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Stabilization of benzene versus oligoacetylenes: not another scale for aromaticity

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ABSTRACT: The energies of a number of oligoacetylenes are compared in a homodesmic reaction with benzene. Assessment of the open vs closed form of a conjugated triene is presented along with a perspective on the pursuit of quantitative scales for 'aromaticity'. Copyright © 2004 John Wiley & Sons, Ltd.
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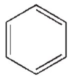
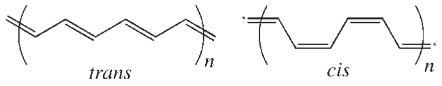
KEYWORDS: benzene; oligoacetylenes; aromaticity scale

Benzene is the archetype of 'aromaticity' and the only molecule for which a consensus about its being aromatic has been reached. For an instructive discussion on this very point, see the discussion proceedings between Heilbronner and Binsch at the Jerusalem Symposium.[1] 'Aromatic' stabilization energy plays a special role in such discussions.[2,3] Polyacetylene shares a bonding representation with multiple repeats of 'open' benzene.[4–6] The energy of an n-unit polyacetylene compared with one of n–$3m$ units plus m benzenes gives an assessment of the relative stability of 'open' vs 'closed' benzene. Can comparison with oligoacetylene yield similar information?

Geometries for benzene (**A**), ethylene (**B**), octatetraene (**C**), tetradecaheptaene (**D**) and icosadecaene (**E**) were optimized at the B3LYP/DZV(2d,p) level of theory, and energies were further assessed at B3LYP/DZV(2d,p), RHF/DZV(2d,p),and MP2/DZV(2d,p) levels at the optimized geometries (see Supplementary material) [structural computations of all compounds were performed using hybrid density functional methods (HDFT). The HDFT method employed Becke's three-parameter functional[7] in combination with non-local correlation provided by the Lee–Yang–Parr expression[8,9] that contains local and non-local terms, B3LYP. Dunning's DZV(2d,p)[10] double-valence basis set was employed. Single-point energy computations were performed on optimized structures using MP2[11] dynamic correlation treatment].[13] Evaluation of a series of six homodesmic reactions (**A** + **B** = **C**; **A** + **C** = **D**; **A** + **D** = **E**; **2*** **A** + **B** = **D**; **2*** **A** + **C** = **E**; **3*** **A** + **B** = **E**) for the all-*cis*, all-*trans* and one mixed *cis*–*trans* oligoacetylene configuration revealed a rapid convergence of values at each level of theory (Table 1).



A



B-E n = 0,1,2,3

The all-*cis* comparison provided higher stabilization energies for benzene (21.2, 29.9 and 24.3 kcal mol^{-1} for HDFT, RHF and MP2, respectively) than the all-*trans* comparison (14.5, 23.9 and 19.0 kcal mol^{-1}). The larger *cis* values could arise from the 1,4-interactions between in-plane hydrogens, which are present in the *cis* but not the *trans* forms nor in benzene . A simple test of this was to compare energetics obtained from $1 + 2 = 3$ using the (*trans*, *trans*), (*cis*, *cis*) and (*trans*, *cis*) forms (Table 2).

In all cases, RHF predicts higher benzene stabilization than oligoacteylene, followed by MP2 and HDFT . These molecules are all highly conjugated and therefore consideration of dynamic correlation is expected to provide a better assessment of the energetics. Clearly, HDFT and MP2 not only provide different ways of accounting for dynamic correlation, but also predict different energetic significance of it. The HDFT methods predict lesser stabilization for the closed benzene form.

Regardless of which analysis one chooses, the results predict either a significant stabilization of the open form within a polyacetylene backbone or, conversely, a much lower aromatic stabilization energy for benzene than generally estimated by classical assessments (ca 36 kcal mol^{-1}).[2] The clear message here is that an open triene within a conjugated polyacetylene is stabilized substantially.

What about higher order annulenes? They too should share this bond representation analogy with polyacetylene.

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Table 1. Relative energetics of oligoacetylenes [kcal mol^{-1} (1 kcal = 4.184 kJ)] using [ethylene + 3·benzene] as reference point[a,c]

Reaction	All-*cis* isomer	All-*trans* isomer	$n-1$ *trans* isomer
E			
B3LYP/DZV(2d,p)	63.3 (21.1)[b]	46.4 (14.5)	48.4 (14.6)
RHF/DZV(2d,p)	87.0 (29.9)	70.6 (23.9)	72.4 (23.8)
MP2/DZV(2d,p)	74.0 (24.3)	60.5 (19.0)	62.0 (19.0)
D + **A**			
B3LYP/DZV(2d,p)	42.1 (21.1)	31.9 (14.7)	33.8 (14.8)
RHF/DZV(2d,p)	57.1 (29.8)	46.7 (23.5)	48.6 (23.4)
MP2/DZV(2d,p)	49.7 (24.4)	41.5 (19.3)	43.0 (19.4)
C + 2(**A**)			
B3LYP/DZV(2d,p)	21.0 (21.0)	17.2 (17.2)	19.0 (19.0)
RHF/DZV(2d,p)	27.3 (27.3)	23.2 (23.2)	25.2 (25.2)
MP2/DZV(2d,p)	25.3 (25.3)	22.2 (22.2)	23.6 (23.6)
B + 3(**A**)	0.0	0.0	0.0

[a] Values in parentheses represent the difference between the entry shown and the corresponding entry in the row below.
[b] Relative to ethylene + 3·benzenes.
[c] All geometries optimized at B3LYP/DZV(2d,p).

