Derivatives of Molecular Valence as a Measure of Aromaticity

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Derivatives of the molecular valence have been calculated ab initio within the new non-finite-difference approach elaborated on earlier for the global hardness and the Fukui function indices. The group of 10 five-membered-ring molecules C_4H_4X has been chosen for a test, using the exaltation of the total magnetic susceptibility (Λ) as a reference measure of their aromaticity. An excellent correlation has been found between the molecular valence derivatives in the nucleophilic regime and the exaltation Λ, for both the aromatic and antiaromatic molecules. Calculation of the valence derivatives provides an absolute measure of aromatic character that is not directly dependent on the size of the molecule and does not require adopting any standard reference molecule.

Introduction

Aromaticity, the property resulting from cyclic conjugation, is an important concept in organic chemistry.[1] Properties implying high aromaticity, i.e., high stability, low reactivity, and sustained induced ring current, are commonly characterized by a number of criteria: geometric (bond length alternation, bond order, and ring current indices), energetic (stabilization energies), and magnetic (^{1}H NMR chemical shifts, diamagnetic susceptibility anisotropy and exaltation, and most recently the nucleus independent chemical shifts, NICS[2]). The magnetic criteria of aromaticity are of particular interest in their relation with the molecular electron density. They stem from the model of interatomic ring currents induced in conjugated cyclic molecules by external magnetic fields as proposed by Pauling.[3] Molecules that sustain the diamagnetic ring current induced by an external magnetic field are termed diatropic and classified as aromatic. By contrast, molecules are antiaromatic if the ring currents are paramagnetic (paratropic systems). An interesting magnetic manifestation of aromaticity is represented by the exaltation of the total magnetic susceptibility (Λ) introduced by Dauben Jr.[4] and extended by Kutzelnigg et al.[5] and von Ragué Schleyer et al.[6] The exaltation of the total magnetic susceptibility Λ is by definition the difference between the magnetic susceptibility of a cyclic conjugated system and that of hypothetical cyclic system with localized double bonds in which the ring current vanishes.[1] For an aromatic ring Λ is negative (diamagnetic), and for an antiaromatic ring Λ is positive (paramagnetic). The diamagnetic susceptibility exaltation is uniquely associated with aromaticity;[7] however, it is highly dependent on the ring size and requires suitable calibration standards.[2]

A new group of criteria of aromaticity directly related to the electronic structure has been formulated not long ago by Parr and co-workers.[8,9] The value of the HOMO−LUMO energy separation, Δ_{HL}, may serve as an index of structural stability[10] and reactivity whenever the HOMO and/or LUMO orbital take part in driving chemical reactions.[11] Parr et al. have demonstrated the linear correlation between Δ_{HL} and resonance energy per π-electron (REPE) for a range of carbocyclic and heterocyclic molecules.[9] The HOMO−LUMO energy gap represents twice the absolute chemical hardness of a molecule; the relative hardness is defined as the difference between the value of absolute hardness for a given molecule and for the corresponding acyclic reference structure. Compounds with large relative hardness are expected to be aromatic, and those with very small relative hardness are predicted to be antiaromatic.

In this paper the aromaticity of the series of five-membered heterocycles C_4H_4X is revisited. On the basis of several aromaticity criteria, the molecules in the series can be ordered in terms of decreasing aromaticity and increasing antiaromaticity for X being CH^-, S, O, SiH^-, PH, CH_2, AlH, BH, SiH^+, CH^+.[6] The aim of this work is to explore if the theoretical as well as computational tools now developed in the density functional theory can be further applied to the description of trends in aromaticity in this classic group. First, the absolute hardness ($^1/_2\Delta_{HL}$) is tested as a measure of the aromaticity of the group members. Second, the new prospective measures of the aromaticity are derived from the concept of molecular valence analyzed in terms of the DFT method, i.e., including its derivatives with respect to the number of electrons. These derivatives have been calculated by the newly developed nonfinite difference approximation for the derivatives with respect to the number of electrons within a Hartree−Fock scheme.[12] The magnetic susceptibility exaltation Λ has been chosen as a reference as its high correlations with the energetical, geometric, and other magnetic criteria are well established.[2,6,7]

Calculation of the Global Reactivity Descriptors in the DFT

Density functional theory (DFT)[13] has provided solid support for traditional chemical ideas of electronegativity[14] and hardness,[15] and it has also introduced new descriptors such as hardness and softness kernels,[16] global and local softness,[17] and the Fukui function.[18] Global and local descriptors in DFT are typically the derivatives with respect to the total number of

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electrons at constant external potential, $(\partial/\partial N)_{\nu(r)}$.[19] The derivatives at some integral value N_0 will in general have different values on the right-hand ($N_0 + \delta$) and on the left-hand side ($N_0 - \delta$). Hence, three sets of indices result: the right-hand-side derivative (reactivity toward nucleophilic reagent), the left-hand-side derivative (reactivity toward electrophilic reagent), and the average (reactivity toward an radical reagent). Electronegativity and global hardness in the DFT framework are the first and the second derivatives, respectively, of the electronic energy with respect to N at a "frozen" geometry of the molecule.

