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On the Destabilization (Strain) Energy of Biphenylene

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Biphenylene is subject to a variety of destabilizing effects (antiaromaticity, ring strain) and resonance stabilization. Careful construction of a group equivalent reaction that isolates the destabilization energy from other chemical effects, notably resonance energy, leads to a revised estimate of the destabilization energy of biphenylene as 57 kcal mol^{-1}. Extension of these ideas to higher homologoues of biphenylene, including starphenylene, point out pitfalls of any approach toward uniquely defining reactions that measure chemical effects.

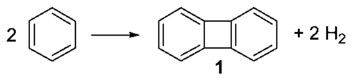
Introduction

Biphenylene (**1**) is a molecule that tests our assumptions concerning a number of essential organic concepts.[1] It lies at the crossroads of aromaticity, antiaromaticity, and strain energy. Coulson and Moffit first estimated a strain energy of about 74 kcal mol^{-1} for **1**.[2] With the refinement of the heat of combustion of **1**, Bedford et al. estimated the strain energy, in reference to biphenyl, as 64.3 kcal mol^{-1}.[3] Using *o*-xylene as the reference, Maksić and co-workers estimate a value of 52.2 kcal mol^{-1}.[4] Schulman and Disch have computed the heats of formation of a series of [*N*]phenylenes, including **1**.[5] These values are in excellent agreement with experiment. Novak recently attempted to refine the value of the strain energy of biphenylene.[6] Our attempt here is to point out difficulties in a number of assumptions made in Novak's and the other studies and to provide a more firmly grounded estimate of the strain energy of biphenylene. We also point out some inherent problems in making these kinds of estimations.

Experimental Methods and Calculations

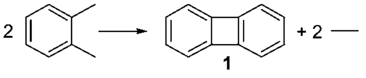
Our approach will be to create balanced chemical reactions where the reactants and products differ by only the particular effect we wish to assess, such as strain energy or resonance energy. To evaluate the energies of these reactions, we have completely optimized all molecules at PBE1PBE/6−311G(d).[7] Each structure was confirmed to be a local energy minimum by vibrational frequency analysis. This also provides the zero-point energy, which we add to the electronic energy without scaling. To assess the validity of these computed energies, the smaller molecules were also computed at G3MP3B3, a composite method that provides excellent thermodynamic properties.[8] Where applicable, comparison with experimental enthalpies are made using the NIST Webbook data.[9] All computations were performed with GAUSSIAN-03.[10]

We begin, as Novak did implicitly,[6] by claiming that biphenylene is strained or stabilized by some amount relative to benzene. We partition this energy difference into two parts: a resonance energy (RE) due to the interaction between the two adjoining phenyl rings and a destabilization energy (DSE) due to the small bond angles at the carbons where the rings join, the strain of a four-member ring, the role of antiaromaticity from the four-member ring, and the reduction of aromaticity within the six-member rings by partial localization to avoid the antiaromatic cyclobutadiene fragment. (Novak and previous authors call this strain energy, but we opt for the label destabilization energy because of the broad range of effects covered by this umbrella term.) We will not attempt to partition the destabilization energy into its components as this cannot be done without invoking significant assumptions. The root problem is that the ring strain and the antiaromaticity will always enter hand-in-hand.[11] So although Reaction 1a does directly compare biphenyl to benzene, the reaction is neither isodesmic nor homodesmotic and, therefore, cannot provide any insight concerning the partitioning of strain versus resonance effects, too many other changes are also involved (such as the unbalanced number of C−C and C−H bonds).



ΔE = 58.66 kcal mol^{-1} (PBE1PBE)
ΔE = 53.72 kcal mol^{-1} (G3MP2 0K)
ΔH = 56.85 kcal mol^{-1} (G3MP2 298K)
ΔH = 60.88 kcal mol^{-1} (expt)

Reaction 1a



ΔE = 47.54 kcal mol^{-1} (PBE1PBE)
ΔE = 50.14 kcal mol^{-1} (G3MP2B3 0K)
ΔH = 50.67 kcal mol^{-1} (G3MP2B3 298K)
ΔH = 51.40 kcal mol^{-1} (expt)

Reaction 1b

Maksić's estimation of the strain energy uses Reaction 1b,[4] which, although being homodesmotic, fails to separate the resonance energy from the destabilization energy. The energy of this reaction underestimates the destabilization energy, since resonance energy is gained. We will employ reactions that are group equivalent reactions,[12] that is, reactions that conserve equivalent groups as defined by Benson.[13] Group equivalent reactions are also, by definition, both isodesmic and homodesmotic.[14]

Novak's approach was to create a reaction where the reactants and products differed solely by the destabilization energy (DSE) and the resonance energy (RE).[6] The RE of **1** he defined as twice the stabilizing energy of two bonded phenyl rings (2RE).

