Average Deviation from Ideal Bond Order as a Measure for Aromaticity. AM1 Commuted Aromatic Properties of Five-Membered C_4H_4X Ring Systems

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Average bond order deviation from that in an ideal aromatic system was proposed as a parameter for evaluation of aromaticity in general. The validity of this approach was examined by studying a series of aromatic five-membered heterocycles. The geometries and bond orders were computed with AM1 semiempirical method. The usefulness of AM1 semiempirical method for computation of these parameters was also discussed.

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Introduction.

Though the formulation of a simple definition of the term "aromatic character" or "aromaticity" presents certain difficulties, from the stand point of organic chemistry it may be said that the most important and distinguishing characteristics of the aromatic compound is associated with its particularly diminished unsaturation and with the pronounced tendency of these substances to form and preserve type [1]. There is no generally acceptable definition of aromaticity but it is generally discussed in terms of energetic, structural and magnetic properties of the molecules. Aromatic stabilization energies as one of the criterion for aromaticity can be obtained both from experimental measurements and from computational studies [1,2]. The C-C bond lengths in aromatic compounds tend to have uniform length midway between those exhibited by single and double bonds. Thus bond length has been also used as a test for aromaticity [3]. Aromatic compounds also exhibit magnetic susceptibility anisotropies [4] and diamagnetic susceptibilities [5].

In this study we will present a very simple approach to determine relative aromaticity for a comprehensive set of five-membered C_4H_4X heterocycles by comparing average bond order deviation from an ideal aromatic system.

Computational Methodology.

All semiempirical calculations were performed on a DEC 7620 computer. Chem-3D Plus on a Macintosh IIfx was used as a graphical interface for drawing and visualizing all structures and for preparing input files for MOPAC [6]. The AM1 [7] semiempirical method with bonds [8] routine was used for optimizating geometries and to compute the bond orders.

Results and Discussion.

Experimentally, it is a problem to obtain results for a wide variety of molecules that are 4π and 6π system. Computational approaches enable 4π electron antiaromatic compounds (X = CH^+, SiH^+, and AlH) and 6π electron aromatic compounds (X = PH, SiH^-, O, S, NH, and CH^-) to be examined together. It is well known that magnetic susceptibility depends on the ring size [5], so we have chosen five-membered heterocycles because their shape is nearly uniform. The geometries of the heterocycles are computed by AM1 semiempirical methods. As one can expect, the accuracy of predicted structures for the five-membered heterocycles depends on AM1 parameterization. The structural parameters for cyclopentadiene, furan, and pyrrole are reproduced very well, deviating from the experimental value less than 2% (Table 1).

Table 1

AM1 Computed (A) and Experimental (B) Bond Distances for Five-Membered Heterocycles

X		C1C2	C2C3	C1X
CH2	A	1.359	1.472	1.509
	B[9]	1.342	1.465	1.505
O	A	1.380	1.448	1.395
	B[9]	1.361	1.431	1.369
NH	A	1.402	1.435	1.392
	B[9]	1.382	1.416	1.370
S	A	1.377	1.432	1.672
	B[9]	1.370	1.423	1.714
PH	A	1.349	1.464	1.703
	B[10]	1.343	1.438	1.783

Because AM1 method does not include *d* orbitals it is not surprising that the structures for thiophene and phosphole are not reproduced well with regard to C-X bond distance. The bond distances deviate 0.04-0.08 Å from the experimental values. First,we want to examine how well the AM1 and MP2 computed homodesmic stabilization energies correlate. The homodesmic reaction (Figure 1) was used to evaluate the aromatic stabilization energies. Because the reference compounds are computed with the same semiempirical method the strain effect should be canceled to a large extent. The Magnetic susceptibility

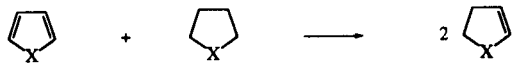

Figure1. The chemical transformation for computation of aromatic stabilization energies.

exaltations and anisotropies are taken from Schleyer and coworkers [2]. They are computed by IGLO on MP2/6-31G* geometries. The Julg parameter *A* [11] defines the degree of aromaticity in terms of the deviation of the individual C-C bond lengths from the mean of C-C bond length computed by following the equation (a). In this

$$A = 1-(255/n)\Sigma(1-r_i/r)^2 \qquad (a)$$

equation *r* is the mean C-C bond length, r_i refers to the C-C bond distance in the examined molecule, *n* is the number of C-C bonds (three in the C_4H_9X systems). *A* = 1 for benzene and the cyclopentadienyl ion. Semiempirical factor 225 provides an aromaticity scale in which *A* = 0 for Kekulé form of benzene with C-C of 1.33 and 1.52 Å.

