such an approach feasible.

The general approach to analyzing magnetic susceptibilities to extract information about nonlocal contributions and their relationship to aromaticity is to first reduce empirically the experimental susceptibilities to local and nonlocal contributions. The bulk susceptibility is given by

$$\chi = \tfrac{1}{3}(\chi_{aa} + \chi_{bb} + \chi_{cc})$$

where χ_{aa}, χ_{bb}, and χ_{cc} are the diagonal elements of the magnetic susceptibility tensor. Each χ_{gg} can be broken into a diamagnetic, χ_{gg}^{d}, and paramagnetic, χ_{gg}^{p}, part giving

$$\chi_{gg} = \chi_{gg}^{d} + \chi_{gg}^{p}$$

The magnetic susceptibility anisotropy is given by

$$\Delta\chi = \chi_{cc} - \tfrac{1}{2}(\chi_{aa} + \chi_{bb})$$

where we take the c axis as the out-of-plane axis for the generally planar molecules considered here. In using χ or $\Delta\chi$ data to evaluate the extent of electron delocalization, one must establish a set of localized atomic, bond, or group values of χ and $\Delta\chi$ which can be added to give the correct experimental values in molecules which are considered to have essentially localized electrons. Thus, the experimental values of χ and $\Delta\chi$ for aromatic molecules or molecules which contain delocalized electrons are obtained by a sum of the local and nonlocal contributions:

$$\chi = \chi^{local} + \chi^{nonlocal}$$

$$\Delta\chi = \Delta\chi^{local} + \Delta\chi^{nonlocal}$$

Benson and Flygare[17] showed that the entire magnetic susceptibility anisotropy cannot be attributed to nonlocal contributions. For example, half the anisotropy of benzene is attributable to local contributions, a consideration that has not always been taken into account.[13,14]

Schmalz et al.[18] have used data obtained from Zeeman measurements on nonaromatic molecules to construct a set of localized bond and atom susceptibility tensors. Applying these local rules to aromatic molecules, they were able to show that the historically recognized, anomalously large bulk susceptibilities (χ) and anisotropies ($\Delta\chi$) were due to an increase in the out-of-plane component (χ_{cc}) of the susceptibility over that expected for a localized model. This work establishes that

$$\Delta\chi^{\text{nonlocal}} = \chi_{cc}{}^{\text{nonlocal}} = 3\chi^{\text{nonlocal}}$$

Another important conclusion is that the change in anisotropy for $(4n + 2)$ π systems is due to a decrease in the paramagnetic contribution to the overall susceptibility anisotropy, while the diamagnetic susceptibility contribution remains relatively constant.[19]

The use of nonlocal bulk susceptibility as a criteria for aromaticity has been developed by Dauben, Wilson, and Laity.[11,20] These workers used the Haberditzl system[21] to calculate the bulk susceptibilities for their local models. In this work, we have used Hameka's formalism[22] to decompose the local susceptibility by completely basing our local models on experimental data. As will be shown, the conclusions obtained from χ^{nonlocal} are very similar to those obtained by measurements of magnetic susceptibility anisotropies.

Determinations of empirical resonance energies have traditionally been the foundation of quantitative measurements of aromatic character.[1,2] In an effort to provide an experimentally based, gas-phase property of the hypothetical models needed for estimates of resonance energies, Beak et al.[10] used the 14.6 ± 1.7 kcal/mol difference in equilibration enthalpy between 1-methyl-2-piperidone and 2-methoxy-3,4,5,6-tetrahydropyridine as the enthalpy difference of the localized models for comparison to the 8.0 ± 2.3 kcal/mol energy difference between 1-methyl-2-pyridone and 2-methoxypyridine.[23-25] The difference in empirical resonance energies of 1-methyl-2-pyridone and 2-methoxypyridine by this analysis is 6.6 ± 4.0 kcal/mol in favor of the pyridine. Cook et al.[26] more recently have used essentially the same type of comparison to determine a value of 6.5 kcal/mol empirical resonance energy in favor of 2-hydroxypyridine relative to 2-pyridone on the basis of tautomeric equilibrium constants with an implicit assumption of cancellation of solvent effects. These workers have extended this approach to a wide variety of heterocyclic and carbocyclic systems.[2,26,27] In an effort to determine if there is a correspondence between the magnetic and thermodynamic criteria of aromatic character, we have made the necessary susceptibility measurements for the 2-methoxypyridine–1-methyl-2-pyridone comparison.

II. Experimental Results

To provide a data base for the extraction of the nonlocal contribution to the magnetic susceptibility of 1-methyl-2-pyridone and 2-methoxypyridine, we have measured the magnetic susceptibility of these compounds and their local model compounds 1-methyl-2-piperidone and 2-methoxy-3,4,5,6-tetrahydropyridine. In cases where the literature measurements were insufficient to determine the Hameka parameters used in establishing local susceptibility values, we have measured the bulk magnetic susceptibilities of additional molecules of certain classes. The measurements include mostly ethers and amines, particularly unsaturated ones for which no literature data appears to be available.

The bulk susceptibility measurements were carried out by the method of Frei and Bernstein.[28] The difference in chemical shifts between Me_4Si in the spherical and cylindrical positions of a sealed reference cell was measured on a Varian A60/56 NMR spectrometer at 40 °C. The instrument was adjusted so that the Me_4Si splitting was 20 Hz for carbon tetrachloride. Liquids of known susceptibility were used to calibrate the volume susceptibility (χ_v) dependence of the Me_4Si splitting.[29] Unknown volume susceptibilities were then calculated from the formula

$$\chi_v = (-0.519 \pm 0.002) + (-0.0076 \pm 0.0001)\delta$$

where δ is the Me_3Si splitting in Hz. Splittings were reproducible to within 1 Hz.

