Calculating stabilization energies for aromatic molecules in schools - quantum chemistry, a valuable tool for teaching and education

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ABSTRACT

While aromaticity is one of the most fundamental concepts in chemistry and is taught in many elementary organic chemistry courses, it is hardly possible to activate pupils and students to learn and explore this topic independently. By applying computational chemistry and especially quantum chemistry, we introduce a possibility to activate students, allowing them to test taught

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concepts and do their own "experiments" cheaply and securely. We have focused in the current report on the structural and energetic aspects of aromaticity, as they are most compatible with other topics of typical chemistry lessons. To evaluate the aromatic stabilization energy, we suggest the simple-to-calculate and easy-to-understand isomerization stabilization energy (ISE) popularized by Paul von Ragué Schleyer and Frank Pühlhofer some 20 years ago. As practical examples, we demonstrate our concept with benzene- and pyridine-based systems and suggest topics for small projects for students and pupils.

Introduction

Aromaticity is one of the fundamental concepts in chemistry, initially explaining the special behavior of benzene (Badger, 1969; Garratt, 1971), nowadays ubiquitous in all chemical subdisciplines (Boldyrev et al., 2005; Chattaraj, 2011; Mercero et al., 2015). In schools, the topic "aromaticity" is taught based on Hückel's theory (Hückel, 1931a; Hückel, 1931b; Hückel, 1932) and the 4n+2 π-rule clearly and simply (McMurry, 2021), leading pupils to the idea that they and all others have understood aromaticity completely. More than 12,000 publications with the keyword "aromaticity" registered in the Web of Science for the last 50 years draw a different picture.

While aromaticity is in school and elsewhere in chemistry-related science, an important concept utilized, *e.g.*, in Biology to understand the NAD^+/NADH-system (Schaller, 2021), the possibilities to enrich the lectures by attractive experiments are very limited and therefore more or less only done in theory by paper and pen or chalk and blackboard. Depending on the scientific level of pupils or students, orbitals are included, or otherwise, the explanation is limited to the theory of single and double bonds. Normally the students get a list of typical characteristics for aromatic systems and the second list of properties related to the aromatic character (McMurry, 2021) (*vide infra: Results and Discussion*), and then the identification of aromatic molecules is typically exercised by homework. Motivating lectures are something different.

A possible alternative way is to illustrate the teaching of this topic, also potentially activating pupils to own work and "independent research" by applying computational, especially quantum chemical, calculations (Simpson et. al., 2020). These methods have many benefits for teaching, i) they utilize equipment handy in many classrooms nowadays, the personal computer, and therefore do not cause extra costs ii) the necessary software is also free of charge and legally accessible and iii) no potentially dangerous chemicals are necessary. In the last years, a lot of money was spent worldwide to equip schools with contemporary personal computers for all kinds of purposes and with computer power allowing quantum chemical calculations. Additional appropriate free software is accessible free of charge, *e.g.*, there are a couple of free quantum

chemical programs like Gamess (Gordon et. al., 2005; Schmidt et al., 1993), Orca (Neese, 2012; Neese, 2017), Dalton (Aidas et al., 2014) or OpenMopac (Stewart, 2016) and also free software for generating inputs and visualizing the outputs, *e.g.*, Avogadro (Hanwell et al., 2012) can easily be obtained.

In this manuscript, some possibilities offered by the application of quantum chemical calculations to enrich the topic of aromaticity in chemistry courses shall be introduced.

Applied Method and Software

The examples introduced here were calculated with Gaussian16 (Frisch et al., 2016), and whenever possible, in G3 (Curtiss et al., 1998) and/or MP2/def2QZVPP (Hehre et al., 1986; Weigand et al., 2005; Weigand, 2006) theory, to get good reference energies. Of course, the standard density functionals like B3LYP (Becke et al., 1993; Lee et al., 1988; Stephens et al., 1994) or ωB97XD (Chai & Head-Gordon, 2008) in combination with standard basis sets like 6-311+G** or 6-31G* (Hehre et al., 1986) lead to sufficient results, too. Semiempiric methods like AM1 (Dewar et al., 1985) are also leading to correct qualitative results and can be done directly in the lecture. The results presented here were calculated with Caddle/Empire (Hennemann et. al., 2020). And beyond quantum chemistry, even MMFF94 (Thomas & Halgren, 1996) force field calculations, as implemented in Avogadro, can illustrate a lecture.