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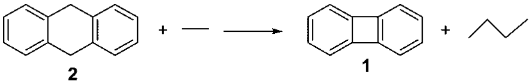
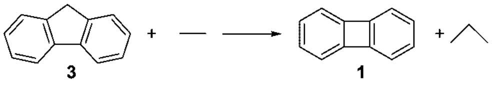
SCHEME 1

The reaction he selected for this purpose is Reaction 2. Implicit here is the assumption that the central six-member ring of (**2**) is strain-free. Novak computed energies at G3MP2/B3LYP (which we have repeated and we use our values herein), and obtained a value of ΔH^{298}(Reaction 2) = 51.19 kcal mol^{-1}. To remove the resonance energy, he next employed Reaction 3. He assumed that the resonance energy of biphenylene is twice the value in fluorene (**3**) and that the destabilization (strain) energy of **3** is negligible. The G3MP2/B3LYP value of ΔH^{298} (Reaction 3) is 50.15 kcal mol^{-1}. He then claimed that the difference in these two energies is the value of the resonance energy RE.



ΔE = 48.30 kcal mol^{-1} (PBE1PBE)
ΔE = 50.96 kcal mol^{-1} (G3MP2 0K)
ΔH = 51.19 kcal mol^{-1} (G3MP2 298K)
ΔH= 52.28 kcal mol^{-1} (expt)

Reaction 2



ΔE = 49.08 kcal mol^{-1} (PBE1PBE)
ΔE = 50.00 kcal mol^{-1} (G3MP2 0K)
ΔH= 50.15 kcal mol^{-1} (G3MP2 298K)
ΔH= 53.63 kcal mol^{-1} (expt)

Reaction 3

Let us examine this more closely. Novak's assumptions lead to the following expressions. From Reaction 2, we obtain the following equation,

$$\Delta \text{H}^{298}(\text{Reaction 2}) = \text{DSE} - 2\text{RE} = 51.19\ \text{kcal mol}^{-1} \tag{1}$$

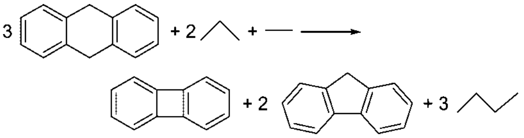
and from Reaction 3 we get eq 2

$$\Delta \text{H}^{298}(\text{Reaction 3}) = \text{DSE} - \text{RE} = 51.15\ \text{kcal mol}^{-1} \tag{2}$$

Because resonance energy is stabilizing, if Novak's assumptions are correct, Reaction 2 should be less endothermic than Reaction 3. This is in fact true if one uses the experimental values for these two reactions derived from NIST[9] data (52.28 kcal mol^{-1} for Reaction 2 and 53.62 kcal mol^{-1} for Reaction 3) or the PBE1PBE values (48.30 and 49.08 kcal mol^{-1} for Reactions 2 and 3, respectively). However, Novak used his G3MP2 computed values, which are in conflict with this assumption. He then subtracts ΔH^{298}(Reaction 3) from ΔH^{298}(Reaction 2), obtaining a value of 1.04 kcal mol^{-1}, and from eqs 1 and 2 we get

$$\Delta E(\text{Reaction 2}) - \Delta E(\text{Reaction 1}) = -\text{RE} = 1.04\ \text{kcal mol}^{-1} \tag{3}$$

Again, this result contradicts the assumption of *RE* being stabilizing. In his next step, Novak doubles this faulty RE value and adds it to ΔH^{298}(Reaction 2) to give a destabilization energy of 53.27 kcal mol^{-1}. In effect, his estimate for DSE is given by Reaction 4, whose derivation is worked out in Scheme 1S (see the Supporting Information). This reaction does not conserve group equivalents. This is readily apparent in that there are 12 $\text{C}_\text{b}-(\text{C})$ groups on the left-hand side but only four of them on the right. It is also clear that this reaction does not cancel out the resonance energy; there are no $\text{C}_\text{b}-(\text{C}_\text{b})$ groups in the reactants whereas there are four $\text{C}_\text{b}-(\text{C}_\text{b})$ groups among the products, and it is this group that accounts for the resonance interaction between connected phenyl rings.