Densities were measured at 40 °C in 2-ml pycnometers calibrated with water. The molar susceptibility, χ_M, was then calculated by the formula

$$\chi_M = \frac{\chi_v M}{d}$$

where M is the molecular weight and d is the density. The experimental results are given in Table I.

Table I. Experimental Bulk Magnetic Susceptibilities

Compound	χ_v[a]	d (g/cm)^3 [b]	χ_m[c]
2-Methoxypyridine	0.620	1.028	65.8
3-Methoxypyridine	0.619	1.060	63.7
4-Methoxypyridine	0.622	1.064	63.8
1-Methyl-2-pyridone	0.640	1.115	62.6
1-Methyl-4-pyridone	0.686[d]	1.354[d]	57.2
1-Methyl-2-piperidone	0.649	1.015	72.4
2-Methoxy-3,4,5,6-tetrahydropyridine	0.618	0.965	72.5
1-Vinyl-2-pyrrolidinone	0.633	1.027	68.5
1-Pyrrolidino-1-cyclopentane	0.675	0.937	98.8
N-Morpholino-1-cyclohexene	0.669	1.009	110.8
2-Oxazoline	0.578	1.048	39.2
2-Methyl-2-oxazoline	0.593	0.990	51.0
1,3-Dimethyl-2-piperidene	0.601	0.843	79.3
N-Ethylurethane	0.585	0.952	72.6
Diisopropylethylamine	0.609	0.739	106.5
N-*n*-Butylmethylaldimine	0.562	0.759	73.5
N-*n*-Propylethylaldimine	0.546	0.734	73.7
Tropone	0.546	1.077	53.8
2-Pyrone	0.562	1.183	45.6
4-Pyrone	0.534	1.195	42.9
Vinylene carbonate	0.609	1.337	39.2
Vinyl formate	0.442	0.918	34.7
Ethylvinyl ether	0.485	0.730	47.9
2,3-Dihydropyran	0.571	0.907	52.9
1,2-Dimethoxyethane	0.552	0.853	58.4
1,1-Diethoxyethane (acetal)	0.575	0.828	82.1
Diethylene glycol, dimethyl ether	0.587	0.937	84.0

[a] Volume susceptibility in mu/cm^3, 40 °C (1 mu = -1×10^{-6} erg/G^2 mol). [b] Density at 40 °C. [c] Molar susceptibility in mu. [d] 36% solution in chloroform.

2-Methyl-2-oxazoline, 1-pyrrolidino-1-cyclopentene, 1-vinyl-2-pyrrolidinone, vinylene carbonate, *N*-morpholino-1-cyclohexene, 1-methyl-2-piperidone, *N*-ethylurethane, diisopropylethylamine, and 2,3-dihydropyran were obtained commercially from Aldrich Chemical Co., vinyl ethyl ether and vinyl formate from ICN, acetal and 1,2-dimethoxyethane from Eastman Chemical Co., and diethylene glycol dimethyl ether from Union Carbide. All compounds were used without further purification other than repeated freeze pumping to remove dissolved gases.

2-Methoxypyridine,[10] 3-methoxypyridine,[30] 4-methoxypyridine,[10] 1-methyl-2-pyridone,[10] 1-methyl-4-pyridone,[10] 1-methyl-2-piperidone,[10] 2-methoxy-3,4,5,6-tetrahydropyridine,[10] 2-oxazoline,[31] 1,3-dimethyl-2-piperidene,[32] *N*-*n*-butylmethylaldimine,[33] *N*-*n*-propylethylaldimine,[33] 2-pyrone,[34] and 4-pyrone[35] were prepared and purified by established procedures and characterized by IR and NMR spectroscopy.

III. Hameka-Type Localized Magnetic Susceptibility Parameters

In order to evaluate the magnetic manifestation of aromaticity, a reliable set of parameters are needed to estimate the

magnetic susceptibilities of the hypothetical localized model. Historically, it has long been recognized that the magnetic susceptibility of nonstrained, nonaromatic molecules can be represented to reasonable accuracy as a sum of contributions from each atom in the molecule. Various sets of constants of this type, called Pascal's constants, appear in the literature.[36] Most contain "constituitive corrections" for double and triple bonds, but these can be considered also as changes in the atomic values due to differences in hybridization. The Pascal system is in general accurate to better than 10%, but it cannot reflect subtle differences in local values caused by interactions with neighboring atoms.[37]

Hameka[22,38] has taken these neighbor group interactions into account by writing the susceptibility of a molecule as the sum of contributions from the bonds, cores, and electron lone pairs in the molecule, plus corrections due to the interactions between bonds to the same atom. He provides theoretical arguments to show that these terms include all large contributions to the molecular susceptibility. Despite the initially large number of parameters, only a few linear combinations for each functional class appear in the final theory, and they can be determined empirically from a reasonable number of molecules. Hameka has illustrated the application of the method to alkanes[22] and in later work has extended it to alcohols, aldehydes, ketones, acids, and esters.[39,40]

In this work we have used Hameka's method to determine the parameters needed to describe alkenes, ethers, and unsaturated oxygen containing molecules, amines, amides, and imines, as well as the classes already treated by Hameka. However, we have adopted several notational conventions which are different from Hameka's. The most noteworthy of these is our decision to define interaction parameters as the negative of those given by Hameka. This results in the susceptibility of a molecule being the sum of the atom and bond contributions *plus* the bond-bond interactions rather than minus bond-bond interactions as in Hameka. It appears to us that this makes the system much easier to use since one need not be concerned with reversing the sign of bond-bond interactions with respect to bonds. We have also dropped the symbol χ and use, for example, CC;CC for the term Hameka would designate as $\chi_{CC;CC}$.