Results and Discussion

In school, aromaticity is explained with the well-known Hückel theory (McMurry, 2021). This is understandable and applicable for pupils, as it allows paper and pen to identify aromatic molecules or aromatic fragments of molecules. As properties originated by the aromatic character and therefore an indication for the aromaticity of a molecule the following four (+ one) topics (Schleyer et al., 1996) are listed below, which, in most cases, expressed without giving pupils or students the chance to verify only one of them easily by themselves.

a) Criterion "Structure": Deals with bond length equalization due to cyclic delocalization.

b) Criterion "Energy": Deals with enhanced stability (large resonance energy).

c) Criterion "Magnetic properties": Tests the "ring current"-effects

d) Criterion "Chemical behaviour": Studies the electrophilic aromatic substitution.

e) Criterion "Smell"

Of course, for security and hazardous reasons, the smell of a compound is no more an applicable criterion to distinguish between an aromatic compound and a non-aromatic one; this criterion nowadays has only historical importance. The flavourful smell of compounds like benzene motivated August Wilhelm Hofmann in 1855 to call such compounds "aromatic" and the phenomena "Aromaticity" (Hofmann, 1855). Even if we know, nowadays there is no general relationship between aromaticity and the olfactory properties of a molecule, a hint to the smell and structure of vanillin (4-hydroxy-3-methoxybenzaldehyde) is still instructive.

Testing chemical reactivity requires lab and laboratory skills. If a lab course is included in the curriculum, it is a good idea to demonstrate and teach it experimentally, too. This is neither possible nor included in the official curriculum in many secondary schools. Additionally, many aromatic molecules do not undergo the typical textbook electrophilic aromatic substitution reactions (McMurry, 2021), *e.g.*, C_{60}. What shall be substituted? One can add bromine to phenanthrene and anthracene to point out two of the most striking examples (Price, 1936).

Of the remaining three criteria, the magnetic criterium is indeed the most difficult and abstract one to teach. The concept of John People et al. is very supportive here to understand the resonance of the alternating single and double bonds, *e.g.*, in benzene as a ring current (People and Untch, 1966). This idea of a ring current can lead pupils with a solid technical and physical background to understand aromatic molecules as a solenoid generating a magnetic field (McMurry, 2021). Surely it needs outstanding pupils to go deeper into this topic, but it is questionable if this is necessary for a secondary school.

Criteria of (a) structure and (b) resonance energy are suited to be taught and exercised by applying quantum chemical calculations during the course or in an extra exercise.

Aromaticity is connected to bond length equalization due to cyclic delocalization. While we draw benzene classically with alternating double and single bonds to explain later to students

that there are no shorter (double) and longer (single) bonds and that we have averaged bond length between the carbon atoms (Figure 1).
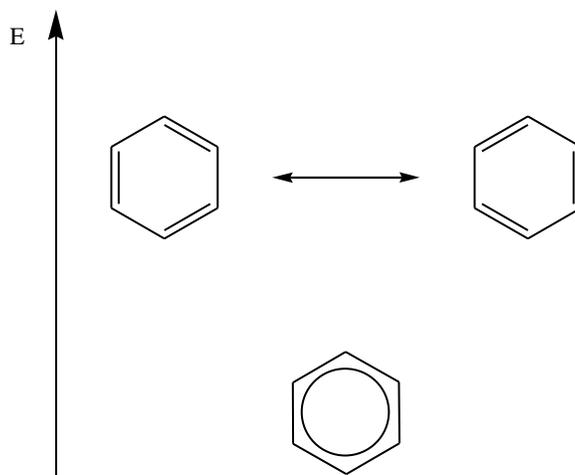
Figure 1. Resonance structures of benzene leading to the structure with bond equalization

This effect can easily be demonstrated or better evaluated by the pupils themselves. No matter how pronounced they make double and single bonds in their input file, they will end up with the well-known high symmetric D_{6h}-structure (within the accuracy of the selected method, normally two significant figures). Additionally, by comparing with simple references like cyclohexane or ethene, they can understand that the resulting bonds are neither single nor double bonds but in-between.

