COOPERATIVE EFFECTS IN THE ANNELATION OF BENZENE BY MULTIPLE ETHENO GROUPS

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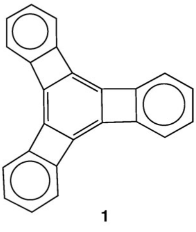
Dedicated to Dr. Zdeněk Havlas on the occasion of his 60th birthday.

The results of B3LYP/6-31G(d) calculations show that there is a strong cooperative effect on the energies that result from annelating benzene with 1, 2, and 3 etheno groups, to form **3**, **4**, and **5** respectively. The etheno annelation energies have been decomposed into two major contributors – etheno annelation, with all the bonds in the six-membered ring constrained to have the same C–C bond length as in D_{6h} benzene, and optimization of the C–C bond lengths in the annelated benzene ring. The energies computed for each of these two steps show that the etheno groups behave cooperatively in both of them. The origin of the cooperativity, calculated for each step, is described and discussed.
Keywords: Cooperative effects; Bond Alternation; Orbital mixing; Mathematical model; Carbocycles, Density functional calculations.

During the past two decades, the effects on bond lengths upon annelation of benzene by small rings have received considerable attention[1]. The interest in this subject was sparked by the experimental findings that the three benzo groups in **1** [2] and the three 1,3-cyclobutano groups in **2** [3] result in localization of the double bonds in the central benzene ring, so that they are exocyclic to each of the annelating groups.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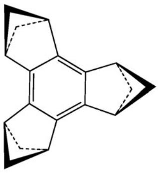
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Three types of explanations have been proposed to explain the cyclohexatriene-like bond length alternations found in **1** and **2**. The first applies to **1** and to other benzenes that are annelated by groups with π bonds. This explanation posits that the bond lengths of the central benzene ring alternate, in order to minimize the anti-aromatic character of the benzocyclobutadiene rings[4]. The second explanation focuses on the σ, rather than on the π bonds of **1**; and, hence, this explanation is also applicable to **2**. This explanation posits that the three strained rings around the periphery of the central benzene ring in **1** and in **2** result the observed alternation of the bond lengths in the benzene ring[5,6]. The third view is that a combination of both π and σ effects in the benzene ring accounts for the bond alternation induced by the annelated small rings[7].

Since unlike the benzo groups in **1**, the annelating cyclobutano groups in **2** have no π bonds, it might seem that some sort of σ effect provides the only possible explanation of the bond localization in **2**. However, many years ago, it was pointed out that the highest occupied (HO)MO of a 1,3-bridged cyclobutane ring resembles the HOMO of ethylene[8]. This fact was initially used to explain the spectroscopy[9] but, subsequently[10], also the unusual chemistry[11] of molecules containing unsaturatively-bridged cyclobutane rings. Houk and Schleyer[12] appear to have been the first to point out that the same types of orbital interactions, which favor butadieno over etheno as a 1,3-cyclobutane bridging group[10], provide an explanation of the bond alternation predicted for and observed in **2** [3].

If orbital interactions do, in fact, explain the cyclohexatriene-like fixation of the double bonds in the central benzene ring of **1** and of **2**, these interactions should be even stronger when benzene is annelated by three etheno groups, as in **5**. Previous computational studies on **3**–**5** have, indeed, found that successive annelation of benzene by etheno groups produces bond alternation of the type observed experimentally in **1** and **2** and that the de-

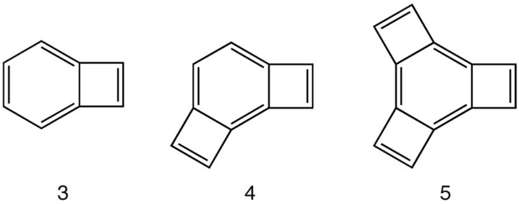


FIG. 1
Resonance structures for the double bonds in the benzene rings of **3**–**5** that avoid having two π bonds in the same four-membered ring

gree of bond alternation becomes more pronounced with increasing numbers of etheno groups on going from **3** to **5** [4,13].

To the best of our knowledge, no one has yet investigated the energy changes that occur on annelation of benzene with 1–3 etheno groups. These energy changes could prove quite interesting, since they might reveal cooperative effects in the formation of **3–5** from benzene. For example, the effect of the first etheno group should be to cause the bond lengths in **3** to begin to alternate as shown in Fig. 1. Therefore, annelation of **3** with a second etheno group, to form **4**, might involve π orbital interactions that are less destabilizing than those involved in forming **3** by annelation of benzene. The same line of reasoning suggests that attachment of a third etheno group to **4**, to form **5**, might entail π orbital interactions that are even less destabilizing than those encountered in the annelation of **3** to form **4**.