In the calculation scheme for derivatives with respect to N in the framework of the Hartree−Fock approximation proposed by Balawender and Komorowski,[12] electronegativity χ is equal to

$$\chi = -\left(\frac{\partial E}{\partial N}\right)_{\nu(r)} = \begin{cases} \chi^{+} = -e_{\mathrm{LUMO}} \\ \chi^{-} = -e_{\mathrm{HOMO}} \end{cases} \tag{1}$$

where e_{HOMO} and e_{LUMO} are frontier orbital energies; (+) and (−) denote the right-hand ($N_0 + \delta$) and left-hand-side ($N_0 - \delta$) derivatives, respectively. The global hardness is thereby expressed as

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{\nu(r)} = \frac{1}{4}J_{\mathrm{FMO}} + \sum_{i}^{\mathrm{vir}}\sum_{i}^{\mathrm{occ}} U_{ij}[2(i, j|\mathrm{FMO}, \mathrm{FMO}) - (i, \mathrm{FMO}|j, \mathrm{FMO})] \tag{2}$$

$J_{\mathrm{FMO}} = (\mathrm{FMO,FMO|FMO,FMO})$ is Coulomb integral for the frontier orbital (FMO), and $(ij|kl)$ stands for a two-electron repulsion integral in MO basis.

The **U** matrix is by definition[12] related to the derivative of the molecular orbital coefficients matrix **C**:

$$\left(\frac{\partial \mathbf{C}}{\partial N}\right)_{\nu(r)} = \mathbf{CU} \tag{3}$$

A calculation scheme for the elements of the **U** matrix has been elaborated; U_{ij} values are directly available from a simple ab initio SCF calculation for a neutral molecule.[12] The result for the electronegativity (eq 1) is identical to the molecular orbital theory approach using Koopmans' theorem; the results for hardness (eq 2) represent a remarkable extension of earlier simplified models. The global hardness in the finite-difference approximation is simply the energy gap between the HOMO and LUMO;[13] in a more refined consideration global hardness was related to the Coulomb integral ($^1/_2 J_{\mathrm{FMO}}$).[20,21] The hardness given by eq 2 contains an additional term corresponding to the relaxation of the electron system, directly resulting from the adopted approximation for $(\partial/\partial N)_{\nu(r)}$ (eq 3). The same method is now applied to the derivatives of another chemically significant quantity, the molecular valence.

Molecular Valence and Its Derivatives

The density matrix in the LCAO method may be formulated as

$$\mathbf{P} = \mathbf{CnC}^{\mathrm{T}} \tag{4}$$

where the element n_i of the diagonal matrix **n** represents the MO occupation (2 for an occupied MO and 0 for a virtual MO for a closed-shell system). The bond order (I_{AB}) has been defined by Mayer[22] as

$$I_{AB} = \sum_{\mu\in A}\sum_{\nu\in B}(\mathbf{PS})_{\mu\nu}(\mathbf{PS})_{\nu\mu} \tag{5}$$

where **S** is the overlap matrix. The definition of the bond order has been explored for the determination of atomic (V_{A})[22] and molecular valence (V_{M}):[23,24]

$$V_{\mathrm{A}} = \sum_{A\neq B} I_{AB} \qquad V_{\mathrm{M}} = \frac{1}{2}\sum_{A} V_{A} \tag{6}$$

The molecular valence can be rewritten in following way:

$$V_{\mathrm{M}} = \frac{1}{2}\sum_{A}\sum_{A\neq B}\sum_{\mu\in A}\sum_{\nu\in B}(\mathbf{PS})_{\mu\nu}(\mathbf{PS})_{\nu\mu} = \frac{1}{2}\left(\sum_{i}^{\mathrm{MO}} n_{\mathrm{i}}^{2} - \sum_{A}\sum_{\mu\in A}\sum_{\nu\in A}(\mathbf{PS})_{\mu\nu}(\mathbf{PS})_{\nu\mu}\right) = \frac{1}{2}\left(\sum_{i}^{\mathrm{MO}} n_{\mathrm{i}}^{2} - \sum_{A} I_{\mathrm{AA}}\right) \tag{7}$$

