Theor Chem Acc (2011) 130:261–268
DOI 10.1007/s00214-011-0970-4

REGULAR ARTICLE

The effects of orbital interactions on the geometries of some annelated benzenes

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Received: 25 March 2011 / Accepted: 27 May 2011 / Published online: 24 June 2011

Abstract In order to investigate C–C bond-length alternation in benzenes, tris-annelated with benzo (**1**), 1,3-cyclobutano (**2**), etheno (**3**), and ethano (**4**) groups, B3LYP/6-31G(d) calculations have been performed. The calculations were carried out not only at the fully optimized geometries of **1**–**4**, but also at partially optimized geometries in which the C–C bond lengths in the benzene rings were all constrained to be $R = 1.397$ Å (the optimized C–C bond length of D_{6h} benzene). This mode of analysis allowed the annelation energies for forming **1**–**4** to be separated into contributions from (a) the effects of the orbital interactions, which, to different extents in **1**–**4**, localize the π bonds in the benzene rings, even at $R = 1.397$ Å and (b) the resulting changes in the C–C bond lengths that lead to the optimized, bond-alternated, geometries. The degree of cooperativity in steps (a) and (b) has been investigated by computing the annelation energies as a function of n, the number of annelating groups. Cooperativity has been found in step (a) for both **1** and **3**, but not for **2**, due to the absence of a low-lying, unfilled orbital in cyclobutane. Cooperativity has been found in step (b) for **1**–**3**, where the energy liberated on allowing the benzene bond lengths to alternate has been found to vary as n^2, the square of the number of annelating groups. The dependence on n of both contributors to the annelation energies is discussed.

Keywords Bond alternation · Orbital interactions · Cooperative effects

1 Introduction

The origin of the alternation of benzene C–C bond lengths, caused by annelated small rings, has been discussed for two and a half decades [1]. In 1986, Diercks and Vollhardt synthesized **1**, which contains three dibenzocyclobutadiene rings [2]. The C–C bond lengths in the central benzene ring of **1** were found to alternate strongly in a manner that minimizes the antiaromatic, four-electron interactions between the π bonds in this ring and those in the three benzo groups that are annelated to it.

Subsequently, Siegel and coworkers reported that fusion of three 1,3-cyclobutano groups to benzene also results in bond-length alternation in the benzene ring of **2** [3]. The X-ray structure of **2** confirmed the prior computational prediction by Baldridge and Siegel that such bond-length alternation would be found in **2** [4].

Computational studies also find that annelation of benzene by three etheno groups causes strong, cyclohexatriene-like fixation of the double bonds in the central benzene ring of **3** [5–8]. In contrast, both calculations [5, 7] and experiments [9–15] find that benzene, tris-annelated by ethano groups, (**4**) shows considerably less bond-length alternation than benzene, annelated by the three etheno groups in **3** [5–8, 16–22], by the three 1,3-butano groups in **2** [3, 4], or by the three benzo groups in **1** [2].

The explanations of the origin of C–C bond-length alternation in benzene, caused by annelation of small rings,

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Dedicated to Professor Shigeru Nagase on the occasion of his 65th birthday and published as part of the Nagase Festschrift Issue.

Electronic supplementary material The online version of this article (doi:10.1007/s00214-011-0970-4) contains supplementary material, which is available to authorized users.

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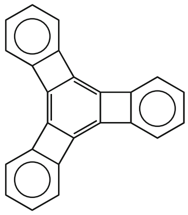
can be generally classified into two types. The first focuses on π interactions. If, as in **1** and in **3**, the annelating groups contain π bonds, the alternation of the C–C bond lengths in the benzene ring may be attributed to minimization of the anti-aromatic character of the benzocyclobutadiene rings in **3** [5–8] and in the dibenzocyclobutadiene rings in **1** [2]. This argument is supported by the comparatively small amount of bond-length alternation found in **4** [9–15], in which the etheno groups in **3** are replaced by ethano groups.

However, like the ethano groups in **4**, the annelating 1,3-cyclobutano groups in **2** contain no unsaturation. Nevertheless, the benzene bond lengths in **2** show a high degree of alternation [3]. It has been argued that σ strain effects can induce some degree of bond alternation [23–26], as they apparently do in **4** [12]; but the difference between the degree of bond alternation in the benzene rings of **2** and **4** is hard to rationalize solely on this basis.