Aside from the above two conventional changes, our parameters A, B, and C, which are sufficient to describe all contributions in alkanes, are the same as Hameka's. The parameter B describes the contribution of a methylene group to the susceptibility. A accounts for end effects in acyclic alkanes. C describes the contribution of a chain branch. The remainder of the parameters defined in Table II extend Hameka's formalism to treat additional classes of molecules. Our parameter D represents the addition of a vinyl group to an alkyl chain. Unlike Hameka, we have consistently defined our atom containing parameters as the contributions necessary to add a particular functional group to an alkyl chain. Thus our alcohol parameters *FO* and *GO* correspond to Hameka's D and E, but our carbonyl parameter *HO* does not follow Hameka's convention. This change allows us to write functional groups such as acids and esters in terms of easily identifiable atom combinations plus appropriate interaction terms. In addition, we have designated the nitrogen parameters as analogues of the correspondingly named oxygen parameters whenever possible. The parameters *KON* and *LON* represent the same interaction between an oxygen and a nitrogen as *KO* and *LO* (or *KN* and *LN*) represent between an oxygen (or nitrogen) and a carbon. We emphasize that since the parameters are all linearly independent, the predictions for the susceptibility of a local structure are independent of the particular linear combinations of atoms, bonds, and interactions used in defining the parameters.

Application of this method assumes additivity of bond interactions with neglect of conjugation, long-range interactions, and ring strain. Conjugation does not appear to be important since conjugated and nonconjugated dienes have the same bulk susceptibilities within experimental error. We also note that no explicit corrections are made for whether an amine is planar or pyrimidal. If this difference is important, it may be reflected in the parameter *KN*.

The values of the parameters defined in Table II are given in Table III. Most were determined from a least-squares fit of 120 nonaromatic molecules listed in the appendix. The standard deviation of the fit was 0.8 mu (1 mu = 1 magnetic unit $= -10^{-6}$ erg/G^2 mol). The remaining values, where indicated, were calculated from individual molecules because insufficient data were available to obtain a meaningful least-squares fit. The molecules *N*-*n*-propylethylaldimine and *N*-*n*-butylmethylaldimine yield the parameter *DN* directly. For reasons to be discussed, we believe that the most accurate determination of *EN* is given by the difference between 2-methyl-2-oxazoline and 2-oxazoline. This value, along with the measured susceptibility of 2-methoxy-3,4,5,6-tetrahydropyridine, gives *KON*. Finally, *N*-ethylurethane was used to evaluate *LON*.

Care must be exercised in the selection of experimental susceptibility measurements to be used in parameterizing the least-squares fit. It is our observation that while magnetic susceptibility measurements from one laboratory are usually selfconsistent with a high degree of precision, there are sometimes relatively large systematic errors between series of measurements from different investigators. Mixing values from several sources can sometimes produce very irregular results. We have tried wherever possible to select only starred (preferred) values of experimental measurements from the Landolt-Börnstein tables,[41] plus those measured in this work, for use in our fit. For certain functional groups this is not possible. In those cases we have examined the original sources and attempted to verify that the values used are reasonable. Of particular note are the values for nitrogen containing molecules. The largest set of measurements on nitrogen containing systems is that of Francois;[42] yet these values seem to be systematically lower than those from any other source. However, they agree quite well with the measurements reported in this work, and we have used them exclusively in Table IV.

Even within the set of starred values by investigators who otherwise generally report consistent measurements, there are occasional values which are so discrepant that we have seen fit to replace or eliminate them. he preferred values of butane, trihexylamine, triheptylamine, propylacetamide, diethylacetamide, and dibutylacetamide do not appear to fit well and were omitted. In addition, the preferred values of dimethyl ether and dioxane seem to be significantly in error. Instead, we believe that the value of 33.0 reported[43] for dimethyl ether and the value of 52.2 for dioxane reported by Venkateswarlu and Sriraman[44] are more likely to be correct. Finally, we note that the value of five-membered rings is many times about 1-2 mu larger than would be expected. For this reason we have not used cyclopentane or cyclopentene in the least-squares fit. We have considered only the difference between two five-membered rings in evaluating the parameter *EN*. We have also excluded the molecule 1-pyrrolidino-1-cyclopentene from the least-squares fit. We note that if the experimental rather than the calculated value for the cyclopentene ring is used, this molecule gives a value of KN in good agreement with that obtained in the fit.

Hameka[39] found a strong dependence of the values of the parameters A, B, and C on the oxygen functional group of the molecule. Values of B varying over the range 11.2 to 11.7 probably reflect real differences in the susceptibilities. It appears that the much larger variations in A observed by Hameka may be due, at least partially, to a failure to decouple the parameter A correctly from the functional group parameter. We

Table II. Definition of Hameka Parameters[a]