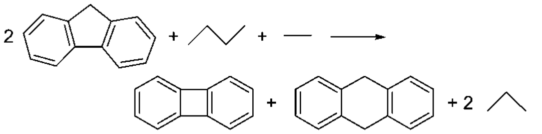
Reaction 4

ΔE = 46.74 kcal mol^{-1} (PBE1PBE)
ΔE = 52.89 kcal mol^{-1} (G3MP2B3 0K)
ΔH = 53.28 kcal mol^{-1} (B3MP2B3 298K)
ΔH = 49.58 kcal mol^{-1} (expt)

It should be noted that eq 3 yields a positive value for RE if the experimental or PBE1PBE values are used. However, use of Reaction 4, regardless of what method is used to obtain the reaction energy, involves a reaction that does not properly remove the resonance energy.

One can make use of Reactions 2 and 3 to construct a group equivalent reaction that does balance the resonance contributions. This is Reaction 5, and its construction is shown in Supporting Information Scheme 2S. This reaction, along with conserving equivalent groups, balances the resonance energy (two such phenyl−phenyl bonds). The PBE1PBE and G3MP3B3 values are in close agreement, but differ from experiment by 5 kcal mol^{-1}.

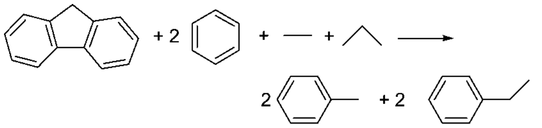
But what about the assumption that the five-member ring of fluorene is essentially strain-free? This is once again difficult to assess since the ring strain and the resonance are intrinsically linked.[11] Reaction 6 assesses the net effect of both the strain and resonance energy of fluorene. This reaction is slightly endothermic with PBE1PBE or experimental values; if the ring



Reaction 5

ΔE = 49.86 kcal mol^{-1} (PBE1PBE)
ΔE = 49.04 kcal mol^{-1} (G3MP2B3 0K)
ΔH = 49.10 kcal mol^{-1} (G3MP2B3 298K)
ΔH = 54.98 kcal mol^{-1} (expt)

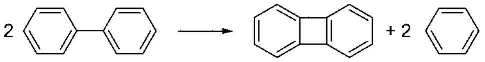
strain were negligible, one might expect a larger endothermicity reflecting the loss of resonance energy. (The reaction is predicted to be slightly exothermic with G3MP2B3, counter to the expectation if the ring were truly strain-free.) As we will see below, the resonance energy is about 4−5 kcal mol^{-1}. This suggests that the destabilization energy of fluorene is about 3 kcal mol^{-1}, and because fluorene appears twice in Reaction 5, the reaction energy includes the release of about 6 kcal mol^{-1} of destabilization energy in fluorene. This makes the estimate for the destabilization energy of **1** about 56 kcal mol^{-1} at PBE1PBE (or about 60 kcal mol^{-1} using the experimental values)



Reaction 6

ΔE = 1.32 kcal mol^{-1} (PBE1PBE)
ΔE = -1.11 kcal mol^{-1} (G3MP3B3 0K)
ΔH = -0.79 kcal mol^{-1} (G3MP3B3 298K)
ΔH = 1.73 kcal mol^{-1} (expt)