Instead, it has been suggested that interactions of the orbitals of the ring bonds of the 1,3-cyclobutano groups with the π bonds of the benzene ring are responsible for the bond alternation found in **2** [27–29]. The HOMO of "Walsh" cyclobutane has 2p AOs at C1 and C3 that are in-phase, like the 2p AOs that comprise the π bond of ethylene [30, 31]. Consequently, orbital interactions favor butadieno over etheno as a 1,3-cyclobutane bridging group [32–34]. The same types of orbital interactions should then favor the observed localization of the benzene π bonds in **2** [3] so that the cyclobutane rings in **2** are each 1,3-bridged by butadieno, rather than by etheno groups.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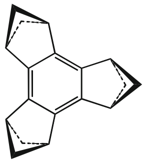
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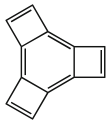
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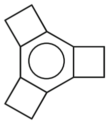
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We recently reported an analysis of the π MOs of **3** and how the three localized π bonds in **3** evolve from the mixing of the delocalized benzene π and π^* orbitals with the π and π^* orbitals of one, two, and three etheno annelating groups [8]. In the course of our calculations on **3**, we discovered the existence of two types of cooperative substituent effects.

The first we traced to a stabilizing interaction between the π^* MOs of the benzene ring and the π^* MOs of the etheno groups. The antibonding π^* MOs of the benzene ring are mixed into the degenerate HOMOs of **3** by interactions with the filled π orbitals of the etheno groups; and the antibonding π^* MOs of the etheno groups are mixed into the degenerate HOMOs of **3** by interactions with the filled π orbitals of the benzene ring. The stabilizing interaction between the π^* MOs of the benzene ring and the π^* MOs of the etheno groups provides a stabilization energy that is non-linear in n, the number of annelating etheno groups [8].

The interactions of the benzene π and π^* MOs with the π and π^* MOs of each of the three etheno groups progressively localizes the benzene π bonds in **3**, even when the C–C bonds in the benzene ring of **3** are all constrained to have the same length as the C–C bonds in D_{6h} benzene. When this constraint is released, the localized π bonds cause **3** to relax to a geometry with alternating bond lengths in the benzene ring. The energy decrease that accompanies bond-length alternation was also found to be cooperative [8].

The size of the geometry change was found to depend linearly on the number of etheno substituents, n; but the decrease in the energy was found to be proportional to n^2. Formulas [35], which were derived in order to model the cooperative and competitive substituent effects in the Cope rearrangement [36], predict both the linear dependence of the degree of bond-length alternation on n and the quadratic dependence of the energy, associated with bond-length alternation, on n^2.

In contrast to **1** and **2**, **3** has not been prepared, so the results of our calculations on **3** are of largely theoretical interest. The benzo annelating groups in **1** and the 1,3-cyclobutano annelating groups in **2** should mix less strongly than the etheno annelating groups in **3** with the benzene π and π^* MOs. In fact, since cyclobutane lacks the relatively low-energy LUMO that is present in ethylene, the cooperative effect that comes from the mixing of the π^* orbitals of the etheno groups in **3** with the π^* orbitals of the benzene ring should be absent in **2**.

In this paper, we report the results of our calculations on the annelation energies of the benzene rings in **1**, **2**, and **4,** with all the benzene bond lengths constrained to be $R = 1.397$ Å. We also compare the three highest energy π MOs of **1**–**4** at $R = 1.397$ Å, in order to see how much each of the different annelating groups causes the three π bonds in the benzene ring to localize, when all the bond lengths in the benzene rings are constrained to be equal. Finally, we report the results of our calculations on how, when this constraint is lifted, the sizes of the geometry changes and of the concomitant energy decreases depend on n, the number of annelating groups.

2 Computational methodology

We performed electronic structure calculations, using the B3LYP density functional method. It is a combination of