The set of above quantities represents a recent generalization of well-established chemical concepts. The index I_{AB} has integer values in the specific case of some homonuclear diatomics (H_2, N_2, and F_2) treated at the minimal basis level. The deviation from the integer values may be due to the nonorthogonality, to delocalization effects, and especially to the partial ionic character of the bonds formed between two atoms of different electronegativities. The V_{A} values for a given atom type differ from molecule to molecule, but they are always very close to classical valence values of this atom.[25] The V_{M} for closed-shell systems is equal to the difference between the total number of electrons and the sum of all one-center bond orders (I_{AA}), which have no chemical significance.

Using eq 7, the molecular valence may be transformed into the sum of orbital valences V_i:

$$V_{\mathrm{M}} = \frac{1}{2}\sum_{i}^{\mathrm{MO}}\left(n_{\mathrm{i}}^{2} - \sum_{A}\sum_{\mu\in A}^{\mathrm{AO}}\sum_{\nu\in A}^{\mathrm{AO}}(\mathbf{P}^{i}\mathbf{S})_{\mu\nu}(\mathbf{PS})_{\nu\mu}\right) = \sum_{i}^{\mathrm{MO}} V_{\mathrm{i}} \tag{8}$$

where $(\mathbf{P}^{i})_{\mu\nu} = c_{i\mu}n_i c_{i\nu}$ and by definition[24]

$$V_{i} = \frac{1}{2}\left(n_{\mathrm{i}}^{2} - \sum_{A}\sum_{\mu\in A}^{\mathrm{AO}}\sum_{\nu\in A}^{\mathrm{AO}}(\mathbf{P}^{i}\mathbf{S})_{\mu\nu}(\mathbf{PS})_{\nu\mu}\right) \tag{9}$$

The MO valence has the following trends: (i) zero or low values for core, antibonding, and lone pair molecular orbitals; (ii) high values for strongly bonding molecular orbitals.

When the approximation introduced for the $(\partial\mathbf{C}/\partial N)_{\nu(r)}$ derivative in eq 3 is applied to the derivative of the valence, the analysis must proceed step by step. The derivative of the density matrix with respect to N at "frozen" geometry is[12]

$$\left(\frac{\partial \mathbf{P}}{\partial N}\right)_{\nu(r)} = \mathbf{C}\left(\left(\frac{\partial \mathbf{n}}{\partial N}\right)_{\nu(r)} + \mathbf{Un} - \mathbf{nU}\right)\mathbf{C}^{\mathrm{T}} = \mathbf{P}^{f} + \mathbf{P}^{U} \tag{10}$$

where

$$\mathbf{P}^{f} = \mathbf{C}\left(\frac{\partial \mathbf{n}}{\partial N}\right)_{\nu(r)}\mathbf{C}^{\mathrm{T}} \qquad \mathbf{P}^{U} = \mathbf{C}(\mathbf{Un} - \mathbf{nU})\mathbf{C}^{\mathrm{T}} \tag{11}$$

The $\mathbf{P}^{f}$ matrix accounts for the effect of changing MO occupations with "frozen" molecular orbital coefficients, and $\mathbf{P}^{U}$ represents the MO relaxation contribution for the frozen MO occupations. The elements of the diagonal matrix **f** are all equal to zero, except the element for the FMO which is equal to unity.

$$f_i = \begin{cases} 1 & i = \mathrm{FMO} \\ 0 & i \neq \mathrm{FMO} \end{cases} \tag{12}$$

The derivative of molecular valence (eq 8) becomes after rearranging

$$\left(\frac{\partial V_M}{\partial N}\right)_{\nu(r)} = \sum_{i}^{\mathrm{MO}} f_i n_i - \frac{1}{2}\sum_{A}\left(\frac{\partial I_{AA}}{\partial N}\right)_{\nu(r)} = \sum_{i}^{\mathrm{MO}} f_i n_i - \sum_{A}\sum_{\mu\in A}^{\mathrm{AO}}\sum_{\nu\in A}^{\mathrm{AO}}\left(\left(\frac{\partial \mathbf{P}}{\partial N}\right)_{\nu(r)}\mathbf{S}\right)_{\mu\nu}(\mathbf{PS})_{\nu\mu} \tag{13}$$