The computed bond order values for five-membered heterocycles are quite different than the theoretical values for an ideal aromatic system. As mentioned above, the computed bond distances for some heterocycles are quite different from experimental values and, consequently, estimation of bond orders should exhibit a similar lack of congruence. The computed values for the five-membered heterocycles clearly demonstrate the expected discrepancy

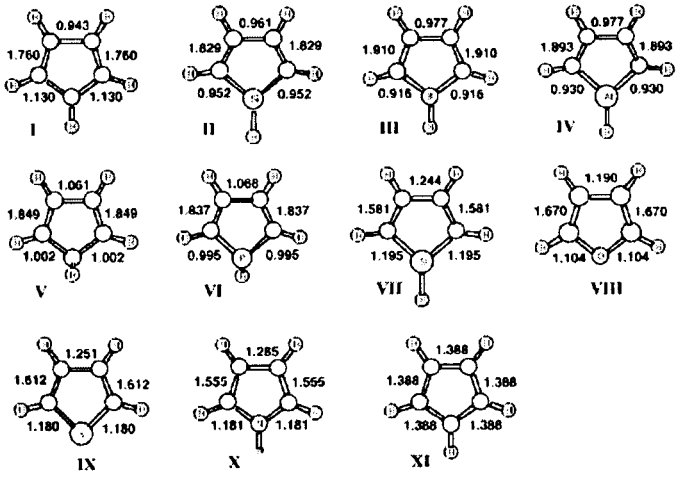

Figure 2. AM1 computed bond orders for five-membered heterocycles.

(Figure 2). For example, heterocycle **VI**, where the P-C bond orders were computed to be 0.995. This value would be expected if the phosphorus lone pair orbitals were not overlapped with carbon p-orbitals at all. To estimate the aromaticity of five-membered heterocycles we are proposing the computation of average bond order deviation from the ideal aromatic system expressed in equation (*b*). Factor 1.5 is chosen for ideal delocalized X-Y bond involved in studied cycle, $b.o_i$ is computed bond order for X-Y,

$$D = \Sigma|(1.5-b.o_i)|/n \qquad (b)$$

and *n* is the number of atoms in cycle. Thus, computed deviation from ideal aromaticity is presented in Table 2.

Table 2

The Computed Magnetic Susceptibility Exaltation Λ, Magnetic Susceptibility Anisotropies χ_{anis}[10^{-6}cm^{3}mol^{-1}], Homodesmic Stabilization/Destabilization Energies ASE[kcalmol^{-1}] and sum of Bond Orders for Five-Membered heterocycles

Heterocycle	Λ	χ_{anis}	ASE(MP2)	ASE(AM1)	D	A
I	32.6	58.1	-56.7	-43.7	0.363	-0.084
II	13.2	-0.8	-24.1	-24.2	0.459	0.346
III	12.8	-5.6	-19.3	-11.4	0.502	0.354
IV	11.2	-11.4	-6.8	-12.5	0.470	0.476
V	-2.4	-31.0	3.7	-2.3	0.427	0.684
VI	-3.3	-35.2	7.0	-1.2	0.423	0.795
VII	-7.7	-41.5	13.8	9.6	0.206	0.926
VIII	-9.1	-36.2	19.8	6.1	0.288	0.900
IX	-10.0	-46.4	22.4	9.4	0.223	0.951
X	-12.1	-41.8	25.5	10.7	0.193	0.967
XI	-17.2	-45.8	28.8	7.0	0.112	1.000

The AM1 computed aromatic stabilization energies are in relatively good correlation with the energies calculated with *ab initio* MP2 method [2e]. The correlation coefficient is 0.9758. Acceptable correlation is what one would expect based upon the parameterization of the AM1