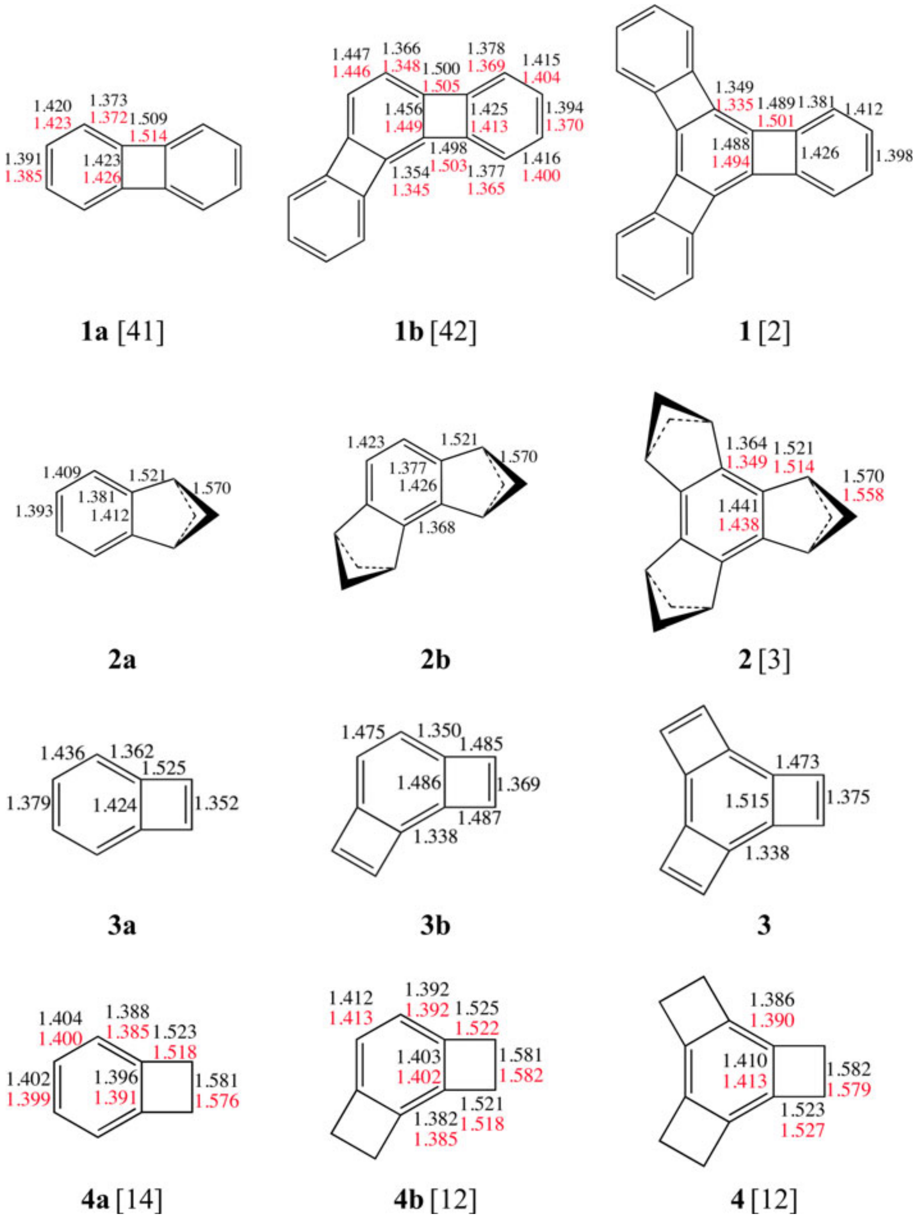
Becke's 3-parameter hybrid functional [37] with the electron correlation functional of Lee, Yang, and Parr (LYP) [38]. The 6-31G(d) basis set [39] was employed in all our calculations. The structures of **1**, **2**, and **4** were fully optimized, and B3LYP/6-31G(d) vibrational analyses were performed, in order to ensure that the optimized structures corresponded to local minima and to obtain zero-point energy corrections. The Gaussian 09 suite of programs [40] was used for all of these calculations and for the calculations in which the geometries of **1**, **2**, and **4** were partially optimized, with the constraint that all of the C–C bonds in the benzene rings had lengths of $R = 1.397$ Å.

3 Results and discussion

3.1 Optimized bond lengths

The changes in the D_{6h} benzene C–C bond lengths ($R = 1.397$ Å at B3LYP/6-31G(d)) that occur on successive annelations to form **1**–**4** can be seen in Fig. 1. Also given, where available, are the experimentally determined bond lengths. Fig. 1 shows that there is generally good agreement between the calculated and the measured bond lengths.

As expected, the etheno groups in **3** are calculated to induce the greatest amount of bond alternation in the



1a [41] **1b** [42] **1** [2]

2a **2b** **2** [3]

3a **3b** **3**

4a [14] **4b** [12] **4** [12]

Fig. 1 Optimized bond lengths (Å) at the B3LYP/6-31G (d) level of theory are given in *black*. The bond lengths of **3a**, **3b**, and **3**, calculated at this level of theory, have previously been reported [8]. Where available, the experimental bond lengths are given in *red*, and references are also provided benzene ring, followed by the benzo groups in **1**, then the 1,3-cyclobutano groups in **2**, and finally, the ethano groups in **4**. The three-fold symmetry of **1**–**4** makes it possible to use the difference between the lengths of the long and short bonds in the benzene ring of each molecule as an accurate measure of the amount of bond-length alternation. These differences in **1**–**4** are, respectively, 0.139, 0.077, 0.177, and 0.024 Å.