The derivative of an orbital valence (eq 9) is

$$\left(\frac{\partial V_i}{\partial N}\right)_{\nu(r)} = f_i n_i - \frac{1}{2}\sum_{A}\sum_{\mu\in A}^{\mathrm{AO}}\sum_{\nu\in A}^{\mathrm{AO}}\left(\left(\left(\frac{\partial \mathbf{P}^i}{\partial N}\right)_{\nu(r)}\mathbf{S}\right)_{\mu\nu}(\mathbf{PS})_{\nu\mu} + (\mathbf{P}^i\mathbf{S})_{\mu\nu}\left(\left(\frac{\partial \mathbf{P}}{\partial N}\right)_{\nu(r)}\mathbf{S}\right)_{\nu\mu}\right) \tag{14}$$

The MO valence derivatives for virtual orbitals vanish, except for the LUMO in the case of a nucleophilic attack (+ derivative). For core orbitals $(\partial V_i/\partial N)_{\nu(r)}$ will be zero or very close to this value. Due to restricted occupation in the HF method

$$(\mathbf{P}^f)_{\mu\nu} = \sum_{i}^{\mathrm{MO}} c_{\mu i} f_i c_{\nu i} = c_{\mu\mathrm{FMO}}c_{\nu\mathrm{FMO}} \tag{15}$$

Using eqs 10, 11, and 15, the molecular valence derivative expression (eq 13) is finally

$$\left(\frac{\partial V_M}{\partial N}\right)_{\nu(r)} = f_{\mathrm{FMO}}n_{\mathrm{FMO}} - \sum_{A}\sum_{\mu\in A}^{\mathrm{AO}}\sum_{\nu\in A}^{\mathrm{AO}}\Big(\sum_{\lambda}^{\mathrm{AO}} c_{\mu\mathrm{FMO}}c_{\lambda\mathrm{FMO}}S_{\lambda\nu}\Big)(\mathbf{PS})_{\nu\mu} - \sum_{A}\sum_{\mu\in A}^{\mathrm{AO}}\sum_{\nu\in A}^{\mathrm{AO}}(\mathbf{P}^U\mathbf{S})_{\mu\nu}(\mathbf{PS})_{\nu\mu} \tag{16}$$

For a nucleophilic attack eq 16 becomes

$$\left(\frac{\partial V_M}{\partial N}\right)^{+}_{\nu(r)} = -\sum_{A}\sum_{\mu\in A}\sum_{\nu\in A}\Big(\sum_{\lambda}^{\mathrm{AO}} c_{\mu\mathrm{LUMO}}c_{\lambda\mathrm{LUMO}}S_{\lambda\nu}\Big)(\mathbf{PS})_{\nu\mu} - \sum_{A}\sum_{\mu\in A}\sum_{\nu\in A}(\mathbf{P}^{U^+}\mathbf{S})_{\mu\nu}(\mathbf{PS})_{\nu\mu} \tag{17}$$

or using eqs 8 and 14

$$\left(\frac{\partial V_M}{\partial N}\right)^{+}_{\nu(r)} = \left(\frac{\partial V_{\mathrm{LUMO}}}{\partial N}\right)^{+}_{\nu(r)} + \sum_{i}^{\mathrm{occ}}\left(\frac{\partial V_i}{\partial N}\right)^{+}_{\nu(r)} \tag{18}$$

The first term represents the contribution to the derivative from the subspace of virtual MO's. The second is contribution from occupied MO's. For an electrophilic attack

$$\left(\frac{\partial V_M}{\partial N}\right)^{-}_{\nu(r)} = 2 - \sum_{A}\sum_{\mu\in A}\sum_{\nu\in A}\Big(\sum_{\lambda}^{\mathrm{AO}} c_{\mu\mathrm{HOMO}}c_{\lambda\mathrm{HOMO}}S_{\lambda\nu}\Big)(\mathbf{PS})_{\nu\mu} - \sum_{A}\sum_{\mu\in A}\sum_{\nu\in A}(\mathbf{P}^{U^-}\mathbf{S})_{\mu\nu}(\mathbf{PS})_{\nu\mu} \tag{19}$$

or

$$\left(\frac{\partial V_M}{\partial N}\right)^{-}_{\nu(r)} = \sum_{i}^{\mathrm{occ}}\left(\frac{\partial V_i}{\partial N}\right)^{-}_{\nu(r)} \tag{20}$$

It is instructive to analyze these results when simplified via Koopmans' theorem (matrix $\mathbf{U} = \mathbf{0}$). The value of the left-hand-side derivative reduces to the valence of the HOMO orbital:

$$\left(\frac{\partial V_M}{\partial N}\right)^{-}_{\nu(r)} \cong V_{\mathrm{HOMO}} \tag{21}$$