Table 1. Calculated C-C-bond length in benzene

Method	C-C bond length in benzene	C-C bond length in cyclohexane[cc]	C-C bond length in ethene
MMF94	1.395 Å	1.526 Å	1.336 Å
AM1	1.395 Å	1.515 Å	1.326 Å
HF/STO-3G	1.387 Å	1.544 Å	1.306 Å
HF/3-21G	1.385 Å	1,541 Å	1.315 Å
B3LYP/6-31G*	1.397 Å	1.537 Å	1.331 Å
B3LYP/6-311+G**	1.395 Å	1.536 Å	1.329 Å

ωB97XD/6-311+G**	1.390 Å	1.530 Å	1.326 Å
MP2(full)/def2QZVPP	1.387 Å	1.518 Å	1.326 Å

cc: chair conformation

As simply observable, we get with all methods an averaged C-C-bond length in benzene of 1.4 Å independent from the applied technique and, therefore, clearly significantly shorter than 1.5 Å in cyclohexane or longer than 1.3 Å in ethene.
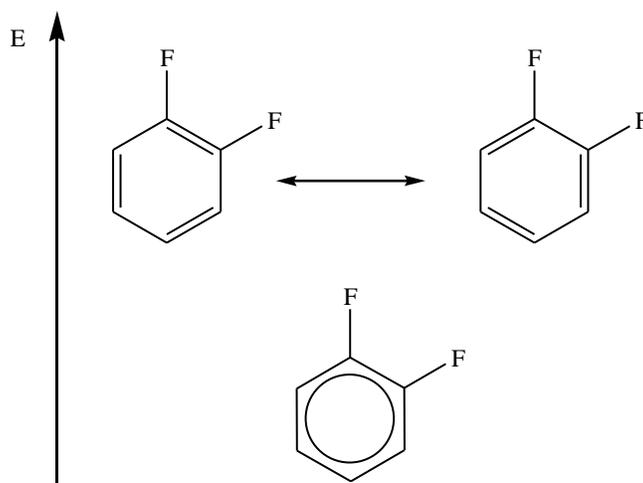
Figure 2. Resonance structures of 1,2-difluorobenzene

Of course, if the resonance structure with alternating single and double bonds would be real structures, one must get two distinguished isomers, *e.g.*, in 1,2-difluorobenzene, one with a single bond between the CF-groups and one with a double bond between the CF-groups. Obviously, only one structure can be found no matter how one tries (Figure 2).

Table 2. Calculated C_FC_F-bond length in 1,2-difluorobenzene

Method	C_F-C_F bond length in benzene (Å)
MMF94	1.397
AM1	1.421
HF/STO-3G	1.407
HF/3-21G	1.375
B3LYP/6-31G*	1.395

B3LYP/6-311+G**	1.391
ωB97XD/6-311+G**	1.388
MP2(full)/def2QZVPP	1.384

A more detailed inspection of the 1,2-difuorobenzene structures shows that the C-C-bonds are not identical anymore, obviously due to the two substituents. Comparing the non-identical bond and the structure, students will still understand that the prerequisite of Hückel's theory is still valid and that a molecule like 1,2-difuorobenzene is still aromatic.

Extending the idea that the structure can undergo perturbation by substituents can easily lead pupils and students to hetero aromatic systems like pyridine (Figure 3). A valuable tool is the application of the concept of isoelectric groups, *e.g.*, N instead CH.
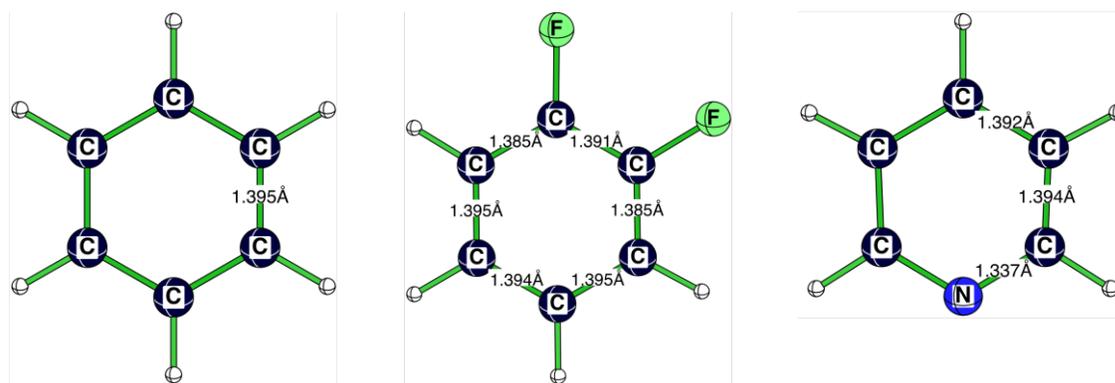

Figure 3. Calculated (B3LYP/6-311+G**) structures of benzene, 1,2-difluorobenzene and pyridine

If computer power and exercise time are available, it can be a nice challenge to ask pupils to design and calculate an aromatic molecule with a maximum bond length alternation.