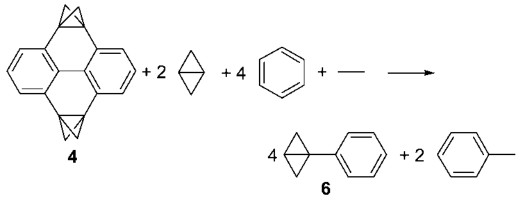
An alternative approach we now explore is to create a group equivalent reaction that balances the resonance energy on both sides of the reaction. Because the resonance energy is due to the interaction of two bonded phenyl groups, biphenyl would be the simplest reference case, as seen in Reaction 7. Assuming that the resonance energy in two biphenyl molecules is equivalent to that in biphenylene, the energy of Reaction 7 equals the destabilization energy of biphenylene, 50.6 kcal mol^{-1} at PBE1PBE and about 3 kcal mol^{-1} larger with G3MP2B3 or experimental values. However, this is a faulty assumption; the two phenyl rings of biphenyl are not coplanar (the angle between the ring planes is 40.9°) and so their resonance interaction is diminished, making the destabilization energy of **1** greater than the energy of Reaction 7.



Reaction 7

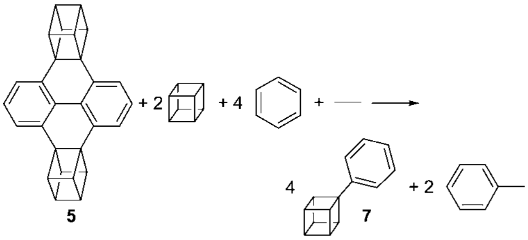
ΔE = 50.61 kcal mol^{-1} (PBE1PBE)
ΔE = 54.73 kcal mol^{-1} (G3MP2B3 0K)
ΔH = 54.74 kcal mol^{-1} (G3MP2B3 298K)
ΔH = 53.08 kcal mol^{-1} (expt)

We next sought out derivatives of biphenyl that bring the phenyl rings coplanar. Compounds **4** and **5** have D_{2h} symmetry, so the rings are rigorously coplanar, allowing for maximal resonance. The energies of Reactions 8 and 9 should measure the resonance energy between two phenyl rings; these reactions should be endothermic if all other effects are properly balanced. However, both of these reactions are exothermic. These reactions are constructed to balance the ring strain energy on each side. So, for Reaction 8 and 9, there are four bicyclobutyl or cubyl moieties on each side. These polycyclic ring fragments are not equivalently strained. The highlighted C−C−C angles in **6** and **7** (see Scheme 1) are 131.8° and 124.4°, respectively. The corresponding angles in bicylobutane and cubane are 128.7° and 125.3°, respectively. However, in our reference molecules, the angles are 119.4° in **4** and 119.0° in **5**. The bicyclobutyl and cubyl fragments in the reference compounds **4** and **5** are thus much more strained than their analogues in Reactions 8 and 9, so these reaction energies reflect not just the resonance energy but also the strain relief.



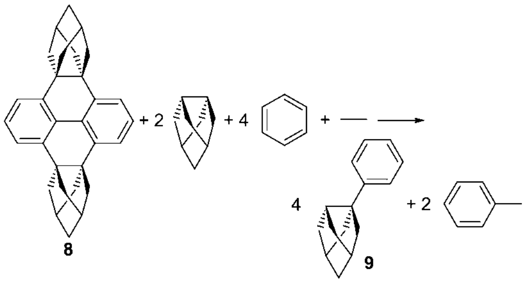
Reaction 8

ΔE = -9.13 kcal mol^{-1} (PBE1PBE)



Reaction 9

ΔE = -0.84 kcal mol^{-1} (PBE1PBE)



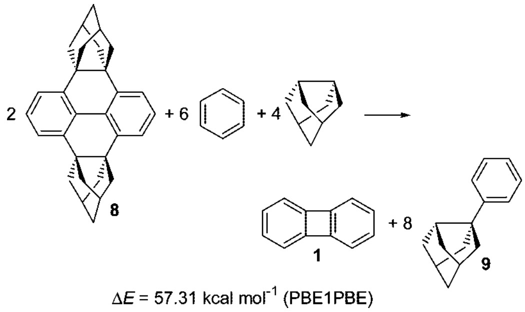
Reaction 10

ΔE = 5.51 kcal mol^{-1} (PBE1PBE)

On the other hand, Reaction 10 is endothermic (ΔE = 5.51 kcal mol^{-1}). The strain energies of the tricyclononane fragments are likely to be quite comparable: the highlighted C−C−C angle in **9** (115.4°) is very similar to that in **8** (116.4°). Reaction 10 predicts that the resonance energy due to the direct bonding between two phenyl rings is 5.5 kcal mol^{-1}.