For addition of electrons one obtains in the same simplifying scheme

$$\left(\frac{\partial V_M}{\partial N}\right)^{+}_{\nu(r)} \cong -\sum_{A}\sum_{\mu\in A}^{\mathrm{AO}}\sum_{\nu\in A}^{\mathrm{AO}}\Big(\sum_{\lambda}^{\mathrm{AO}} c_{\mu\mathrm{LUMO}}c_{\lambda\mathrm{LUMO}}S_{\lambda\nu}\Big)(\mathbf{PS})_{\nu\mu} = 2\left(\frac{\partial V_{\mathrm{LUMO}}}{\partial N}\right)^{+}_{\nu(r)} \tag{22}$$

The lack of symmetry between the two derivatives (±) is striking. Comparing eq 22 and eq 18 leads to an interesting conclusion approximately valid only for the right-hand-side derivative:

$$\left(\frac{\partial V_{\mathrm{LUMO}}}{\partial N}\right)^{+}_{\nu(r)} \cong \sum_{i}^{\mathrm{occ}}\left(\frac{\partial V_i}{\partial N}\right)^{+}_{\nu(r)} \tag{23}$$

Comparing this result to eq 21 fully exposes the unsymmetry between the two sets of derivatives of the molecular valence (±), applicable for the nucleophilic and electrophilic attack, respectively.

Calculations and Results

The geometry of all molecules was optimized at the MP2/6-31G* ab initio level with the Gaussian 94 package[26] running on the CRAY J916/8-1024 computer of the Brussel's Free Universities Computer Center. All calculations for molecules were performed at their singlet states in accordance with previous works.[6] Input data for calculations of the **U** matrix have been obtained at the RHF/6-31G* ab initio level with the GAMESS package[27] running on the same computer. The magnetic susceptibility exaltations calculated with the IGLO method[28] and basis set II were taken from ref 4.

Neither the global electronegativity (eq 1) nor the global hardness as defined by eq 2 shows correlation with the aromaticity index. In Table 1 the average values for (+) and (−) derivatives are reported. The calculated HOMO−LUMO gap (Δ_{HL}) known to produce linear correlation with standard quantitative aromaticity criteria in many groups of molecules[8,9,29] reveals a remarkable linear correlation with Λ for the com-

TABLE 1: Calculated Magnetic Susceptibility Exaltations Λ [ppm], Average Electronegativity, the Half of LUMO−HOMO Energy Gap ($\Delta_{\mathrm{HL}}/2$), and Average Hardness (All in eV)

X	sym	Λ[a]	χ	$\Delta_{\mathrm{HL}}/2$	η
CH^+	C_{2v}	32.6	10.711	4.226	1.544
SiH^+	C_{2v}	13.2	10.048	4.478	1.437
BH	C_{2v}	12.8	3.581	4.814	1.427
AlH	C_{2v}	11.2	3.642	4.690	1.281
CH_2	C_{2v}	−2.4	2.207	5.929	1.395
PH	C_s	−3.3	2.969	5.668	1.306
SiH^-	C_s	−7.7	−3.372	4.705	1.313
O	C_{2v}	−9.1 (−8.9)	1.962	6.528	1.549
S	C_{2v}	−10.01 (−13)	2.574	6.139	1.399
NH	C_{2v}	−12.11 (−10.4)	1.178	6.640	1.498
CH^-	D_{5v}	−17.2	−6.085	6.725	1.321

[a] Experimental estimate in parentheses, ref 3.

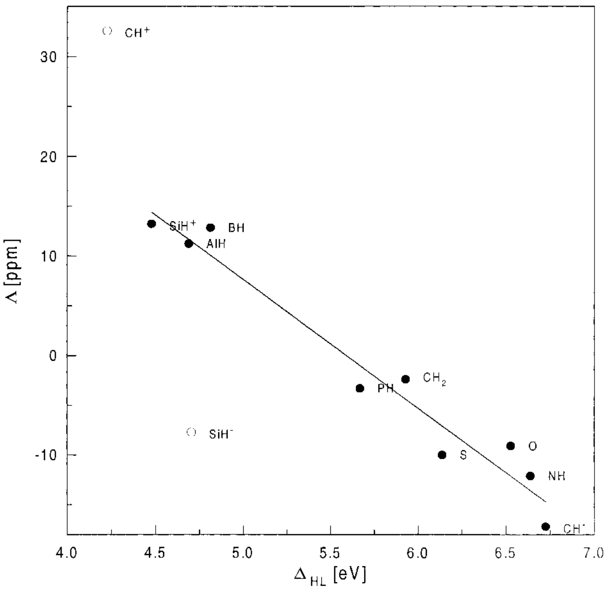

Figure 1. Plot of the magnetic susceptibility exaltations Λ versus Δ_{HL} for C_4H_4X rings. The correlation coefficient of the regression line ($\Lambda = -12.93\Delta_{HL} + 72.28$) is $R = 0.98$ (empty circles, compounds omitted in correlation).