	Parameter Definition
A	C + 4CH − CC;CC + 5CH;CH + 2CH;CC
B	C + CC + 2CH + CC;CC + CH;CH + 4CH;CC
C	CC;CC + CH;CH − 2CH;CC
D	2C + CC* + CC + 2CH + 2CH;CC + 2CC;CC* + 2CH;CC*
E	CH;CC* − CC;CC* + CC;CC − CH;CH
FO	O + CO + OH − CH − 2CH;CH − CH;CC + CC;CO + 2CH;CO + OC;OH
GO	CC;CO − CH;CO + CH;CH − CH;CC
HO	C + O + CO* + CC + CC;CC + 2CC;CO*
IO	CH;CO* − CC;CO* + 2CH;CC − 2CH;CH
JO	O + 2CO − CC − 2CC;CC − 4CH;CC + 2CC;CO + 4CH;CO + OC;OC
KO	CO;CC* + CC;CC + CH;CC − CC;CC* − CC;CO − CH;CO
LO	CC;CC + CO;CO − 2CC;CO
MO	CO;CO* − CC;CO* + 2CH;CC − 2CH;CO
DN	C + N + CN* + CN + CH − CC;CC − CH;CC + CC;CN* + CH;CN* + NC;NC* + CC;CN + 2CH;CN
EN	CH;CN* − CC;CN* + CC;CC − CH;CH
FN	N + CN + 2NH − CH − 2CH;CH − CH;CC + CC;CN + 2CH;CN + 2NC;NH + NH;NH
GN	CC;CN − CH;CN + CH;CH − CH;CC
JN	N + 2CN + NH − CC − 2CC;CC − 4CH;CC + 2CC;CN + 4CH;CN + NC;NC + 2NC;NH
KN	CN;CC* + CC;CC + CH;CC − CC;CC* − CC;CN − CH;CN
MN	CN;CO* − CC;CO* + 2CH;CC − 2CH;CN
TN	NC;NC + NH;NH − 2NC;NH
DON	C + O + N + CN* + CO − CN + NO + CH − CC;CC − CH;CC + CC;CN* + CH;CN* + NO; NC* − NC;NC* + CC;CO − CC;CN + 2CH;CO − 2CH;CN + OC;ON
KON	CO;CN* + CC;CC + CH;CC − CC;CN* − CC;CO − CH;CO
LON	CO;CN − CC;CO + CC;CC − CC;CN

[a] Parameters *A*, *B*, and *C* are the same as defined by Hameka (ref 22) except that the sign convention for bond interactions has been changed. Others are closely related (see text). The asterisk indicates a double bond.

Table III. Least-Squares Fit Values of Hameka Parameters

Parameter	Value	Std dev
A	17.10	0.15
B	11.48	0.03
C	0.52	0.07
D	14.11	0.17
E	0.40	0.16
FO	4.84	0.12
GO	0.73	0.11
HO	5.68	0.13
IO	0.25	0.15
JO	3.55	0.12
KO	0.73	0.26
LO	0.66	0.34
MO	4.94	0.16
DN	10.6[a]	
EN	0.6[a]	
FN	7.38	0.27
GN	0.92	0.18
JN	6.50	0.37
KN	0.62	0.53
MN	3.86	0.31
TN	1.12	0.73
DON	14.4[a]	
KON	1.1[a]	
LON	0.0[a]	

[a] Determined from the average susceptibilities of a limited number of molecules assuming the least-squares fit values for the other parameters.

find no great variation in *A* among oxygen functional groups if only monoesters and monoacids are included in the fit. However, the use of diacids and diesters to differentiate between *A* and the acid or ester parameter leads to significant deviations. Again, the problem of comparing measurements from two different sources arises, but the work of Angus and Stott[45] shows that if selfconsistent values are used, the alkyl chain contributions in diesters and esters are identical but that the functional group remainder yields a dramatically different value of *A* from esters than from diesters *A*.

IV. Nonlocal Magnetic Susceptibility

As noted in the introduction, the correlation between nonlocal magnetic susceptibility and aromaticity has been widely discussed.[5-12] To calculate accurately the nonlocal contribution, we must have a reliable set of local rules to evaluate the localized structure used as the nonaromatic reference. The system of Haberditzl[21] was used by Dauben et al.[11,20] to estimate magnetic susceptibilities. This system has a separate contribution for core electrons, lone pairs, π bonds, and σ bonds. The σ bond value depends not only on the hybridization of the atoms in the bond, but also on neighboring atoms. While there are enough parameters to describe any conceivable interaction, the parameters cannot be determined uniquely and some effects are arbitrarily partitioned into two or more parameters. Due to a lack of experimental data, the values of all π bond contributions were assumed to be the same as the C–C π bond. We feel that the Hameka parameters evaluated in Section III are at present the best method of calculating the local contributions to the bulk susceptibility.

We have calculated the local and nonlocal contributions to the magnetic susceptibility for some cyclic compounds, and the results are given in Table V. We note that the two Kekulé structures of 2-substituted pyridines are described by different Hameka parameters, and the two structures are predicted to have slightly different local susceptibilities. In the absence of any accurate method of weighting the different forms, we have merely averaged the two results.

We estimate the uncertainty of our nonlocal susceptibilities by the following method. The standard deviation of the fit of the local values to the nonaromatic molecules in Table IV is about 0.8 mu. The experimental uncertainty in the bulk susceptibility measurement is about 0.5 to 1.0 mu. Our resultant uncertainty is therefore at most 1.8 mu, or 15% of the nonlocal value of benzene.

We also compare our nonlocal susceptibilities with the "magnetic susceptibility exaltations", Λ, calculated by Dauben et al.[11,20] The two determinations are in reasonable agreement. In addition, the value of 7.5 for χ^{nonlocal} of 1-methyl-2-pyridone is in good agreement with Dauben's value of 7.0 for Λ of 1-ethyl-2-pyridone. The only major discrepancy is the case of pyridine. Our local value for the CN double bond is based on experiment, while Dauben et al. had to assume that the π contribution of a CN double bond was equal to that in a CC double bond. The value we use for the susceptibility of the CN double bond is also larger than that calculated from Pascal's rules. However, Pascal's value is derived from measurements on benzilidenemethylamine and benzilidene aniline.[46] These molecules have been remeasured more recently,[42] and the newer values of the susceptibilities are much larger, in agreement with the results of this work.