3.2 Molecular orbitals

Fig. 2 shows the three highest energy π MOs in **1**–**4**, calculated with the C–C bonds in the benzene rings all fixed at $R = 1.397$ Å, but with all the other bond lengths and bond angles optimized. (The geometries of these partially optimized structures are available in the Supporting Information for this manuscript). The MOs in Fig. 2 leave no doubt that interactions between the π bonds of the benzene ring and those of the annelating groups are responsible for the bond-alternated equilibrium geometries of **1**–**3**.

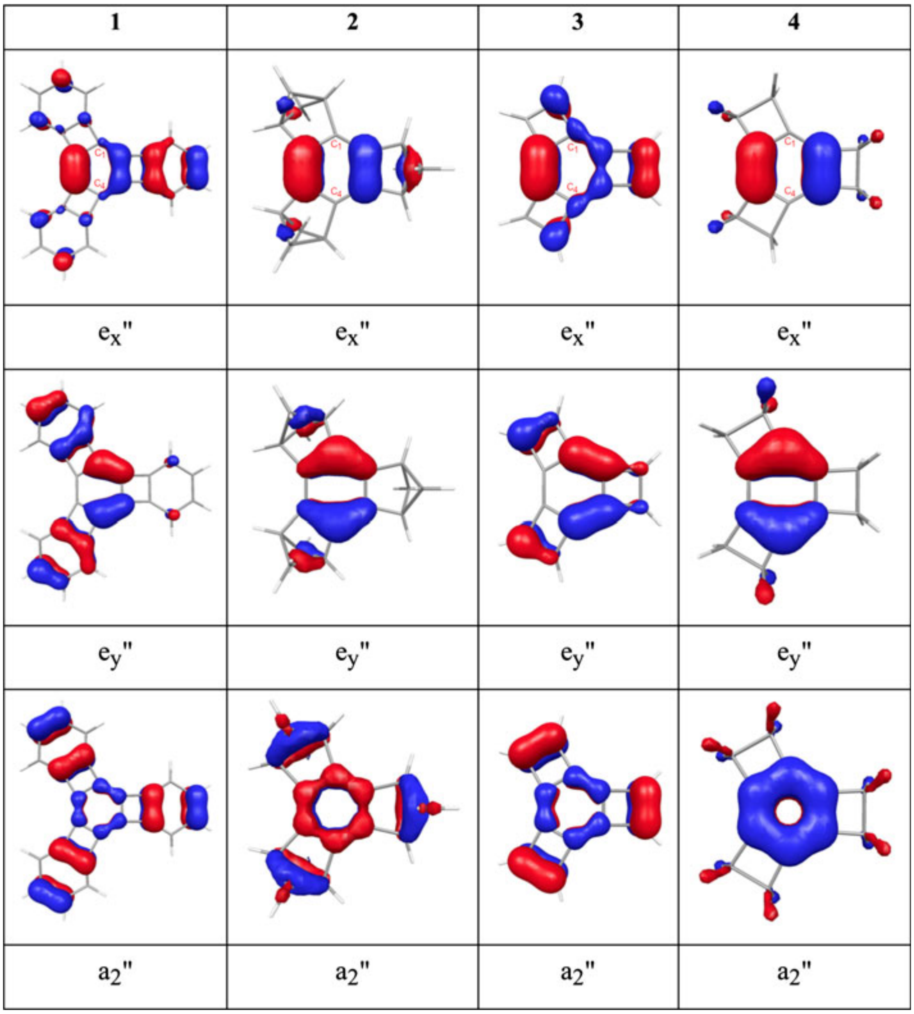
The D_{3h} point group is common to all the molecules that are shown in Fig. 2. The MOs on the first line belong to the e_x'' representation of D_{3h}; hence, they are degenerate by symmetry with the e_y'' MOs, which are shown on the second line. The MOs on the third line belong to the a_2'' representation of D_{3h}.

The π MOs that are shown for **4** in Fig. 2 are essentially the same as the unperturbed π MOs of benzene. At the other extreme, the π MOs of **3** are essentially the symmetry combinations of three double bonds in the six-membered ring, localized exocyclic to the four-membered rings [8].

