The Estimation of the Aromaticity of Five-Membered and Benzo Fused Five-Membered Rings by the Hybrid DFT Computed Magnetic Properties

Branko S. Jursic

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148
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The structures of thiophene, pyrrole, furan, and their benzo derivatives were generated with the hybrid B3LYP density functional theory (DFT) methods employing a 6-31G* basis set. Their magnetic susceptibility anisotropies were calculated on these geometries with a continuous set of gauge transformations. The aromaticity of the heterocycles was discussed in light of their structural uniformity and magnetic susceptibility. The computed structural parameters, order of aromaticity, stability, and reactivity is in excellent agreement with the experimental results. The usefulness of this approach to determine the reactivity is discussed.

Introduction.

Although, the aromaticity has been widely used by the organic chemist to explain the unusual behavior and reaction outcome [1] of molecules, a general definition is lacking [2]. Originally, the aromaticity was associated with a special chemical reactivity. The aromatic hydrocarbons were unsaturated compounds that underwent substitution reactions in preference to addition. In terms of the MO terminology, the cyclic structures that have a particular stable arrangement of occupied π-molecular orbitals, expressed as in the *Hückel* rule, are referred to as aromatic. Experimentally, the aromaticity was determined by the heat of combustion or by the heat of hydrogenation [3]. This isodesmic reaction approach has also been applied to calculations of the resonance stability of conjugated cyclic polyenes [4].

The nmr spectroscopy also provides an experimental tool capable of assessing aromaticity of the structure. Aromatic compounds are characterized by their capacity to exhibit a diamagnetic ring current. The ring current effect is responsible for the large magnetic anisotropy in the aromatic compounds. The nuclei in the cone above and below the plane of an aromatic ring are shielded by the induced field and appear at the higher field region in the nmr spectrum. However, the nuclei in the ring occur at relatively low field positions. This effect can be taken as evidence for the aromaticity, although, this criterion should be applied with some care [5].
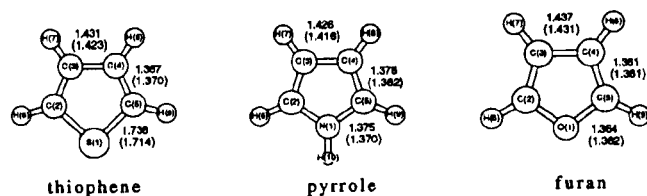
Recently, Schleyer and coworkers used the *ab initio* calculated diamagnetic susceptibility exaltations to evaluate the aromaticity of five-membered aromatic heterocycles [6]. Here, we present the results of the B3LYP DFT computation of magnetic properties for five-membered and benzo five-membered aromatic compounds with the purpose of evaluating their relative aromaticities.

Computational Methods.

All of the calculations were performed with the GAUSSIAN 94 [6] on RISC/6000 computers by Becke's three parameter hybrid method [7] using the LYP correlation functional [8] (B3LYP). The nmr shielding tensors and magnetic properties were calculated using the continuation set of gauge transformations (CSGT) [9], single origin, and IGAIM methods [9]. The standard gaussian 6-31G* [10] basis set was also used.

Results and Discussion.

We have demonstrated that the B3LYP is a reliable method when the geometries and energies of chemicals are computed [11]. The structures for thiophene, pyrrole and furan are presented in Figure 1. As demonstrated again, an excellent agreement between the B3LYP/6-31G(d) and the highly accurate microwave spectroscopy determined structures in gas phase was observed [12].

Now, we have turned to the computation of magnetic susceptibility anisotropies (cgs) of five-membered heterocyclic compounds (Table 1). The computed values were

Figure 1. The lengths of the five-membered heterocyclic bonds at the B3LYP/6-31G(d) level (experimental values [12] are given in the parentheses).

Table 1

The Heat of Combustion (kJ/mol) and the Computed Magnetic Susceptibility Anisotropies (cgs)

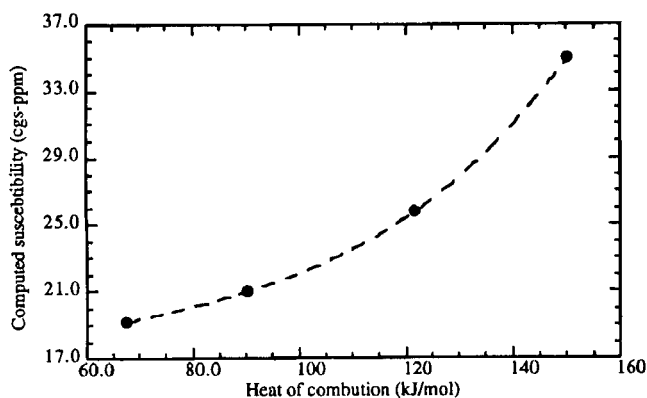| Compounds	combustion [13]	IGAIM	CSGT
benzene	150.2	34.9	34.9
thiophene	121.8	25.8	25.8
pyrrole	90.4	21.0	21.0
furan	67.8	19.2	19.2

Figure 2. The correlations between the B3LYP/6-31G* CSGT computed magnetic susceptibility with an experimentally determined heat of combustion.