In Table VI we compare the nonlocal bulk susceptibility with $\chi_{cc}^{\text{nonlocal}}$ and $\Delta\chi^{\text{nonlocal}}$ determined from the molecular Zee-

Table IV. Details of Least Squares Fit

Compound	Hameka formula	Obsd	Calcd
	Alkanes		
Propane	$A + 2B$	39.6	40.1
Isobutane	$A + 3B + C$	51.7	52.1
Pentane	$A + 4B$	63.2	63.0
Isopentane	$A + 4B + C$	63.1	63.5
Neopentane	$A + 4B + 3C$	63.1	64.6
Hexane	$A + 5B$	74.1	74.5
2-Methylpentane	$A + 5B + C$	75.3	75.0
3-Methylpentane	$A + 5B + C$	75.5	75.0
2,2-Dimethylbutane	$A + 5B + 3C$	76.2	76.1
Heptane	$A + 6B$	85.3	86.0
2,4-Dimethylpentane	$A + 6B + 2C$	87.5	87.0
Octane	$A + 7B$	96.8	97.5
	Alkenes		
Propene	$A + D + E$	31.5	31.6
2-Butene	$A + B + D$	43.0	42.7
Isobutene	$A + B + C + D$	44.4	43.2
Pentene	$A + 2B + D + E$	54.6	54.6
2-Methyl-2-butene	$A + 2B + C + D - E$	54.7	54.3
Hexene	$A + 3B + D + E$	66.4	66.0
2,4-Dimethyl-2-butene	$A + 3B + 2C + D - 2E$	65.9	65.9
Heptene	$A + 4B + D + E$	78.0	77.5
Octene	$A + 5B + D + E$	88.8	89.0
2-Methyl-4-heptene	$A + 5B + C + D$	88.0	89.1
2,4-Dimethyl-4-hexene	$A + 5B + 2C + D - E$	88.5	89.3
Nonene	$A + 6B + D + E$	100.1	100.5
2-Methyl-2-octene	$A + 6B + C + D - E$	100.0	100.2
2,5-Dimethyl-4-heptene	$A + 6B + 2C + D - E$	100.6	100.7
2-Methyl-1,3-butadiene	$A + C + 2D + E$	46.0	46.2
2,3-Dimethyl-1,3-butadiene	$A + B + 2C + 2D$	57.1	57.8
	Alcohols		
Methanol	$A + C + FO - GO$	21.4	21.7
Ethanol	$A + B + FO$	33.6	33.4
Propanol	$A + 2B + FO$	45.2	44.9
Isopropanol	$A + 2B + FO + GO$	45.8	45.6
Butanol	$A + 3B + FO$	56.2	56.4
sec-Butanol	$A + 3B + FO + GO$	57.3	57.1
Isobutanol	$A + 3B + C + FO$	57.2	56.9
tert-Butyl alcohol	$A + 3B + C + FO + 2GO$	57.4	58.4
2-Pentanol	$A + 4B + FO + GO$	69.1	68.5
Isopentanol	$A + 4B + C + FO$	69.0	68.4
Hexanol	$A + 5B + FO$	79.2	79.3
4-Methyl-2-pentanol	$A + 5B + C + FO + GO$	80.4	80.6
Allyl alcohol	$A + D + E + FO$	36.7	36.4
Ethylene glycol	$A + B + 2FO$	38.8	38.3
1,6-Hexandiol	$A + 5B + 2FO$	84.3	84.2
	Ketones		
Acetone	$A + B + HO$	33.9	34.3
Methyl ethyl ketone	$A + 2B + HO$	45.6	45.7
Diethyl ketone	$A + 3B + HO$	57.3	57.2
Ethyl propyl ketone	$A + 4B + HO$	69.0	68.7
Methyl isobutyl ketone	$A + 5B + C + HO$	70.0	69.2
Dipropyl ketone	$A + 5B + HO$	80.5	80.2
Diisopropyl ketone	$A + 5B + 2C + HO$	81.1	81.2
Ethyl butyl ketone	$A + 5B + HO$	80.7	80.2
Methyl pentyl ketone	$A + 5B + HO$	80.5	80.2
2,5-Hexandione	$A + 3B + 2HO$	62.5	62.9
	Aldehydes		
Ethanal	$A + HO + IO$	22.7	23.0
Propanal	$A + B + HO + IO$	34.3	34.5
Butanal	$A + 2B + HO + IO$	46.1	46.0
Isobutanal	$A + 2B + C + HO + IO$	46.4	46.5
Hexanal	$A + 4B + HO + IO$	69.4	69.0
Heptanal	$A + 5B + HO + IO$	81.0	80.4
	Ethers		
Diethyl ether	$A + 3B + JO$	55.1	55.1
Dioxane	$4B + 2JO$	52.2	53.0
Diisopropyl ether	$A + 6B + 2GO + JO$	79.4	79.5
Dimethoxymethane	$A + 2B + 2C - 2GO + 2JO + LO$	47.2	47.4

Table IV. (Continued)

