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A phenomenological use of benzene tip to probe aromaticity

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ABSTRACT

Interaction of a C–H tip of benzene with a monocyclic aromatic compound studied using M062X functional in DFT, yields a tilted T-shaped conformation with a tilt angle θ. For a set of ten monohetero five-membered rings C_4H_4X (X = BH, AlH, SiH_2, CH_2, O, S, SiH^-, PH, NH, CH^-), θ^{-1} is found to be linearly related to NICS(0), Mo-Schleyer resonance energy and Shannon's aromaticity in excellent manners. Consequently θ can be used as an index of aromaticity of the system with which benzene is interacting. The larger the θ, the larger the aromaticity. The angle θ, which can vary from 90° to 180°, seems to have a threshold value of ~115°; a θ value below 115° means non-aromaticity. The index shows that borazine, the inorganic benzene is aromatic. It reveals that cyclopropane is aromatic while cyclobutane is not. The present approach faces problems in polycyclic aromatic hydrocarbons as the benzene probe tends to span two adjacent rings. Finally, to test the efficacy of Truhlar's functional M062X in DFT in describing non-bonded interactions, the case of benzene dimer has been studied. It is found that M062X/LanL2DZ or M062X/6-311++G(2d,p) can reproduce the experimental binding energy of the benzene dimer quite well, while B3LYP and BP86 cannot.

1. Introduction

Planar, cyclic molecules having a complete delocalization of $4n + 2$ π electrons which can undergo electrophilic substitution are chemically said to be aromatic [1]. These are designated to possess extra thermochemical stability (resonance energy). The term "aromaticity" was first introduced by Kekule in 1865 [2]. But it is still a nebulous concept, mainly because there is no unique experimental method for its determination. The value of the resonance energy depends on the isodesmic/homodesmotic reaction taken as the reference. Thus over the period of time, a range of 22–75 kcal mol^{-1} has been obtained experimentally for benzene, the archetype of all aromatic molecules, as its resonance energy [1,3–6]. So far the value of 36 kcal mol^{-1} obtained by Kistiakowsky et al. [6] in 1936 is most widely accepted and quoted. They determined it from the following equation using experimental enthalpies:

$$\text{Benzene} + 2\text{cyclohexane} = 3\text{cyclohexene} + 36\ \text{kcal mol}^{-1}$$

This happens to be the first attempt to determine resonance energy experimentally. The case of benzene, in a way, epitomizes the overall experimental situation. Hence there has been a need for a theoretical index of aromaticity. Again a number of theoretical indices, based on structural, magnetic, energetic, electronic, or spectroscopic criteria, are now available [1,7–14]. Other than adding to the controversies, these approaches show that aromaticity can be linked with a number of physico-chemical properties. Hence the present surge for developing a suitable index for it. While testing the efficacy of Truhlar's functional M062X [15] in Density Functional Theory in describing non-bonded interactions [16,17], we have found that a benzene ring prefers a shifted, parallel conformation in the interaction with cyclobutadiene but a tilted T-shaped orientation while interacting with another benzene molecule. It then occurred to us whether the tilt angle can be correlated with aromaticity. The results are reported here.

2. Computational

All calculations have been done using GAUSSIAN 09W suite of programs [18]. All binding energies (BE) reported here are corrected for basis set superposition error and zero point energy. There are reports [19,20] where imaginary frequencies lower than $60i$ cm^{-1} in magnitude have been arbitrarily ignored in DFT calculations. But we have not ignored any imaginary frequency encountered in the geometry optimizations, however low it is in magnitude. The associated structures are designated as saddle points of various orders depending on the number of imaginary frequencies. Various confor-mations for benzene's interaction with another molecule are obtained by starting with different

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geometries. Nucleus independent chemical shift (NICS) for silole at the center of the five membered ring has been calculated by us using the method prescribed by Schleyer and co-workers [7].

3. Results and discussion

Experimental measurements in the gas phase have shown the stabilization enthalpy of the benzene dimer to range from -1.6 ± 0.2 kcal mol^{-1} [21] to -2.4 ± 0.4 kcal mol^{-1} [22]. A number of theoretical studies have appeared [23,24]. It was felt in 2000 that density functional approaches are not equipped to study systems whose intermolecular interactions are dominated by dispersion [23]. We have found that M062X is quite capable of reproducing experimental binding energy of benzene dimer (Table 1). As found by Podeszwa et al. [25] from a six dimensional potential energy surface search, both T-shaped and stacked geometries are saddle points in our M062X calculations carried out with LanL2DZ and 6-311++G(2d,p) basis sets (Table 1; Fig. 1). An angular geometry with a tilt angle 150–160° and a parallel displaced geometry are found to be likely for the benzene dimer. Similar calculations for the interaction of benzene with cyclobutadiene, which is anti-aromatic, show that a parallel displaced geometry is possible (Table 1; Fig. 2). As mentioned above, possible implications are that when benzene interacts with an aromatic system, an angular conformation is possible but such angular interaction is not possible

Table 1
Geometry optimization parameters obtained for the non-bonded interactions of benzene with another benzene molecule and cyclobutadiene in our DFT calculations[a].