The localization of the double bonds in **3** is apparent even in the a_2'' MO, which has no nodes, apart from the node in the molecular plane. The localization of the electrons in this MO is due to a contribution from 3d AOs on carbon. The 3d AOs polarize the 2p AOs, so that there is much more electron density exocyclic, rather than endocyclic to the four-membered rings in the a_2'' MO of **3**.

The MOs of **1** are intermediate between those of **3** and **4**. As is the case in unsubstituted benzene, the node in the e_x'' MO of **4** passes through two atoms (C-1 and C-4). In **3,** the

Fig. 2 The three highest energy filled π MOs of **1**–**4**. The MOs were computed at a bond length of $R = 1.397$ Å for all the C–C bonds in the benzene rings of **1**–**4.** The representation of the D_{3h} point group to which each MO belongs is shown under it. The three filled π MOs in the six-membered ring of **4** are essentially the same as those in benzene; whereas, the π MOs in the six-membered ring of **3** are essentially those for three double bonds that are localized exocyclic to the four-membered rings [8]



node passes through the middle of the bonds between C-1 and C-2 and C-3 and C-4. (The numbering of the carbons in the benzene rings of **1–4** in Fig. 2 is counterclockwise from C-1). In **1,** the node in e_x'' is in an intermediate position. It passes to the left of C-1 and C-4, but to the right of the centers of the bonds between C-1 and C-2 and C-3 and C-4.

Like the e_x'' MO, the e_y'' MO in **4** is indistinguishable from the e_y'' MO in unsubstituted benzene, with coefficients of equal magnitude at C-2, C-3, C-5, and C-6. At the other extreme, the e_y'' MO in **3** is the out-of-phase combination of π bonds between C-1 and C-6 and C-4 and C5, with no contribution from the 2p AOs at C-2 and C-3 [8].

In **1,** the e_y'' MO extends toward C-2 and C-3; but, unlike the case in **4**, the coefficients of this MO at these two carbons are clearly far smaller than the coefficients at C-5 and C-6. The appearance of the a_2'' MO of **1** is also much closer to that of **3** than of **4**, although it is hard to tell whether or not the a_2'' MO of **1** is less localized than the a_2'' MO of **3**.

One also has to look closely to see that the MOs of **2** and **4** really are different. However, careful inspection of the e_x'' MO of **2** reveals more π bonding between C-2 and C-3 than between C-5 and C-6. Similarly, examination of e_y'' shows stronger π antibonding between C-5 and C-6 than between C-2 and C-3.

Finally, although the a_2'' MO of **2** resembles that of **4**, the a_2'' MO of **2** has slightly more bonding between pairs of exocyclic carbons (C-1 and C-6, C-2 and C-3, and C-4 and C-5) than between pairs of endocyclic carbons (C-1 and C-2, C-3 and C-4, and C-5 and C-6). In contrast, the a_2'' MO of **4** can be seen to have essentially equal bonding between each pair of adjacent carbons.

It is to be emphasized that the MOs of **1–4** in Fig. 2 were computed with all the C–C bond lengths in the benzene ring fixed at $R = 1.397$ Å. Consequently, the partial localization of the π MOs of **1–3** that is seen in Fig. 2 is a consequence of interactions of the π and π^* MOs of the benzene ring with the annelating groups in these three molecules. The partial localization of the π bonds in **1–3** at $R = 1.397$ Å is the cause of the alternation of the C–C bond lengths in the benzene rings of **1–3** that can be seen in the fully optimized geometries in Fig. 1.

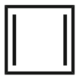
3.3 The energetics of annelation reactions that form **1–4**

We previously compared the energetics of the successive annelations of benzene to form **3a**, **3b**, and **3** by computing the energies of the three reactions that transfer one, two, and three etheno groups to benzene [8]. Since it is the differences between the energies of the annelation reactions that were of interest, the choice of the annelation reactions was arbitrary. We chose isodesmic reactions that transfer etheno groups from one, two, and three molecules of rectangular cyclobutadiene (**5**), because the energies of this series of reactions provide information about the extent to which the π interactions between the benzene ring and the annelating etheno groups in **3a**, **3b**, and **3** are less destabilizing than the interactions between the two ethylenic π bonds in **5**. The energies of these three isodesmic reactions, although published previously [8], are given in Table 1, so that they can be compared with the triads of isodesmic reactions that culminate in the formation of **1**, **2**, and **4**.