Calculating the resonance energy includes more thinking about science than playing with science, but usually students and pupils are motivated to investigate a topic new to them independently. Traditionally the aromatic stabilization energy (ASE) is calculated by model equations.

In the middle of the 20th century, Wheland suggested calculating the resonance energy by equation 1 (Wheland, 1955).
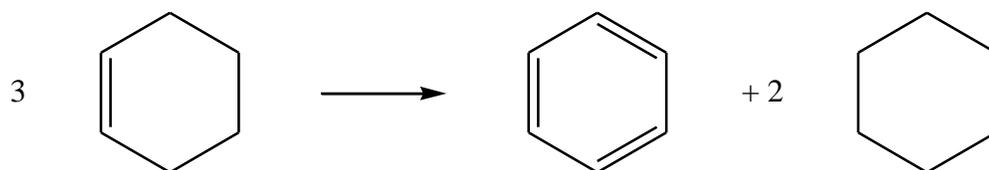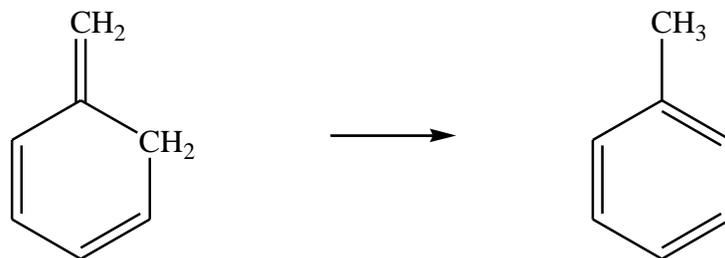

Equation 1

This equation allows measuring the total stabilization referencing to a hypothetical system without resonance. The weakness of this equation is it does not include influences like strain, hyperconjugation, differences in the types of bonds, *etc.* (Dewar and Schmeising, 1959). Stepwise new equations were suggested and applied to include all necessary effects, leading to the homodesmotic equation 2 (Schleyer and Pühlhofer, 2002).
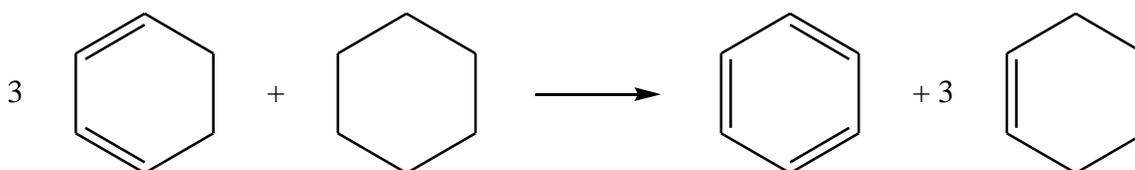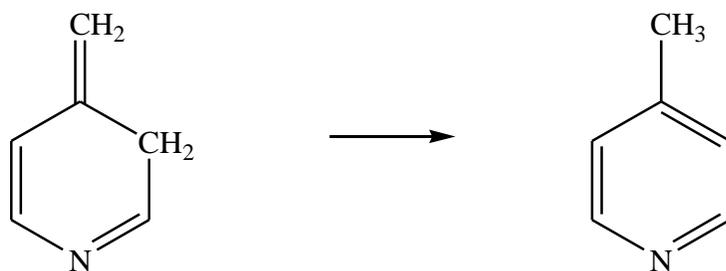

Equation 2

While accurate energy values can be calculated by all kinds of computational methods, the idea of this equation can be applied to all kinds of aromatic molecules. The significant disadvantage of a homodesmotic equation like 2 is that for the simple molecule benzene, one needs three different molecules besides benzene; in the case of pyridine, even six reference structures are necessary beside pyridine. This is for scientists unpleasant and for educational purposes prohibitive. The simple and nearly self-explanatory solution was introduced by Paul von Ragué Schleyer and Frank Pühlhofer in 2002, inspired by earlier work (Schleyer & Pühlhofer, 2002). They isomerized 5-methylenecyclohexa-1,3-diene by a hydrogen shift to methylbenzene (toluene) (equation 3) and calculated the isomerization stabilization energy (ISE). The energy difference of both isomers is the stabilization caused by cyclic electron delocalization (Schleyer & Pühlhofer, 2002).