pounds under study in this work (Figure 1, $R = 0.98$; the cyclopentadienyl cation and silolyl anion have been omitted). $^1/_2\Delta_{HL}$ for antiaromatic molecules is around 4.5 eV including the cyclopentadienyl cation, which is, however, inconsistent with the exceedingly high Λ value for this molecule. $^1/_2\Delta_{HL}$ for the silolyl anion, aromatic by Λ and other criteria (see ref 6), is in the range typical for antiaromatic compounds. High absolute hardness ($^1/_2\Delta_{HL}$) is associated with high stability and low reactivity, typical features of aromatic compounds. Also, the dependence of the paramagnetic term upon the energy gap has been reported elsewhere.[30]

The total valencies for the molecules (V_M) as well as those for HOMO orbital (V_{HOMO}) are reported in Table 2. All V_{HOMO}'s are around 1 with the notable exception of the silolyl anion. Neither V_{HOMO} nor V_M parallels the trends given by Λ the chosen measure of aromaticity.

Properties of $(\partial V_M/\partial N)^+_{\nu(r)}$ and $(\partial V_M/\partial N)^-_{\nu(r)}$ appear distinctly different (eqs 17−23); this has been further tested through the numerical results. The plot of left-hand-side derivative $(\partial V_M/\partial N)^-_{\nu(r)}$ versus magnetic susceptibility exaltations Λ is shown in Figure 2. As expected from eq 21, the derivative shows a rather weak variation within the group of molecules; the approximate character of eq 21 is clearly seen in the data for $(\partial V_M/\partial N)^-_{\nu(r)}$ and V_{HOMO} in Table 2.

In contrast to $(\partial V_M/\partial N)^-_{\nu(r)}$, the right-hand side derivative of the molecular valence $(\partial V_M/\partial N)^+_{\nu(r)}$ shows remarkable correlation with the magnetic susceptibility exaltations Λ (Figure 3, $R = 0.98$; the cyclopentadienyl cation omitted). Better still, a plot of the magnetic susceptibility exaltations Λ versus the sum of

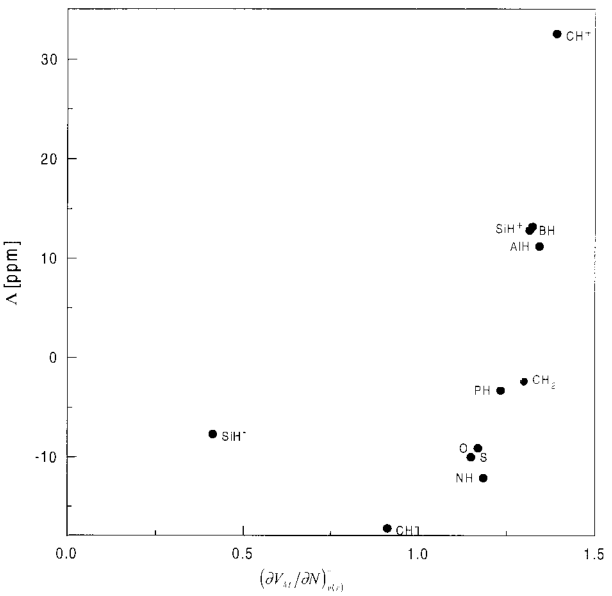

Figure 2. Plot of the magnetic susceptibility exaltations Λ versus $(\partial V_M/\partial N)^-_{\nu(r)}$ for C_4H_4X rings.