Basis set	Functional	Conformation	Tilt angle	Binding energy
Benzene–benzene				
LanL2DZ	B3LYP	Angular	179.7[b]	−0.09
			158.4[b]	−0.12
		Stacked	–[b]	0.46
		PD	–[b]	0.00
	BP86	Angular	179.8[b]	0.12
			157.8	0.07
		Stacked	–[b]	0.57
		PD	–[b]	−0.07
	M062X	Angular	179.6[b]	−1.46
			153.0	−1.57
		Stacked	–[b]	0.09
		PD	–	−1.42
6-311++G(2d,p)	B3LYP	Angular	179.6	0.16
			158.4	0.16
		Stacked	–	0.51
		PD	–[b]	0.00
	BP86	Angular	179.5[b]	0.17
			157.0[b]	0.23
		Stacked	–[b]	0.36
		PD	–[b]	0.20
	M062X	Angular	179.6[b]	−1.84
			152.0	−2.11
		Stacked	–[b]	−0.88
		PD	–	−2.22
Benzene–cyclobutadiene				
LanL2DZ	B3LYP	Angular	179.3[b]	0.13
		Stacked	–[b]	0.24
	BP86	Angular	179.2[b]	0.49
		Stacked	–[b]	0.03
	M062X	Stacked	–[b]	−1.34
		PD	–	−1.42
6-311++G(2d,p)	B3LYP	Angular	179.7[b]	0.08
		Stacked	–[b]	0.02
	BP86	Angular	179.4[b]	0.46
		Stacked	–[b]	0.14
	M062X	Stacked	–	−1.80
		PD	–	−1.93

[a] PD = parallel displaced. Units used: tilt angle, deg; binding energy, kcal mol^{-1}.
[b] Has one or more imaginary frequencies.

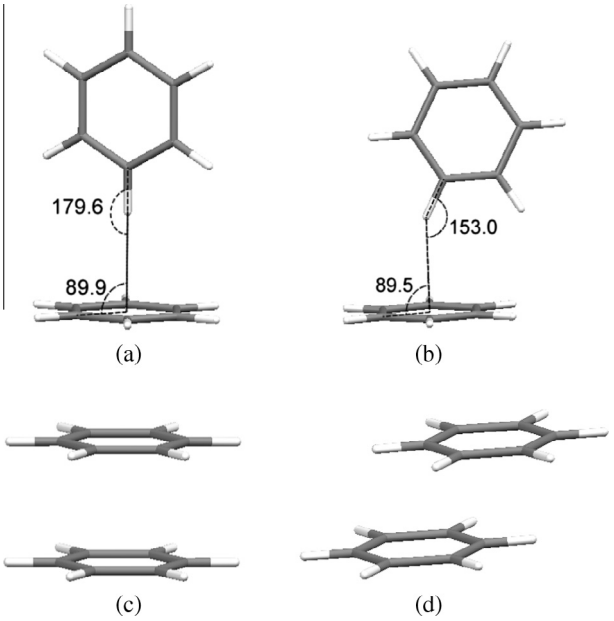

Fig. 1. Various conformations of benzene dimer obtained from M062X/LanL2DZ calculations. Conformation (a) has one imaginary frequency of 30.5*i* cm^{-1}, (b) no imaginary frequency, (c) two imaginary frequencies of 59.0*i* and 44.0*i* cm^{-1} and (d) no imaginary frequency. At M062X/6-311++G(2d,p) level, (a) with one imaginary frequency of 27.7*i* cm^{-1}, (c) with three imaginary frequencies of 72.3*i*, 57.9*i* and 28.3*i* cm^{-1}, (b) and (d) with no imaginary frequency are obtained; the tilt angles in (a) and (b) are 179.6° and 152.0° respectively.

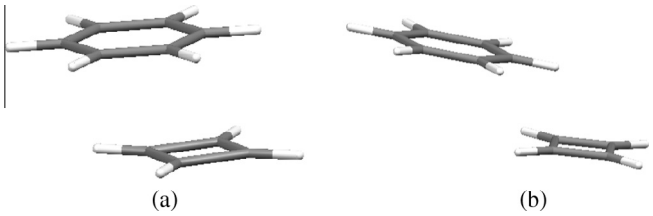

Fig. 2. Various conformations of benzene's interaction with cyclobutadiene obtained from M062X/LanL2DZ calculations. (a) Has one imaginary frequency of 7.8*i* cm^{-1} and (b) no imaginary frequency. At M062X/6-311++G(2d,p) level, (a) and (b) do not have any imaginary frequency.

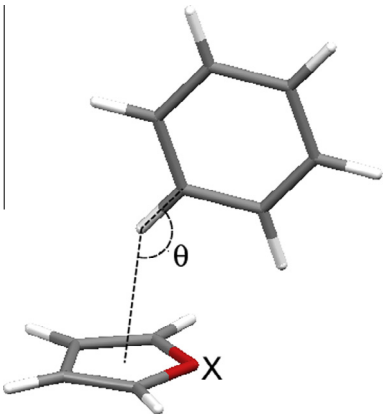

Fig. 3. Angular interaction of a benzene ring with a five-membered ring heterocycle of the type C_4H_4X.