Equation 3

Following Schleyer and Pühlhofer's approach, even for cases like pyridine, simple and fast equations are accessible, allowing students to recalculate the resonance energy themselves.
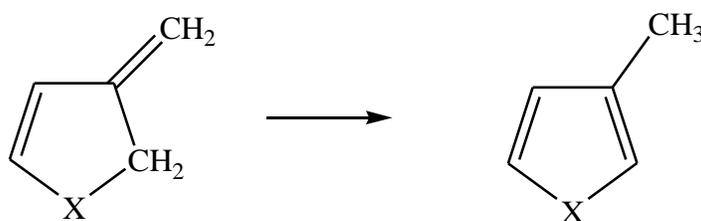

Equation 4

Table 3. Calculated isomerization stabilization energies (ISE) to derive the aromatic stabilization energy for benzene and pyridine

Method	ISE benzene (equation 3) (kcal/mol)	ISE pyridine (equation 4) (kcal/mol)
AM1	-24.25	-22.11
HF/STO-3G	-40.03	-38.35
HF/3-21G	-35.97	-34.99
B3LYP/6-31G*	-34.64	-33.87
B3LYP/6-311+G**	-33.24	-32.41
ωB97XD/6-311+G**	-33.77	-32.97
MP2(full)/def2QZVPP	-37.49	-36.29
G3	-32.00	-31.29

A potential problem can be the position of the CH_2 group in the reference molecule relative to the methylene moiety. As demonstrated by Schleyer and Pühlhofer, impressively are, all necessary effects included in the ISE as long as the two relevant CH_2 moieties are adjacent.

At this point, students and pupils can start with small independent projects.

a) Investigating the ISE of larger annulenes starting from benzene, *via* [10] annulene, [14] annulene, *etc.* The results one can expect are published by Schleyer et al. (2003).

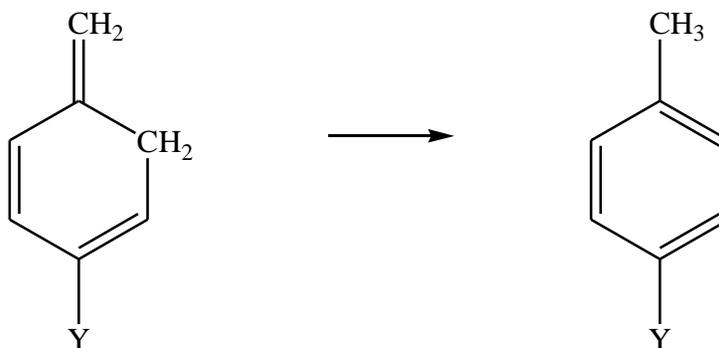b) Calculating the ISE for smaller heteroaromatic systems ring.

Equation 5

Table 4. G3 ISE values for heteroaromatic ring systems according to equation 5

X	BH	$^+$CH	$^-$CH	NH	PH	O	S	Se
ISE kcal/mol	+11.14	+21.37	-27.01	-21.85	-6.07	-15.50	-18.55	-14.57

c) Studying the influences of substituents on the ISE.

Equation 6

Table 5. G3 ISE values for differently substituted benzene rings according to equation 6

Y	CH_3	F	Cl	Br	OH	SH	SeH	NH_2
ISE kcal/mol	-31,29	-31.90	-31,82	-31,79	-31,38	-31.09	-31,20	-31,86

Conclusion

Based on two typical criteria for aromaticity, structure (bond length equalization), and enhanced stability, we designed some simple and fast experiments for pupils and students based on computational chemistry, especially quantum chemistry. Without any hazards, the students can calculate structures and evaluate energies. While classical concepts in deriving aromatic stabilization, energies tend to be complex and time-consuming, we recommend for educational use the simple and nearly self-explanatory isomerization stabilization energy (ISE), a simple concept established for common use by Paul von Ragué Schleyer and Frank Pühlhofer. Only an H-atom is shifted from a methyl group to a carbon atom in the aromatic ring, and consequently, the ring current is stopped by the CH_2- and the exocyclic $=CH_2$ group. Small projects based on the structural and energetic criteria for aromaticity are suggested for the learners.

Acknowledgment

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