Compound	Hameka formula	Obsd	Calcd
1,2-Dimethoxyethane	$A + 3B + 2C - 2GO + 2JO$	58.4	58.2
Diethylene glycol, dimethyl ether	$A + 5B + 2C - 2GO + 3JO$	84.0	84.8
1,1-Diethoxyethane (acetal)	$A + 5B + 2JO + LO$	82.1	82.3
Ethyl vinyl ether	$A + B + D + E + JO + KO$	47.9	47.4
Dihydropyran	$3B + D + JO + KO$	52.8	52.8
	Esters		
Methyl formate	$A + 2C - 2GO + HO + IO + JO + MO$	31.0	31.1
Ethyl formate	$A + B + C - GO + HO + IO + JO + MO$	42.7	42.8
Propyl formate	$A + 2B + C - GO + HO + IO + JO + MO$	55.0	54.3
Isobutyl formate	$A + 3B + 2C - GO + HO + IO + JO + MO$	66.8	66.3
Methyl acetate	$A + B + C - GO + HO + JO + MO$	42.6	42.5
Ethyl acetate	$A + 2B + HO + JO + MO$	54.1	54.2
Isopropyl acetate	$A + 3B + GO + HO + JO + MO$	67.0	66.4
Methyl propionate	$A + 2B + C - GO + HO + JO + MO$	54.1	54.0
Ethyl propionate	$A + 3B + HO + JO + MO$	65.8	65.7
Methyl butyrate	$A + 3B + C - GO + HO + JO + MO$	65.8	65.5
Ethyl butyrate	$A + 4B + HO + JO + MO$	77.4	77.2
Methyl methacrylate	$A + B + 2C + D - PO + HO + JO + MO$	57.3	57.2
Vinyl formate	$A - B + C + D + E - GO + HO + IO + JO + KO + MO$	34.7	35.1
Vinyl acetate	$A + D + E + HO + JO + KO + MO$	46.4	46.5
	Acids		
Acetic acid	$A + FO + HO + MO$	31.8	32.5
Propionic acid	$A + B + FO + HO + MO$	43.4	44.0
Butyric acid	$A + 2B + FO + HO + MO$	55.2	55.5
Isobutyric acid	$A + 2B + C + FO + HO + MO$	56.1	56.0
Pentanoic acid	$A + 3B + FO + HO + MO$	66.9	67.0
Hexanoic acid	$A + 4B + FO + HO + MO$	78.5	78.5
Heptanoic acid	$A + 5B + FO + HO + MO$	89.7	90.0
Octanoic acid	$A + 6B + FO + HO + MO$	101.6	101.4
	Miscellaneous oxyhydrocarbons		
Methyl acetoacetate	$A + 2B + C - GO + 2HO + JO + MO$	59.6	59.7
Ethyl acetoacetate	$A + 3B + 2HO + JO + MO$	71.7	71.4
Methyl-2-methoxy-2-methyl propionate	$A + 4B + C + HO + 2JO + MO$	81.9	81.3
Diethyl carbonate	$A + 3B + HO + 2JO + LO + 2MO$	75.4	74.9
Vinylene carbonate	$D + HO + 2JO + 2KO + LO + 2MO$	39.2	38.9
	Amines		
Butylamine	$A + 3B + FN$	58.9	58.9
Isobutylamine	$A + 3B + C + FN$	59.8	59.4
Pentylamine	$A + 4B + FN$	69.4	70.4
Isopentylamine	$A + 4B + C + FN$	71.6	70.9
Heptylamine	$A + 6B + FN$	93.2	93.4
Dibutylamine	$A + 7B + JN$	103.7	104.0
Diisobutylamine	$A + 7B + 2C + JN$	105.7	105.0
Di-*sec*-butylamine	$A + 7B + JN + 2GN$	105.9	105.8
Dihexylamine	$A + 11B + JN$	148.9	149.9
Diheptylamine	$A + 13B + JN$	171.5	172.8
Triethylamine	$A + 5B - FN + 2JN + TN$	81.4	81.2
Diisopropylethylamine	$A + 6B - FN + 2GN + 2JN + TN$	106.5	106.0
1,3-Dimethyl-2-piperidene	$5B + 2C + D - E - FN - GN + 2JN + KN + TN$	79.3	78.6
N-Morpholino-1-cyclohexene	$A + 9B + D - E + JO - FN + GN + 2JN + KN + TN$	110.8	111.8
	Amides		
Formamide	$A - B + C + HO + IO + FN - GN + MN$	22.0	22.4
Acetamide	$A + HO + FN + MN$	34.1	34.0
Oxamide	$A - B + 2HO + 2FN + 2MN$	40.1	39.4
Succinamide	$2B + 2HO + 2JN + 2MN$	61.8	62.4
Isopropyl acetamide	$A + 3B + HO + GN + JN + MN$	68.7	68.5
Butyl acetamide	$A + 4B + HO + JN + MN$	80.2	79.1
Isobutyl acetamide	$A + 4B + C + HO + JN + MN$	78.9	79.6
Dimethyl acetamide	$A + 2B + 2C + HO - FN - 2GN + 2JN + MN + TN$	56.1	55.5
1-Methyl-2-piperidone	$5B + C + HO - FN - GN + 2JN + MN + TN$	72.5	73.3
1-Vinyl-2-pyrrolidone	$3B + D + E + HO - FN + 2JN + KN + MN + TN$	65.8	65.8

man effect. For benzene we have used the susceptibility anisotropy derived by Sutter and Flygare[47] by extrapolation of the fluorobenzene anisotropies. This results in a slightly higher nonlocal anisotropy than had been derived earlier from single crystal measurements on benzene[18] and is in much better agreement with the bulk result. The anisotropy of pyridine confirms our bulk result that pyridine has ca. three-fourths the nonlocal character of benzene. All three indicators also show