We can now employ **8** as a reference for comparison with **1**. Reaction 11 is a group equivalent reaction that conserves the resonance interactions between phenyl rings. The energy of Reaction 11 should therefore be a reasonable estimate of the destabilization energy of biphenylene: 57.3 kcal mol^{-1}.

Because there is no unique reaction that provides a measure of the destabilization energy of biphenylene, we next present a couple of alternatives. If we relax the requirement that the two phenyl rings must be rigorously coplanar and settle instead for rings that are closer to coplanar than in biphenyl, we can use **10** or **11** as reference compounds. Despite the fact that the dihedral angle between the two phenyl ring planes is 17.7° in **10**, and so one might expect some reduction in the overlap between the π-systems of the two rings, the resonance energy predicted by Reaction 12 (5.4 kcal mol^{-1}) is nearly identical to

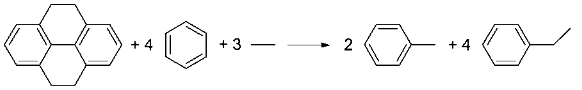


Reaction 11

ΔE = 57.31 kcal mol^{-1} (PBE1PBE)

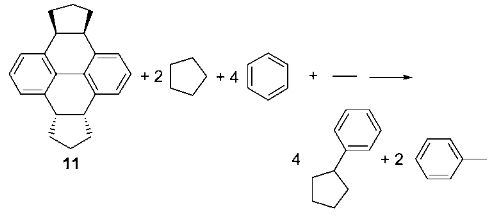
that predicted by Reaction 10 (5.5 kcal mol^{-1}). The saturated carbons of **10** appear to be essentially unstrained: the C_b−C−C angle is 111.0°, and the conformation is staggered. As an aside, we note that the experimental prediction for the enthalpy of Reaction 12 is significantly larger (11.6 kcal mol^{-1}) than either the PBE1PBE or G3MP2B3 estimates. This value appears to be too large; it would suggest an exceptionally strong resonance energy, one that, if correct, would lead to a more planar biphenyl molecule than actually is found.

The phenyl rings are closer to planarity in **11** (14.6°) than in **10** (17.7°). Nonetheless, Reaction 13 predicts a slightly smaller resonance energy (4.0 kcal mol^{-1}) than does Reaction 12. The three predictions (from Reactions 10, 12, and 13) for the resonance energy range from 4.0 to 5.5 kcal mol^{-1}, quite reasonable agreement.



Reaction 12

ΔE = 5.36 kcal mol^{-1} (PBE1PBE)
ΔE = 3.63 kcal mol^{-1} (G3MP2 0K)
ΔH= 4.20 kcal mol^{-1} (G3MP2 298K)
ΔH= 11.58 kcal mol^{-1} (expt)

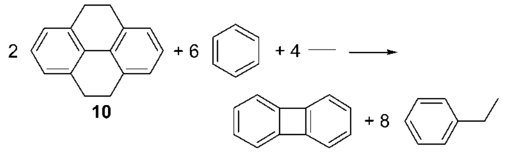


Reaction 13

ΔE = 3.97 kcal mol^{-1} (PBE1PBE)

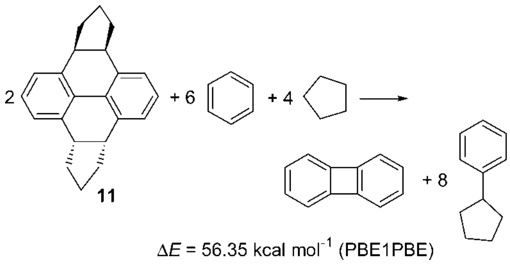
Using **10** and **11** as reference molecules, we can now employ Reaction 14 and 15 to predict the destabilization energy of biphenylene. Again, both of these reactions conserve group equivalents (and thereby conserve resonance energy), so the reaction energy should be the destabilization energy. Once again, we see general agreement between the PBE1PBE and G3MP2B3 results for Reaction 14, whereas the experimental value is significantly larger. The large value for the energy of Reaction 14 using the experimental values casts some doubt on the validity of the experimental ΔH_f value of **10.** If there is an error in the experimental[15] ΔH_f value of **10**, that error would be magnified in Reaction 14 because it appears twice.