correlated with the experimentally determined heat of combustion [13]. An excellent correlation between the computed and the experimental values was obtained (Figure 2), demonstrating that this method can correctly estimate the relative magnetic properties of five-membered heterocycles. It is well known that thiophene is the most aromatic heterocycle in this series, with furan as the most reactive. In a continuation of our study, we have extended this approach to evaluate the relative stability and reactivity of fused five-membered heterocycles and benzene, based on the computed physical properties of their ground states. The computed structures are presented in Figure 3. There are also other physical measurements that give evidence of the aromaticity. The spectroscopic methods or X-ray diffraction can also provide bond-length data. Aromatic molecules consistently show bond lengths in the range 1.38-1.40 Å, and are quite uniform around the ring. In contrast, the localized polyenes show an alternation between the typical sp^2 single-bond and sp^2 double-bonds along the conjugated chain [14]. It is reasonable to expect that the aromaticity for benzene in fused heterocycles will be high if the bond distances of the benzene ring does not
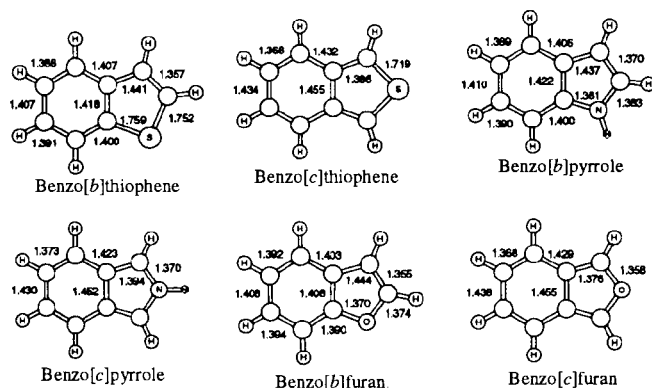
deviate considerably from benzene itself. The B3LYP/-6-31G* calculates the benzene C-C bond distance to be 1.396 Å, which is quite close to the experimental value of 1.39 Å [14]. In b and c benzo heterocycles the b heterocycle is much closer to the benzene structure (Figure 3). Particularly, a large distortion is obtained for benzo[c]-furan and benzo[c]thiophene. In contrast, the benzo[c]-furan benzene ring has a maximal C-C bond discrepancy if compared to the isolated benzene, which is only 0.012 Å. This suggests, that the energy difference between the two benzofurans should be high.

To confirm this finding based on the degree of the benzene ring C-C distortion, we have computed the magnetic susceptibility anisotropies and the relative energies for the benzene fused five-membered heterocycles (Table 2). A similar approach was used by Schleyer and coworkers [15] to evaluate the aromaticity of five membered heterocycles using the *ab initio* methods. As one would expect, the computed magnetic susceptibility anisotropies for the fused rings follow the same order as do the aromatic five-membered heterocycles. It is interesting to mention, the sum of benzene and furan magnetic susceptibility anisotropies is 6.3 cgs smaller than the sum computed for the benzo[b]furan. This indicates a very high π molecular orbital delocalization that exists between the two aromatic rings of benzo[b]furan. Conversely, this is not present in the same degree for the benzo[c]furan, making it the less stable isomer (ΔE = -14.4 kcal/mol). The magnetic susceptibility anisotropies for the benzopyrrole isomers are very close, indicating a small difference in the aromaticity and energy (ΔE = -9.3 kcal/mol). According to both the computed magnetic susceptibility anisotropies and relative energies, the benzothiophenes lie between the benzopyrroles and benzofurans: the benzo[c]thiophene should be more stable than the benzo[c]furan; benzo[b]-thiophene should be the more stable isomer.

There is no direct experimental data for the computed values presented in this paper, however, there is plenty of experimental evidence that fully supports our findings. The existence of benzo[c]furan has been clearly demonstrated [16]. The benzo[c]furan is unstable in solutions and reacts almost instantaneously with typical dienophiles to give the corresponding Diels-Alder adducts [17]. The

Figure 3. The B3LYP computed geometries of the benzene fused five-membered heterocycles.

Table 2

The Heat of Combustion (kJ/mol) and the Computed Magnetic
Susceptibility Anisotropies (cgs)

Compounds	IGAIM	CSGT	E/a.u.	ΔE/kcal mol⁻¹
Benzo[b]thiophene	55.7	55.7	-706.6536216	-11.2
Benzo[c]thiophene	53.9	53.9	-706.6357470	
Benzo[b]pyrrole	51.9	51.9	-363.8166877	-9.3
Benzo[c]pyrrole	51.3	51.3	-363.8018371	
Benzo[b]furan	49.6	49.6	-383.6733932	-14.4
Benzo[c]furan	46.8	46.8	-383.6503658	

structure is then stabilized by the electron withdrawing or delocalizing substituents. On the other hand, the benzo[b]furan is a very stable compound and can be obtained by various synthetic methods [18]. Both of the benzopyrroles are stable molecules and have very similar chemical properties [19], due to the predicted identical aromaticity. Of the two benzothiophenes, the benzo[c]thiophene is more reactive [20] as it was predicted by the computed magnetic susceptibility anisotropies (Table 2).

Since an excellent agreement with the experimental evidence is obtained, we believe that this simple approach can be used to determine the stability of the fused aromatic rings. Especially, when their relative stability or reactivity is investigated. A further application of this approach may be used in other systems, such as transition state structures.

Conclusion.

It can be concluded, that the B3LYP/6-31G* will produce high quality structural parameters for the five-membered rings and their benzo derivatives. Based on the structural uniformity principle and magnetic susceptibility anisotropies, the predicted relative aromaticity of these systems is found to be a reliable approach. From the computed values, the relative stability of this system is accurately predicted.

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