In order to probe for possible cooperative effects on the energies of bis- and tris-annelation of benzene, we have carried out DFT calculations on **3–5**. The results of these calculations are described in this paper.

COMPUTATIONAL METHODOLOGY

We have performed electronic structure calculations, using the B3LYP density functional method. It is a combination of Becke's 3-parameter hybrid functional[14] with the electron correlation functional of Lee, Yang, and Parr (LYP)[15]. The 6-31G(d) basis set[16] was employed in all our calculations. The structures of **3–5** were fully optimized, and B3LYP/6-31G(d) vibrational analyses were performed, in order to ensure that the optimized structures corresponded to local minima. The Gaussian 09 suite of programs[17] was used for all of these calculations.

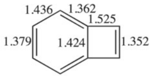
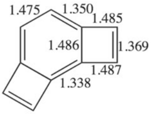
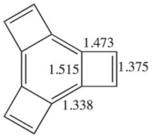
RESULTS AND DISCUSSION

Cooperative substituent effects have been found, both experimentally and computationally, in the activation enthalpies for the Cope rearrangements of 1,5-hexadienes[18]. These effects can be quantitatively modeled by a simple formula[19]. In order to see if the energetic effects, calculated for multiple annelations of benzene to form **3–5**, can be similarly modeled, we have decomposed the overall energies of the annelation reactions into three steps: (i) etheno annelation(s) with the C–C bonds in the six-membered ring all constrained to have the same length as in D_{6h} benzene, (ii) uniform lengthening of the C–C bonds in the benzene ring to the average length that they have in the optimized geometries of the annelated molecules, and (iii) relaxation of the identical lengths of the C–C bonds in the benzene ring to the lengths that these bonds have in the fully optimized geometries of **3**–**5**.

Bond lengths in **3**–**5**. The fully optimized C–C bond lengths of **3**–**5** are given in Table I. The C_1–C_2 bond length is calculated to increase from 1.397 Å in benzene to 1.424 Å in **3**, while the C_2–C_3 bond length is calculated to shorten to 1.362 Å. In **4** the C_1–C_2 bond length further lengthens to 1.486 Å, while the C_2–C_3 bond length further shortens to 1.350 Å. In **5** these two bond lengths are computed to be 1.515 and 1.338 Å, respectively. The B3LYP/6-31G(d) bond lengths computed for the benzene rings of **3**–**5** are qualitatively similar to those obtained previously by RHF calculations[4,13].

The increasing alternation of the C–C bond lengths in the benzene rings of **3**–**5** is accompanied by small increases in the lengths of the double bonds of the annelating etheno groups (from 1.352 Å in **3** to 1.375 Å in **5**) and also by larger decreases in the lengths of the C–C bonds joining the etheno groups to the benzene ring (from 1.525 Å in **3** to 1.473 Å in **5**). The shortening of the C–C bonds that join the etheno groups to the benzene ring indicates that, with increasing exocyclic localization of the double bonds of the benzene ring, the π bonding between the etheno groups and

TABLE I
Bond lengths and bond length changes (Å) in the benzene rings of **3**–**5**

	$R_{avg} = (\Sigma R_i)/6^a$	$R' = R_{avg} - 1.397$ Å^b	$\Delta R = (\Sigma\|R_i - R_{avg}\|)/6$
	1.400	0.003	0.032
	1.414	0.017	0.068
	1.427	0.030	0.089

[a] R_i is each of the fully optimized C–C bond lengths in the benzene ring of **3**–**5**; [b] 1.397 Å is the B3LYP/6-31G(d) C–C bond length in benzene.

the benzene ring increases. Presumably, with increasing bond alternation in the benzene ring, the π bonding between the etheno groups and the benzene ring increases because the π interaction between them loses its cyclobutadienoid character and becomes more like that in dimethylenecyclobutene.

Table I shows that, in addition to the obvious increase in bond length alternation with increasing etheno annelation, the average of the C–C bond lengths in the benzene rings of **3**–**5** increases from R_{avg} = 1.397 Å in benzene to R_{avg} = 1.400 Å in **3**, to 1.414 Å in **4**, and 1.427 Å in **5**. After accounting for the increases in the average of the C–C bond lengths in the benzene rings of **3**–**5**, Table I reveals that the deviation of the individual benzene bond lengths from these averages shows a nearly linear increase in the amount of bond length alternation with the number of annelating etheno groups. ΔR, the average of the absolute values of the differences between each C–C bond length and R_{avg}, increases from 0.032 Å in **3**, to 0.068 Å in **4**, and 0.089 Å in **5**. We will defer commenting, until a subsequent section, on the significance of the observation that the ratios of the ΔR values in **3**–**5** are approximately the same as the number of annelating etheno groups.