Reactions 14 and 15 predict a destabilization energy of **1** of 59.1 and 56.4 kcal mol^{-1}, respectively; their difference is a reflection of the differing value of the resonance energy seen in Reactions 12 and 13. These values are in nice agreement with the values from Reaction 11 (57.3 kcal mol^{-1}) and from the adjusted destabilization energy from Reaction 5 (56 kcal mol^{-1}). We settle on a destabilization energy of approximately 57 kcal mol^{-1}, a value 4 kcal mol^{-1} greater than that suggested by Novak. The G3MP2B3 energies for Reactions 14 and 5 (58.8 and 60 kcal mol^{-1}, respectively) suggest the destabilization energy might perhaps be a little larger.



Reaction 14

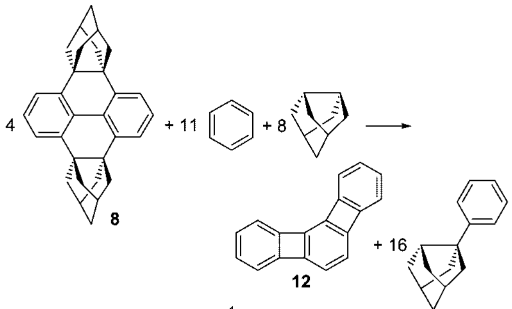
ΔE = 59.13 kcal mol^{-1} (PBE1PBE)
ΔE = 57.73 kcal mol^{-1} (G3MP2B3 0K)
ΔH = 58.78 kcal mol^{-1} (G3MP2B3 298K)
ΔH = 75.44 kcal mol^{-1} (expt)



Reaction 15

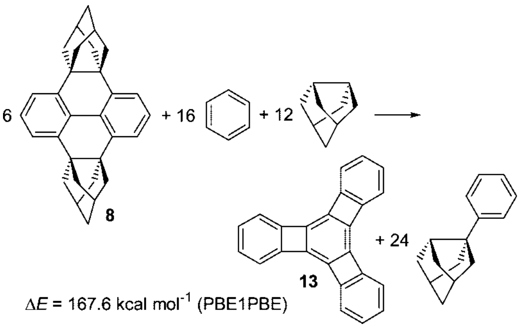
ΔE = 56.35 kcal mol^{-1} (PBE1PBE)

We conclude by applying these ideas to two higher homologues of biphenylene: **12** and **13**. Reactions 16 and 17 employ **8** as the reference compound, allowing us to use these reaction energies as a measure of the destabilization energy of **12** and **13**. As one might expect,**12** is much more strained than **1**: 115 kcal mol^{-1}, just over twice the strain of **1**. Fusing on another ring to create starphenylene **13** increases the strain further; Reaction 17 predicts the destabilization energy is 167.6 kcal mol^{-1}.



Reaction 16

ΔE = 115.4 kcal mol^{-1} (PBE1PBE)

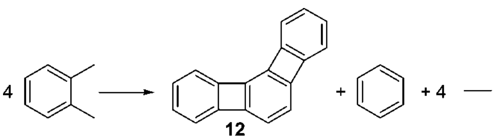


Reaction 17

ΔE = 167.6 kcal mol^{-1} (PBE1PBE)

These destabilization energies can be compared with previous estimates. Maksić employed Reaction 18 to estimate the strain energy of **12**.[4] His estimate, at MP2/6−31G*//HF/6−31G* was 101.2 kcal mol^{-1}, whereas our estimate at PBE1PBE (which includes correction for zero-point vibrational energy, absent in

Macsic's work) is 91.6 kcal mol^{-1}. This is significantly less than the value obtained with Reaction 16, but Reaction 18 accounts for not just the destabilization energy but also the resonance energy of **12**. Vollhardt and co-workers[16] have estimated the strain energy by comparing its experimental heats of formation with that estimated by summing up the Benson group equivalents. This gave strain energy values of 99.7 kcal mol^{-1} for **12** and 147.9 kcal mol^{-1} for **13.**