Table 1 Isodesmic annelation reactions and the amount of energy (ΔE, kcal/mol) that is predicted by B3LYP/6-31G(d) calculations to be liberated by each reaction in the formation of **1a**, **1b**, **1**, **2a**, **2b**, **2**, **3a**, **3b**, **3**, **4a**, **4b**, and **4**

Eq.	Isodesmic reaction	$-\Delta E$	$-\Delta E_0$	$-\Delta E_{\text{geom}} = -\Delta E + \Delta E_0$
1	C_6H_6 + **6** → **1a** + C_2H_4	6.6	5.6	1.0
2	C_6H_6 + *2* **6** → **1b** + *2* C_2H_4	16.3	12.4	3.9
3	C_6H_6 + *3* **6** → **1** + *3* C_2H_4	29.6	20.5	9.1
4	C_6H_6 + **7** → **2a** + C_2H_4	4.8	4.4	0.4
5	C_6H_6 + *2* **7** → **2b** + *2* C_2H_4	9.4	8.2	1.2
6	C_6H_6 + *3* **7** → **2** + *3* C_2H_4	13.9	11.4	2.5
7 [8]	C_6H_6 + **5** → **3a** + C_2H_4	14.9	12.8	2.1
8 [8]	C_6H_6 + *2* **5** → **3b** + *2* C_2H_4	40.8	31.7	9.1
9 [8]	C_6H_6 + *3* **5** → **3** + *3* C_2H_4	73.9	56.6	17.3
10	C_6H_6 + **8** → **4a** + C_2H_4	−2.3	−2.4	0.1
11	C_6H_6 + *2* **8** → **4b** + *2* C_2H_4	−4.9	−5.0	0.1
12	C_6H_6 + *3* **8** → **4** + *3* C_2H_4	−7.8	−8.0	0.2

The energies, ΔE_0, are calculated with fixed C–C bond lengths of $R = 1.397$ Å in the benzene rings of the annelated molecules. For each isodesmic reaction, subtraction of ΔE_0 from ΔE, the energy of the reaction with the product geometries fully optimized, gives ΔE_{geom}



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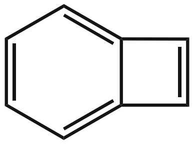

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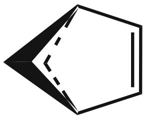

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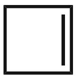

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Table 1 provides the energies of the isodesmic reactions that form: **1a**, **1b**, and **1** by transfers to benzene of benzo groups from the requisite numbers of molecules of benzocyclobutadiene (**6**), **2a**, **2b**, and **2** by transfers of 1,3-cyclobutano groups from molecules of bicyclo[2.1.1]hex-2-ene (**7**), and **4a**, **4b**, and **4** by transfers of ethano groups from molecules of cyclobutene (**8**). Table 1 gives not only the annelation energies (ΔE) but also the annelation energies with all of the C–C bonds of the benzene rings in the annelated molecules constrained to have $R = 1.397$ Å (ΔE_0). The difference between ΔE and ΔE_0 is ΔE_{geom}, the energy liberated by allowing the C–C bonds in the benzene rings to relax from $R = 1.397$ Å to the lengths that they have in the fully optimized geometries of the annelated molecules.

Since ΔE_0 and ΔE_{geom} both involve an energy that is computed at a constrained geometry, ΔE_0 and ΔE_{geom} cannot be corrected for zero-point energy differences (ΔE_{ZPE}). Therefore, in order to make $\Delta E = \Delta E_0 + \Delta E_{\mathrm{geom}}$ in Table 1, the values of ΔE in this table cannot be corrected for ΔE_{ZPE} either. However, a version of Table 1, containing both the ΔE and the $\Delta E + \Delta E_{\mathrm{ZPE}}$ values for the isodesmic reactions in Eq. 1–12, can be found in the Electronic Supplementary Material for this manuscript.

Table 1 shows that each of the isodesmic reactions that culminate in the formation of **1**, **2**, and **3** is energetically favorable. Among these, the most energetically favorable set is the reactions in Eqs. 7–9, which trade the destabilizing interactions between the two π bonds in rectangular cyclobutadiene (**5**) for the far less destabilizing π interactions between the etheno groups and the benzene rings in **3a**, **3b**, and **3**.

Much less energetically favorable is the set of reactions in Eqs. 4–6, which exchange the destabilizing interactions between the four-membered ring and the etheno bridge in bicyclo[2.1.1]hex-2-ene (**7**) for the less destabilizing interactions between the 1,3-butano groups and the benzene rings in **2a**, **2b**, and **2**. The reason for the large differences between the energies of these two sets of annelation reactions is that, although the Walsh HOMO of a 1,3-bridged cyclobutane ring does bear some resemblance to the bonding π MO in ethylene [30, 31], the HOMO of the four-membered ring interacts much less strongly with π bonds than the π bond of ethylene does.