Cooperativity in the energetics of the etheno annelations in **3**–**5**. Since it is the differences between the energies of etheno annelation reactions that interest us, the choice of which annelation reaction to use is actually quite arbitrary. For example, we could have computed all of the annelation energies relative to the reaction of benzene with ethylene to form benzocyclobutadiene (**3**) plus two molecules of H_2. However, we chose, instead, to use as our reference annelation reaction the transfer an etheno group from rectangular cyclobutadiene to benzene to form **3** + ethylene.

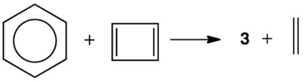
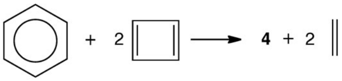
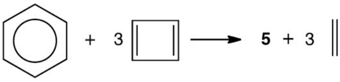
There are two reasons for this choice. First, this reaction allows comparison of the energies of the interactions between the π bonds of the annelating etheno groups and the π bonds of the benzene ring with energies of the same numbers of interactions between pairs of ethylenic π bonds in the appropriate number of rectangular cyclobutadiene rings. Second, since transfer of an etheno group from cyclobutadiene to benzene is an energetically favorable reaction, the increase in the magnitude of ΔE for formation of **3**, **4**, and **5** provides a convenient way to measure the favorable effect of increasing π bond localization in the benzene ring on the energies of the annelation reactions.

Table II shows that, when the ethylene group from a single cyclobutadiene ring is annelated onto benzene to form **3**, our B3LYP/6-31G(d) calculations find that 14.9 kcal/mol are predicted to be liberated. When, by removing an etheno group from each of two cyclobutadiene rings, benzene is angularly bis-annelated to form **4**, the amount of energy that is calculated to be liberated is 40.8 kcal/mol. This is 11.0 kcal/mol greater than would be predicted if the bis-annelation reaction in Eq. (*2*) liberated the same amount of energy as twice that of the mono-annelation reaction in Eq. (*1*).

This 11.0 kcal/mol represents the cooperative energetic effect of two etheno groups in localizing the double bonds in the benzene ring of **4**[20]. This cooperativity makes the bis-annelation reaction in Eq. (*2*) of Table II 37% more energetically favorable than if the bis-annelation energy of benzene for forming **4** were twice the mono-annelation energy in Eq. (*1*) for forming **3**.

The 73.9 kcal/mol that is computed to be liberated by the isodesmic reaction in Eq. (*3*) is 29.2 kcal/mol larger than three times the energy of the isodesmic reaction in Eq. (*1*). The energetic benefit of the cooperativity between three etheno groups in localizing the double bonds in the benzene ring of **5** makes the reaction in Eq. (*3*) 65% more energetically favorable than the 44.7 kcal/mol that would be expected from additivity, based on the energy calculated for the isodesmic reaction in Eq. (*1*). The energetic benefit of cooperativity is, as expected, much higher for the three etheno groups in **5** than for the pair of etheno groups in **4**.

TABLE II
Three isodesmic annelation reactions and the amount of energy (kcal/mol) that is predicted by B3LYP/6-31G(d) calculations to be liberated by each reaction

Eq.	Isodesmic reaction	–Δ*E*
(*1*)		14.9
(*2*)		40.8
(*3*)		73.9

Contributors to ΔE *for annelation*. There are two possible contributors to the cooperative effects that are seen in the $-\Delta E$ values in Table II for bis-annelation of benzene to form **4** and tris-annelation to form **5**. One possible contributor is that, with the C–C bond lengths in the benzene ring fixed at 1.397 Å, annelation with one or more etheno groups causes the wave function for the π electrons in benzene to partially localize, and that such localization of the π wave function is cooperative. The other possible contributor to the cooperative effects, seen in the $-\Delta E$ values in Table II, is that the changes in the C–C bond lengths in the benzene ring, which occur upon complete geometry optimization, are cooperative.

By carrying out calculations on the reactions in Eqs (*1*)–(*3*), with the C–C bond lengths in the six-membered ring fixed at 1.397 Å, it is possible to obtain the energy (which we call ΔE_0) that is associated with the first of these two contributions. Then by subtracting ΔE_0 from the appropriate ΔE value in Table II, the stabilization energy (ΔE_{geom}) that is associated with the change in the lengths of the benzene C–C bonds, can be obtained, since, by definition, $\Delta E = \Delta E_0 + \Delta E_{\text{geom}}$.