Table V. Nonlocal Susceptibility of Some Cyclic Compounds

Compound	Hameka formula	χ^{calcd}	χ^{obsd}	$\chi^{nonlocal}$	Λ^c
Benzene	$3D$	42.3	54.8[a]	12.5	13.7, 14.5
Toluene	$3D + B + C - E$	53.9	66.1[a]	12.2	12.8
Anisole	$3D + B + C - E + JO + KO$	58.2	72.1[a]	13.9	
Phenol	$3D - E + FO + GO + KO$	48.2	60.2[a]	12.0	
Aniline	$3D - E + FN + GN + KN$	50.9	62.4[a]	11.5	
Pyridine	$2D + DN + KN$	39.4	48.5[a]	9.1	13.4
2-Methylpyridine I	$2D + B + C + DN - EN + KN$	50.9	60.3[a]	9.3	
II	$2D + B + C - E + DN + KN$	51.1			
2-Methoxypyridine I	$2D + B + C + DN - EN + JO + KN + KON$	55.5	65.8[b]	10.2	
II	$2D + B - E + DN + JO + KO + KN + GN + LON$	55.7			
3-Methoxypyridine	$2D + B + C - E + DN + KN + JO + KO$	55.3	63.7[b]	8.4	
4-Methoxypyridine	$2D + B + C - E + DN + KN + JO + KO$	55.3	63.8[b]	8.5	
Pyrrole	$2D + JN + 2KN$	35.9	48.6[a]	12.7	10.2
1-Methylpyrrole	$2D + B - C + 2JN - FN + TN + 2KN - GN$	46.2	58.6[a]	12.4	
2-Methylpyrrole	$2D + B - E + GN + JN + 2KN$	47.9	60.1[a]	12.3	
1-Methyl-2-pyridone	$2D + B + C + 2JN - FN + TN + KN - GN + HO + MN$	55.1	62.6[b]	7.5	
1-Methyl-4-pyridone	$2D + B + C + 2JN - FN + TN + 2KN - GN + HO$	51.9	57.2[b]	5.3	
Fulvene	$3D + C$	42.8	42.9[a]	0.1	1.1
Cyclopentadiene	$2D + B$	39.7	44.9[a]	5.2	6.5
Cycloheptatriene	$3D + B$	53.8	59.8[c]	6.0	8.1
Furan	$2D + JO + 2KO$	33.2	43.1[a]	9.9	8.9
Isoxazole	$D + DON + KO$	29.2	38.0[d]	8.8	
2-Pyrone	$2D + JO + HO + KO + MO$	43.1	45.6[b]	2.5	
4-Pyrone	$2D + JO + HO + 2KO$	38.9	42.9[b]	4.0	
Tropone	$3D + HO$	48.0	53.8[b]	5.8	7.8
Tropolone	$3D + HO + FO + GO + KO - E$	53.9	61.0[a]	6.1	9.4
2-Methoxytropone	$3D + HO + B + C + E + JO + KO$	63.9	71.0[a]	6.1	
Benzoquinone	$2D + 2HO$	39.6	38.2[a]	−1.2	

[a] Reference 41. [b] This work. [c] Reference 11. [d] Reference 29.

Table VI. Comparison of Various Magnetic Criteria[a]

Compound	$\chi^{nonlocal}$	$\frac{1}{3}\chi_{CC}^{nonlocal}$	$\frac{1}{3}\Delta\chi^{nonlocal}$
Benzene[b]	12.5	12.4	12.2
Pyridine	9.1		9.5[c]
Thiophene	13.0[d]	11.3	11.2
Pyrrole	12.7	11.5	11.5
Furan	9.9	7.9	7.7
Isoxazole	8.8	6.7	7.3
Cyclopentadiene	5.2	5.7	5.9
Tropone	5.8	1.5	−0.3
2-Pyrone	2.5	0.5	0.4
4-Pyrone	4.0	−0.8	−1.0

[a] Calculated from average susceptibilities in Table V, local rules from reference 18 and anisotropies from ref 15, except as noted. [b] $\Delta\chi$ = 62.5 from ref 47. [c] Local rules for nitrogen from J. R. Davidson, A. K. Burnham, B. Siegel, P. Beak, and W. H. Flygare, *J. Am. Chem. Soc.*, **96**, 7394 (1974). [d] Reference 11.

thiophene, pyrrole, and furan to be substantially aromatic, in agreement with recent spectroscopic evidence,[48] while fulvene and the pyrones are effectively nonaromatic.

One of the interesting results in Tables V and VI is the high nonlocal susceptibility of cyclopentadiene, cycloheptatriene, and the tropones. The nonlocal magnetic properties of cyclopentadiene have been rationalized as a manifestation of hyperconjugation,[49] although ring strain might also contribute. The possibility of ring strain causing the entire effect of 6.5 mu seems remote since cyclopentane and cyclopentene have susceptibilities only about 2 mu greater than that predicted by local rules and vinylene carbonate and cyclopentanone fit the rules well. Cycloheptatriene has been shown to have a nonplanar boat structure by microwave spectroscopy[50] and electron diffraction,[51] as well as crystallographic studies of a derivative.[52] Its high nonlocal susceptibility is therefore difficult to analyze in terms of aromatic character unless there is substantial electron delocalization through space in the nonplanar structure, which seems unlikely.

In contrast to the bulk susceptibility, the anisotropy of tropone shows little nonlocal character in spite of the fact that this molecule is essentially planar.[9] It is unlikely that the measured bulk susceptibility of tropone is significantly in error; the bulk susceptibility measured in this work is in good agreement with a previous determination.[53] It is, of course, possible that the Zeeman anisotropy measurements of tropone are in error. Tropone is undoubtedly the most difficult Zeeman measurement yet attempted due to the extremely weak low J lines which were measured. On the other hand, it is also possible that both measurements are correct and that the difference between the two results reflects a real molecular effect other than aromaticity which results in a large average susceptibility but which does not change the anisotropy significantly. An understanding of the magnetic properties of seven-membered rings seems best regarded as an unresolved problem.

Norris et al.[9] have suggested that formal insertion of a carbonyl group into an aromatic ring leads to complete suppression of the nonlocal magnetic susceptibility. On the basis of the present results, it appears, however, that a suppression of 6.5 ± 2.0 mu is observed for this formal transformation (see Table VII). Accordingly, whether the suppression is complete or not will depend on the nonlocal susceptibility of the aromatic ring.