In contrast to the energetic favorability of the annelation reactions in Eqs. 1–9 of Table 1, the set of reactions in Eqs. 10–12, which transfer an ethano group from cyclobutene (**8**) to benzene, are energetically unfavorable by an average value of 2.5 kcal/mol for each ethano group transferred. A reasonable explanation is that the four-membered ring in benzocyclobutene (**4a**) is more strained than in cyclobutene. The C=C–C bond angle of 94.4° in the ring of **8** results in a large value of 133.6° for the exocyclic H–C=C bond angle. In contrast, the geometrical constraints imposed by the six-membered ring in benzocyclobutene make the corresponding exocyclic bond angle in **4a** 122.3°, which is 11.3° smaller than the H–C=C bond angle in **8**.

The π interactions between the ethano groups and benzene in benzocyclobutenes **4a**, **4b**, and **4** may, in fact, be more favorable than those between the ethano group and the π bond in cyclobutene. However, this presumably small effect is completely masked by the increase in ring strain in the isodesmic reactions in Eqs. 10–12.

3.4 Cooperative effects on ΔE_0

As we have discussed previously [8], both the ΔE_0 and the ΔE_{geom} values for formation of **3a** and **3** deviate from additivity. For example, based on $-\Delta E_0 = 12.8$ kcal/mol for the isodesmic reaction in Eq. 7, which forms **3a**, additivity would give $-\Delta E_0 = 25.6$ kcal/mol and $-\Delta E_0 = 38.4$ kcal/mol for the reactions that form **3b** and **3**, respectively. The actual energies for the isodesmic reactions in Eqs. 8 and 9 in Table 1 are $-\Delta E_0 = 31.7$ and $-\Delta E_0 = 56.6$ kcal/mol, respectively. Thus, the deviations of $-\Delta E_0$ from additivity are 6.1 kcal/mol for formation of **3b** and 18.2 kcal/mol for formation of **3**.

We have described in detail how favorable interactions between the π* MOs of benzene and the π* MOs of the annelating ethylenes lead to the cooperative effects that result in the deviations from energetic additivity in the formation of **3b** and **3** [8]. The same type of effect, albeit smaller by a factor of about five, leads to the deviations from additivity of 1.2 and 3.7 kcal/mol in the formation of, respectively, **1b** and **1**.

The deviation from additivity for tris-annelation of benzene, compared with bis-annelation, is a factor of three larger for both etheno and benzo annelating groups. The factor of 3 increase reflects the increase in the extent to which the π* orbitals of benzene and the π* orbitals of the annelating groups are mixed into the filled MOs of **1** and **3**, compared, respectively, to the filled MOs of **1b** and **3b**.

The values of ΔE_0 in Eqs. 4–6 of Table 1 for annelation of benzene by 1,3-cyclobutano groups, however, show no indication of any cooperativity. For the isodesmic reaction in Eq. 4 to form **2a**, the calculated $-\Delta E_0$ is 4.4 kcal/mol. For the formation of **2b** and **2**, additivity would give $-\Delta E_0 = 8.8$ kcal/mol and $-\Delta E_0 = 13.2$ kcal/mol for the isodesmic reactions in Eqs. 5 and 6, respectively. The actual energies, $-\Delta E_0 = 8.2$ and $-\Delta E_0 = 11.4$ kcal/mol for Eqs. 5 and 6 (Table 1), respectively, are slightly smaller than the expected additivity values, suggesting no cooperativity in ΔE_0 for annelation of benzene by 1,3-cyclobutano groups.

Cooperativity in annelation of benzene by etheno and by benzo groups comes from mixing between π* MOs of benzene and the π* MOs of the annelating groups. Therefore, the absence of a low-lying unfilled MO of the right symmetry in cyclobutane should make ΔE_0 in Eqs. 4–6 of Table 1 strictly additive. Our computational results confirm this previously published prediction [8].

3.5 Cooperative effects on ΔE_{geom}

On allowing the C–C bond lengths in the annelated benzenes to relax from 1.397 Å to their optimized values, the energies of the annelated benzenes, of course, go down. The values of ΔE_{geom} in Table 1 for **1**–**3** show that these energy decreases are strongly cooperative, i.e.; they are not linear in the number of annelating groups. Indeed, the values of ΔE_{geom} appear to vary approximately as the square of, *n*, the number of annelating groups.