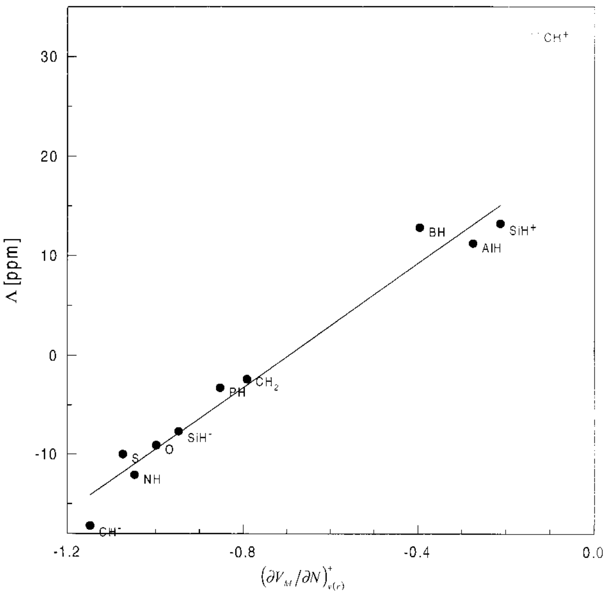

Figure 3. Plot of the magnetic susceptibility exaltations Λ versus $(\partial V_M/\partial N)^+_{\nu(r)}$ for C_4H_4X rings. The correlation coefficient of the regression line ($\Lambda = 31.16(\partial V_M/\partial N)^+_{\nu(r)} + 21.65$) is $R = 0.98$ (empty circles, compounds omitted in correlation).

TABLE 2: Molecular Valency and Its Right- and Left-Side Derivatives

X	V_M	V_{HOMO}	$(\partial V_M/\partial N)^-$	$(\partial V_M/\partial N)^+$	$(\partial V_{LUMO}/\partial N)^+$	$\Sigma_i^{occ}(\partial V_i/\partial N)^+$
CH^+	11.349	1.027	1.392	−0.134	−0.281	0.147
SiH^+	11.546	1.015	1.324	−0.212	−0.208	−0.004
BH	11.594	1.015	1.316	−0.395	−0.289	−0.106
AlH	11.459	1.026	1.344	−0.274	−0.172	−0.102
CH_2	12.436	0.989	1.299	−0.791	−0.527	−0.264
PH	11.529	0.976	1.234	−0.852	−0.533	−0.319
SiH^-	11.633	0.431	0.413	−0.947	−0.544	−0.403
O	10.482	0.953	1.170	−0.998	−0.609	−0.389
S	10.729	0.928	1.150	−1.074	−0.629	−0.445
NH	11.486	0.924	1.185	−1.047	−0.655	−0.392
CH^-	12.138	0.809	0.912	−1.148	−0.567	−0.581

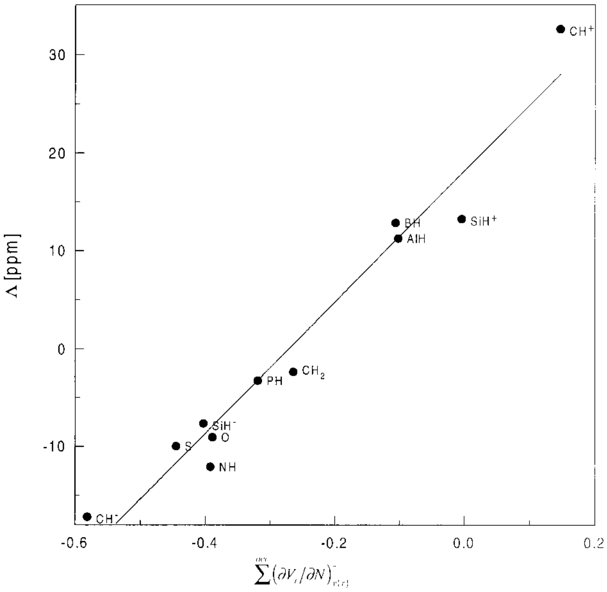

Figure 4. Plot of the magnetic susceptibility exaltations Λ versus $\sum_i^{\text{occ}}(\partial V_i/\partial N)^+_{\nu(r)}$ for C_4H_4X rings. The correlation coefficient of the regression line ($\Lambda = 67.01\sum_i^{\text{occ}}(\partial V_i/\partial N)^+_{\nu(r)} + 18.13$) is $R = 0.98$.

the right-hand-side derivatives of the occupied MO valencies $\sum_i^{\text{occ}}(\partial V_i/\partial N)^+_{\nu(r)}$ shows an excellent linear correlation that extends from the highly antiaromatic singlet cyclopentadienyl cation to the highly aromatic cyclopentadienyl anion (Figure 4, $R = 0.98$). The calculated Λ (column 3 in Table 1) can be confronted with Λ given by the linear correlation in Figure 4. The cyclopentadienyl cation is the most antiaromatic molecule ($\Lambda = 32.6$, predicted 28 ppm); the predicted anitaromaticity of the alumol and the borol is almost equal to (11 ppm) the calculated values being 11.2 and 12.8, respectively. Cyclopentadiene and phosphole are "borderline" aromatics[6] (by Λ). They may be classified as nonaromatic compounds, as suggested by other analyses.[9] The aromaticity order shown by the $\sum_i^{\text{occ}}(\partial V_i/\partial N)^+_{\nu(r)}$ derivative is furan < pyrrole < thiophene, which corresponds to the estimated experimental values of Λ rather than to calculated ones (Table 1).