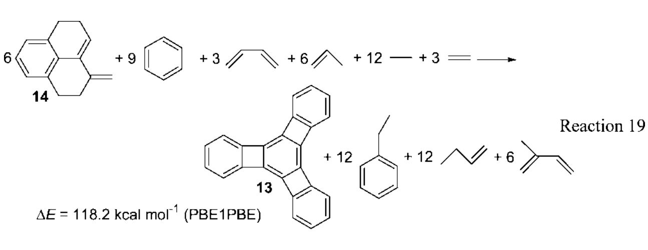


Reaction 18

ΔE = 91.64 kcal mol^{-1} (PBe1PBE)

The case for starphenylene **13** highlights the difficulties in choosing appropriate reference compounds. Vollhardt and co-workers[16] suggested that the central ring of **13** is in fact a cyclohexatriene moiety, based on the heat of hydrogenation of **13** and the bond lengths (1.481 and 1.343 Å at PBE1PBE/6−311G(d)). This actually contradicts their method for estimating the strain energy of **13**; they employed 12 C_b−(H) and 12 C_b−(C_b) equivalents, when the cyclohexatriene model requires 12 C_b−(H), 6 C_b−(C_d), and 6 C_d−(C_b)(C) equivalents. Using these equivalents (see Supporting Information Scheme 3S), the strain energy of **13** is 124.4 kcal mol^{-1}.

The use of **8** as a reference implicates the central ring as a normal aromatic species. The bonds in the four-member rings of **13** might be better modeled as C_b−C_d (given the cyclohexatriene nature of the center ring) so **14** can serve as a model compound. The butadiene fragment of **14** is not planar, nor is it coplanar with the phenyl ring, contrary to their arrangement in **13**. Distortions of this kind are present in **10** too, but this proved a reasonable reference compound in the evaluation of the destabilization energy of **1**. Nonetheless, use of **14** as reference may lead to an underestimation of the destabilization energy of **13**. Reaction 19 provides an estimate of the total destabilization energy of **13** as 118.2 kcal mol^{-1}. This value is in reasonable accord with the revised strain energy using group equivalents (124.4 kcal mol^{-1}).



Reaction 19

ΔE = 118.2 kcal mol^{-1} (PBE1PBE)

Neither model is ultimately satisfactory. Use of **8** compares the central ring to a typical aromatic ring, and so Reaction 17 is too endothermic, including loss of aromatic character along with the destabilization energy. Use of **14** implies that the central ring of starphenylene has no aromatic character, so the energy of Reaction 18 might underestimate the destabilization energy of **13**. Any attempt to select a reference compound (or a set of reference compounds) will require assumptions that cloud the result, principally by creating reactions where reactants and products differ by more than one chemical effect. This example highlights the situation that for some cases a suitable choice of reference compounds may be extraordinarily difficult to determine and ultimately quite arbitrary. In cases like these, definitive isolation of a single effect may not be possible. It is for these reasons that one cannot separate out the many effects (detailed at the beginning of this paper) that make up the total destabilization energy of biphenylene.

It should also be pointed out that homodesmotic and group equivalent reactions can potentially involve large numbers of molecules, such as in Reaction 19 where (among others) 12 molar equivalents of ethane and ethylbenzene are used. Any inherent errors in evaluating the energies of these molecules, whether by experiment or computation, can become magnified, leading to large errors in the overall reaction energy. Caution is advised in interpreting these situations.

Conclusion

By employing carefully constructed reactions that conserve group equivalents, we are able to estimate the destabilization energy of biphenylene as 57 kcal mol^{-1}, a value somewhat greater than that recently proposed by Novak. When a chemical reaction energy is used to measure the consequence of a chemical effect, we strongly encourage the use of the group equivalent reaction[12] to ensure isolation of just that single chemical effect.

Acknowledgment. I thank Nancy Mills for helpful discussions and the two referee for helpful suggestions.

Supporting Information Available: Schemes 1S, 2S, and 3S, full citation of Reference 10, the optimized PBE1PBE/6−311G(d) coordinates and energies of **1**−**14**, and G3MP3B3 energies of selected molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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