This fact was previously noted in the results of our calculations on **3a**, **3b**, and **3** [8]. It was pointed out that the magnitude of the average deviation of the equilibrium C–C bond lengths in the annelated benzenes from equality, $\Delta R = (\sum|R_i - 1.397|)/6$, depends on *n*, the number of annelating groups; and the energy lowering on geometry relaxation depends on both *n* and ΔR. Consequently, the quadratic dependence of ΔE_{geom} on *n* is readily understandable [8] and can, in fact, be derived mathematically [35].

Nevertheless, it is significant that the values of ΔE_{geom} for benzenes that are annelated with both benzo and 1,3-cyclobutano groups are calculated to have the same type of approximate n^2 dependence as the values of ΔE_{geom} for benzenes that are annelated with etheno groups. This finding provides further evidence that the bond-alternated geometries, found experimentally for **1** [2] and **2** [3], have the same origin as the bond-alternated geometry calculated for **3**.

4 Conclusions

It is convenient to think of the C–C bond-length alternation, found in the benzene rings of **1** [2], **2** [3, 4], and **3** [5–8] as having its origin in avoidance of anti-aromatic π interactions between filled orbitals of the annelating groups and the filled π MOs of benzene. However, interactions between filled MOs do not change wave functions; so this explanation of the bond-length alternation in **1**–**3** is not, strictly speaking, correct. Instead, the localization of bonding π MOs of the benzene rings, which can be seen in Fig. 2 to occur to different extents in **1**–**3**, is actually due to the mixing between filled orbitals of the annelating groups and π* orbitals of the benzene ring [8].

Mixing between filled π MOs of the benzene ring and the π* orbitals of the annelating groups also occurs in **1** and **3**. The effects of this mixing are most visible in the desymmetrization of the ethylenic portions of the e_x'' and e_y'' MOs of **3**. In fact, the π* orbital of the unique etheno annelating group can actually be seen in the e_y'' MO of **3** in Fig. 2.

The less localized π and π* MOs in benzo, compared with etheno annelating groups, are responsible for the much smaller values in Table 1 of the annelation energies ($-\Delta E_0$) at $R = 1.397$ Å for **1a**, **1b**, and **1** than for **3a**, **3b**, and **3**. It has also previously been shown [8] that bonding interactions between the π* orbitals of the benzene ring and π* orbitals of the annelating groups are responsible for the non-linearity of $-\Delta E_0$ with *n*, the number of annelating groups. Consequently, the less localized π and π* orbitals in benzo, versus etheno, are also responsible for the smaller percentage deviation of the $-\Delta E_0$ values from linearity with *n* for **1b** and **1** than for **3b** and **3**.

The absence of low-lying π*-like orbitals from 1,3-cyclobutano groups is at least partly responsible for the fact that the $-\Delta E_0$ values for **2a**, **2b**, and **2** are even smaller than the corresponding $-\Delta E_0$ values for **1a**, **1b**, and **1**. In addition, the absence of low-lying π*-like orbitals from the 1,3-cyclobutano groups in **2a**, **2b**, and **2** causes the $-\Delta E_0$ values for **2b**, and **2**, to deviate from linearity with *n* in the opposite direction from the $-\Delta E_0$ values for **1b** and **1** and for **3b** and **3**. Nevertheless, the 1,3-cyclobutano groups in **2** do have high-lying filled MOs [30–34], and Fig. 2 shows that the mixing of these filled MOs with π* orbitals of the benzene ring does, in fact, result in some localization of the benzene π orbitals.

It is the localization of the benzene π orbitals at $R = 1.397$ Å, which is shown in Fig. 2, that is responsible for the C–C bond-length alternation, found experimentally in the benzene rings of **1** [2], **2** [3], and predicted for **3** at its fully optimized geometry [5–8]. Because the amount of π localization in the benzene ring depends on the number of annelating groups, the average deviation of the bond lengths from equality at the optimized geometries is linear in *n*. Then, because the net energy lowering on allowing the benzene C–C bond lengths to alternate depends on *n* through both amount of distortion and the energy lowering due to it, the dependence of ΔE_{geom}, on *n* in Table 1 is, as expected [35], approximately quadratic in *n*.

Acknowledgments This research was supported by grants from the National Science Foundation (CHE-091027) and the Robert A. Welch

Foundation (B-0027). This manuscript is dedicated to Professor Shigeru Nagase on the occasion of his 65th birthday. *Omedetou gozaimasu*!

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