Discussion and Conclusion

Of the two available measures of global hardness, $^1/_2\Delta_{\text{HL}}$ and η, only $^1/_2\Delta_{\text{HL}}$ shows general correlation with aromaticity. Analytical hardness η shows a correlation with Λ for the aromatic group only, X being O, S, NH, and CH^- (Table 1). This observation confirms a much different character of both measures of hardness;[12] the meaning of the analytical hardness η (eq 2) is yet to be discovered. It is quite possible that subtleties of η are masked by the J_{FMO} integral dominating analytical hardness η (eq 2).

The exaltation of the total magnetic susceptibility (Λ) is by definition the difference between the magnetic susceptibility of a conjugated system and that of the corresponding cyclic system with localized double bonds ($\Delta\chi$). The level of conjugation is directly related to the molecular valence, so Λ may be roughly proportional to the difference between the molecular valence of the conjugated system and the molecular valence of the cyclic system with localized double bonds (ΔV_{M}). It is quite interesting to see in the results of this work that this difference is well approximated by the derivatives of the valence with respect to the number of electrons at frozen geometry.

A very interesting result of this work is the distinct difference between the (+) and (−) derivatives of molecular valence, in describing the aromaticity. The left-hand-side (−) derivative describes the effect of the electrophilic attack (eqs 19−21). The major part of this index is the valence of the HOMO orbital, as shown by eq 21, its validity being confirmed by the data in Table 2. Typically, the HOMO orbital is bonding in nature; hence, these derivatives do not show any significant variation even for highly different molecules. Calculated values of $(\partial V_M/\partial N)^-_{\nu(r)} \cong V_{\text{HOMO}}$ are all around 1.2 (except for the silolyl anion), corresponding to fact that the HOMO orbital is delocalized and has strongly bonding nature. Departure of the silolyl anion from that trend can be readily explained. The ground-state conformation of the silolyl anion is a pyramidal C_s structure, and the electron delocalization is significantly reduced in the C_s as compared to the to the C_{2v} form.[31] The planar form is more aromatic, but the gain in aromaticity is insufficient to overcome the energy required for planarization. Hence, the character of the HOMO orbital (localized on Si) is more like the silicon lone pair orbital rather than a bonding molecular orbital; this is reflected by the left-hand-side derivative equal 0.413, much less than for a molecular bonding orbital (Table 2). (In the PH derivative of the same symmetry the HOMO is not localized on the phosphorus atom.)

The right-hand-side (+) derivative of molecular valence with respect to *N* measures reactivity toward a nucleophilic reagent (the increasing number of electrons). The data in Table 2 confirm the rough validity of eq 22 for the aromatic molecules only; it is obviously inapplicable for the antiaromatics. The peculiar character of the sum $\sum_i^{\text{occ}}(\partial V_i/\partial N)^+_{\nu(r)}$ in describing the aromatic, as well as antiaromatic character of a molecule is striking. The sum may be considered as a "valence probe": it reflects the changes in valences of all MO's (whose occupancies are not altered) upon disturbance by the addition of an electron to the empty LUMO orbital. This "valence probe" can only be applied to the nucleophilic attack. When electrons are extracted from the system's HOMO (electrophilic attack), the original electron system that could produce the probe effect is disintegrated by the drastic change in HOMO's occupancy and the probe system collapses.

Changing the valence of LUMO is a gross effect that accounts for the large part of the change in overall valence. Variation in $\sum_i^{\text{occ}}(\partial V_i/\partial N)^+_{\nu(r)}$ is certainly a more subtle effect, yet seems to contain the essence of the aromatic properties. Analysis of that effect became only possible as a result of the novel approximation for the derivative of LCAO coefficients, eq 3, for which this present work provides further support. Two facts are important with respect of aromaticity. (i) The "valence probe" of aromaticity seem to describe properly full spectrum of molecules, aromatic, and antiaromatic as well as nonaromatic. (ii) No reference is needed and the probe can be applied to any molecule. Working with the formulas for orbital, atomic, and molecular valences may open a way to applications of the "valence probe" to a reasonably chosen part of any molecule as well. This aspect of the "valence probe" makes it worth further investigation, despite the relative complexity of the computational apparatus.

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