V. Comparison of Magnetic and Thermodynamic Criteria

The relationship of the magnetic determination of aromatic character to previous thermodynamic measures of aromaticity

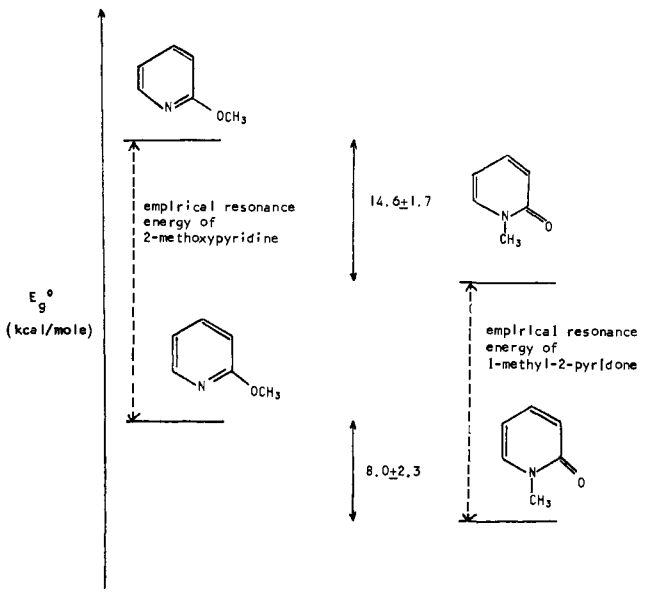

Figure 1. Differences in empirical resonance energies for 1-methyl-2-pyridone and 2-methoxypyridine.

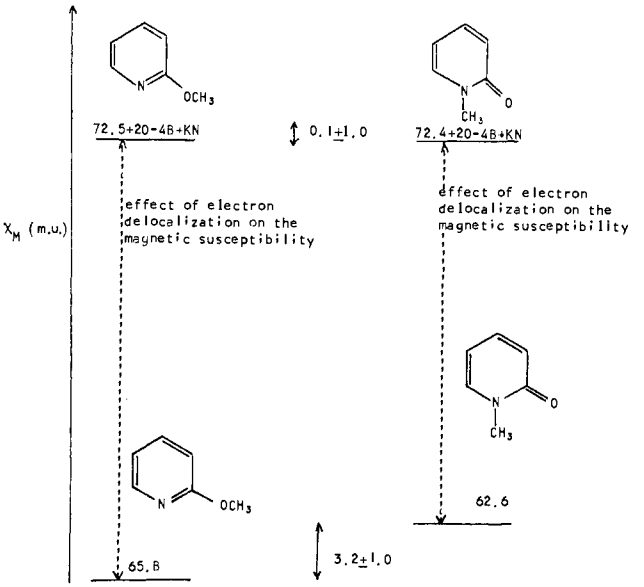

Figure 2. Differences in bulk magnetic susceptibilities for 1-methyl-2-pyridone and 2-methoxypyridine.

Table VII. Effect of Carbonyl Insertion on $\chi^{nonlocal}$

System	Decrease in $\chi^{nonlocal}$
Benzene-tropone	6.7
Phenol-tropolone	5.9
Anisole-methoxytropone	7.8
1-Methylpyrrole-1-methyl-2-pyridone	4.9
1-Methylpyrrole-1-methyl-4-pyridone	7.1
Furan-2-pyrone	7.4
Furan-4-pyrone	5.9

is of considerable interest.[5-10] In an effort to keep our comparisons as experimentally based as possible, we have chosen to use empirical resonance energies for comparisons.[54]

George[55] has recently analyzed the thermodynamic determination of resonance energies in detail. The model dependence of such values is illustrated by the fact that the resonance energy of benzene ranges from 32 to 49 kcal/mol depending on the reaction used for comparison. Using parallel criteria, he finds that the resonance energy of pyridine ranges from 34 to 52 kcal/mol although there is a substantially smaller data base than for benzene. Further, we note that the conclusion that pyridine is as aromatic as benzene according to thermodynamic criteria is by no means unanimous.[54]

Beak et al.[10] attempted to circumvent the problems associated with hypothetical localized models by using the scheme shown in Figure 1 to show that 2-methoxypyridine has a resonance energy 6.6 ± 4.0 kcal/mol greater than 1-methyl-2-pyridone. It was assumed that the difference in the localized polyene structures could be approximated by the difference in energy of 1-methyl-2-piperidone and 2-methoxy-3,4,5,6-tetrahydropyridine.[15] With the magnetic susceptibilities of the reference compounds in Table I and the Hameka parameters, we are able to make an analogous comparison by the bulk susceptibility criterion, which is shown in Figure 2. Using the same localized models, we find that $\chi^{nonlocal}$ for 2-methoxypyridine is 3.2 ± 2.0 mu greater than that of 1-methyl-2-pyridone.

We have chosen benzene as the reference compound for both magnetic and thermodynamic criteria. If an intermediate value of 36 kcal/mol is used for the resonance energy of benzene, we find that by the thermodynamic criterion the difference between 2-methoxypyridine and 1-methyl-2-pyridone corresponds to 18 ± 11% of the nonlocal character of benzene. Using $\chi^{nonlocal}$ of benzene equal to 12.5 mu, we find the difference in aromatic character for the same isomers is 26 ± 16% according to the magnetic criterion. The close correspondence between the magnetic and thermodynamic criteria for the pyridine–pyridone comparison should lend credence to the semiquantitative use of both approaches.

However, it should be recognized that cases which do not correlate do exist. For example, cyclopentadiene, which has been shown by both the Zeeman and present work to have magnetic properties consistent with electron delocalization of the aromatic type, structurally does not fit the formal requirements for an aromatic comund and has only a nominal resonance energy.[56] Moreover, it at least is debatable whether a more quantitative measure of aromatic character is desirable. The concept has been extraordinarily fruitful in both its qualitative and semiquantitative forms, and it may be that little would be gained by more rigorous definitions. In any case, it is clear that resolution of the fundamental problem of model selection must be achieved if any quantitative approach is to gain general acceptance.

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