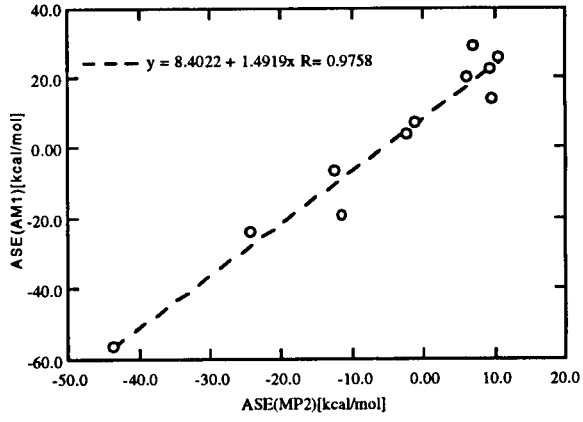

Figure 3. Correlation of AM1 and MP2 computed aromatic stabilization energies.

methods calibrated to reproduce the heat of formation for organic molecules. Schleyer and coworkers [2e] obtained excellent correlation (r = 0.99) between the magnetic susceptibility exaltations (Λ) and the MP2/6-31G* computed aromatic stabilization energy. If aromatic stabilization energies were computed with AM1, the correlation factor would be 0.964. The obtained agreement is not so bad if we consider the fact that computation was obtained with AM1 semiempirical methods not incorporating *d* orbitals necessary for computation of compounds with P and S. Furthermore, our deviation of bond orders from aromatic-

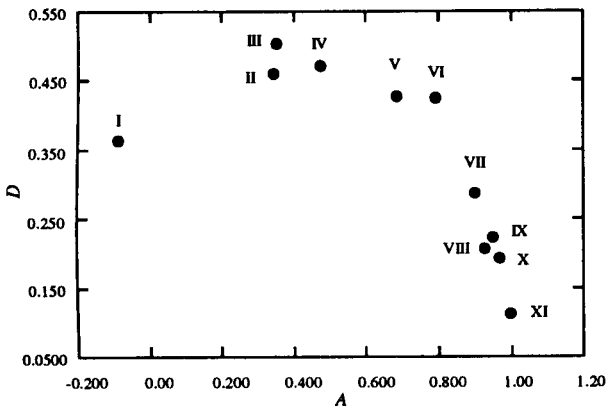

Figure 4. Plot of average bond order deviation from ideal aromaticity (*D*) versus Julg parameters (*A*)

ity (*D*) is comparable with the Julg parameter (*A*) (Figure 4). If we assume the Julg parameters are reliable for evaluating aromaticity as demonstrated by Schleyer and coworkers [2e], then it is reasonable to use these parameters for evaluating the capability of the AM1 semiempirical method to estimate aromaticity through average bond order deviation from ideal aromaticity. With semiempirical methods there is always the problem of parameterization. For example, AM1 method is parameterized to reproduce heat of formations, and it is not surprising that a relatively good correlation between AM1 and MP2 computed aromatic stabilization energies are obtained. The geometric parameters and consequently bond orders do not follow the same accuracy (Table 1 and Figure 4). Nevertheless, there are some interesting observations with regard to computed average bond order deviations. If only compounds with aromatic character (heterocycles **VI-XI**) are considered, then excellent correlation (r = 0.98) between *D* and *A* is observed. For non-aromatic and antiaromatic compounds, however, the correlation was not as good; The correlation decreased as increasingly antiaromatic species were analyzed with our method. Thus, the cyclopentadienyl cation, with the highest antiaromatic nature, deviates the most.

Conclusion.

We believe that the proposed approach to evaluate aromaticity through the average bond order deviation from an ideal aromatic system is one that should be considered. The advantage of our method over the Julg parameters is that our calculations need not determine structure experimentally, it is only necessary to compute bond orders. Although AM1 semiempirical methods cannot correctly predict geometries for charged and highly charge localized molecules (like **I-IV**), we have demonstrated that relative comparison of aromaticity of aromatic compounds is possible. With computational methods that can properly handle the charged molecules, an excellent agreement between aromaticity and our deviation parameters is anticipated. We are continuing to explore the average bond order deviation parameters with both *ab inito* and DFT methods.

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