For example, [18]-annulene (**F**) plus **B** should equate to **E**. This equation shows **F** to be a mere 10 kcal mol^{-1} more stable as a closed 'aromatic cycle' than as an open unit within a conjugated polymer. Similarly, prediction of the energy of the homodesmic reaction for **F** plus six ethylenes going to form three butadienes plus three hexatrienes using HDFT methods yields 17.9 kcal mol^{-1} (22.9 kcal mol^{-1} with zero point corrections) and agrees reasonably well with the experimental value of 19.0 kcal mol^{-1}.[13,14] Indeed, the entire [18]-annulene with three times the extent of benzene has about the same stabilization energy per mole.[15] A related homodesmic comparison between three benzenes and **F** reveals that **F** is much less stable per conjugated unit.[16]

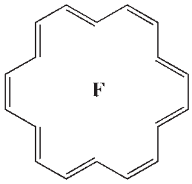

Table 2. Calculated bond separation reactions (kcal mol^{-1})

Reaction	All-*cis* isomer	All-*trans* isomer	$n-1$ *trans* isomer
D + **A** → **E**			
B3LYP/DZV(2d,p)	−21.2	−14.5	−14.5
RHF/DZV(2d,p)	−29.9	−23.9	−23.8
MP2/DZV(2d,p)	−24.3	−19.0	−19.0
C + **A** → **D**			
B3LYP/DZV(2d,p)	−21.1	−14.8	−14.9
RHF/DZV(2d,p)	−29.8	−23.5	−23.4
MP2/DZV(2d,p)	−24.4	−19.3	−19.3
B + **A** → **C**			
B3LYP/DZV(2d,p)	−21.0	−17.2	−19.0
RHF/DZV(2d,p)	−27.3	−23.2	−25.2
MP2/DZV(2d,p)	−25.3	−22.2	−23.6

What should we make of these specific predictions? They are certainly testable and could have implications in the design of conjugated materials.[5] However, does this represent a new definition for a quantitative assessment of aromaticity? No! …nor does any existing scheme purporting to do so.

Arguments over definitions are often the most personal and counterproductive aspects of science. Defining scales of aromaticity creates special problems as aromaticity has a long colloquial multicultural history, an ambiguous or multivariate correlation to experiment and an idiomatic usage.[17–19] There are numerous historical aromatic qualities of benzene. From studies on benzene,[20] semi-quantitative definitions of 'aromaticity' have arisen using structure, stability, reactivity, magnetic character and spectroscopy, to name but a few.[21–25] In every case, benzene is the standard, although in each case a different physical chemical property is measured. Some of these properties loosely correlate with one another for selected subsets of compounds, but for the most part, each has its own general importance to understanding chemistry.

Why would anyone (a) force the use of an *ad hoc* multivariate equation of the phenomena to rank 'aromaticity' or (b) chose to redefine a perfectly respectable single experimental measurable as a rank for 'aromaticity'? Perhaps this comes from a common misconception that quantitative science is always more rigorous and therefore better than qualitative science. Perhaps there is an irrational drive to quantify 'aromaticity' motivated by the emphasis of the term's importance rather than the chemistry.

If someone talks about *a* being more 'aromatic' than *b*, what does this communicate chemically? At present, it might mean that the 'ring current', as gauged from an NMR property, is large, or that the relative heat of formation compared with a 'non-aromatic' reference is lower, or …*it* depends on the context of the statement and the intent of the author. Without a clear understanding of *these*, the usage is ambiguous. So then, would it not be *great* to have a unique definition of aromaticity, you might ask? Well, let us look at the two scenarios presented above: forcing an *ad hoc* multivariate equation; or selecting and redefining an existing experimental measure.

In the first approach presented above, we could assemble together all of (or some agreed upon subset of) the characteristics ever used to characterize aromaticity and scale them. Then, we could create a weighted multivariate equation that would uniquely give a value to the aromatic character of each compound. Now, when someone says *a* is more aromatic than *b*, you would be sure there was a unique solution. But, so what? In order to *get* anything chemically meaningful from the comparison you would have to go and look up the equation, consider the scaling and weighting of parameters and filter them into your chemical situation. As pilpul for a Talmudic scholar, this might deserve praise, but it is counterproductive obfuscation by a scientist because the mutlivariate

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equation merely assembles parameters, but does not condense them in a physically meaningful way (pilpul: a dialectic method of Talmudic study, consisting of examining all of the arguments pro and con in order to find a logical argument for the application of the law and at the same time sharpen the wit of the student).

In the second approach, one might find a quantitative physical property, X, that was convenient to measure or compute for general compounds. If that property, X, was also exceptional for benzene, one might then define that greater (or lower) values of X implies more aromatic character. Now, when someone says that *a* is more aromatic than *b*, you would know the precise meaning and even the chemical relevance. Again, so what?

'But', you might object to our cynicism, 'here we have a unique order and chemical significance, what more do you want?' Nothing, we would reply; however, we already have those features in X alone and to assign the term 'aromatic' to X merely adds jargon to the language and relegates a useful qualitative 'concept of abstraction' such as aromaticity to an arbitrary single observable or *ad hoc* admixture of observables . The addition of jargon and the conceptual restriction of aromaticity are undesirable complications to our science.

So, where are we with aromaticity? Should we ban it from the classroom, lecture hall, journal, and text? We think not. Perhaps we need to understand that the importance of aromaticity is its 'fuzzy' character, which began and has evolved historically as an integral part of our investigations into molecular properties of benzene (for a discussion of 'fuzziness' in chirality, see Ref. 26). If we may, aromaticity is a term of 'poetic' importance in organic chemistry as well. Its use should be contextually well defined by, and reserved for, enhancing the texture of our discussion of 'benzene-like' molecules, but let us leave the quantitative scaling of aromaticity to the disciples of Sisyphus (for similar arguments in favor of qualitative definitions for terms such as 'aromaticity', see Ref. 27).

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