The values of ΔE_0 in Table III were computed with only the lengths of the C–C bonds in the benzene rings in **3**–**5** fixed. All of the other geometric parameters, including the etheno bond lengths and the lengths of the bonds joining the etheno groups to the benzene ring, were fully optimized. Comparison of the non-benzenoid C–C bond lengths at R = 1.397 Å in Table III with those at the fully optimized geometries in Table I, indicates that, on allowing bond-length alternation in the benzene ring, the changes in the non-benzenoid C–C bond lengths are relatively small. Therefore, the values of ΔE_{geom} are largely, although not exclusively, associated with alternation in the C–C bond lengths in the benzene rings on going from R = 1.397 Å to the fully optimized geometries[22].

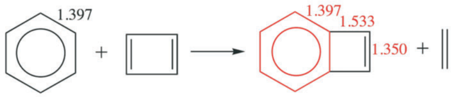
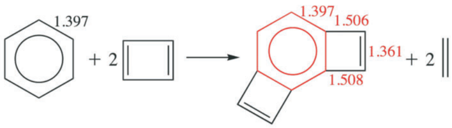
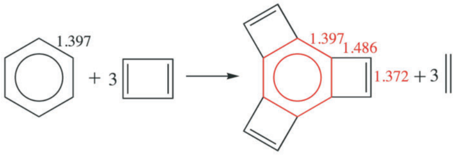
An important conclusion that can be drawn from the results in Table III is that both the alteration of the benzene π wave function by etheno annelation, with the benzene bond lengths fixed at R = 1.397 Å, and the geometry changes in the benzene ring that occur upon etheno annelation, make substantial contributions to the cooperativity seen in the $-\Delta E$ values for **4** and **5** in Table II. For example, Table III shows that, in the bis-annelation of benzene to form **4**, ΔE_0 contributes $31.7 - 2 \times 12.8 = 6.1$ kcal/mol to the 11.0 kcal/mol of cooperativity; and ΔE_{geom} contributes $9.1 - 2 \times 2.1 = 4.9$ kcal/mol. In the tris-annelation of benzene to form **5**, ΔE_0 contributes $56.6 - 3 \times 12.8 = 18.2$ kcal/mol to the 29.2 kcal/mol of cooperativity, and ΔE_{geom} contributes $17.3 - 3 \times 2.1 = 11.0$ kcal/mol.

Origin of the cooperativity in the values of ΔE_0. The origin of the cooperativity, seen in the B3LYP/6-31G(d) values of ΔE_0 for **3–5** in Table III, must reside in changes in the π wave functions as benzene is successively annelated by 1, 2, and 3 etheno groups. In Fig. 2 the three highest energy π MOs of **3–5** [23] are compared with the corresponding π MOs of benzene.

Benzene and **5** each have a three-fold axis of symmetry, and in the D_{3h} point group that is common to both molecules, the MOs on the first and third lines of Fig. 2 have different symmetries. The MOs of benzene and **5** 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 of benzene and of **5** on the third line belong to the a_2'' representation of D_{3h}.

TABLE III

Three isodesmic reactions and their calculated energies, ΔE_0 (kcal/mol), with fixed C–C bond lengths of R = 1.397 Å in the benzene rings in both the reactants and products. For each isodesmic reaction, subtraction of ΔE_0 from ΔE, the energy change with the product geometries fully optimized, gives ΔE_{geom}, the energy lowering due to the optimization of the C–C bond lengths in the benzene ring, plus any other changes in bond lengths and bond angles that complete geometry optimization engenders

Eq.	Isodesmic reaction	$-\Delta E_0$	$\Delta E_{geom} = -\Delta E + \Delta E_0$
(*4*)		12.8	2.1
(*5*)		31.7	9.1 (9.5)[a]
(*6*)		56.6	17.3 (17.6)[b]

[a] Starting from R = 1.414 Å, rather than from R = 1.397 Å; [b] starting from 1.427 Å, rather than from R = 1.397 Å.

Unfortunately, **3** and **4** have only C_{2v} symmetry, and the MOs on the top and bottom lines of Fig. 2 both belong to the b_1 representation of this point group. The symmetry of these two molecules is low enough that, in the b_1 MOs of **3** and **4**, the orbitals of the benzene rings do not look very much like e_x'' and a_2'' MOs of benzene. However, taking the sums and differences of filled MOs has no effect on the total energy of a molecule; and the sums and differences of the b_1 MOs of **3** and of **4** do give π orbitals for the benzene ring that look much more like the e_x'' and a_2'' MOs of benzene.

In the C_{2v} symmetry of **3** and **4**, the MOs in the second row of Fig. 2 belong to the a_2 representation; so these MOs do not mix with the b_1 π orbitals in the first and third rows of Fig. 2. Therefore, it is easy to follow

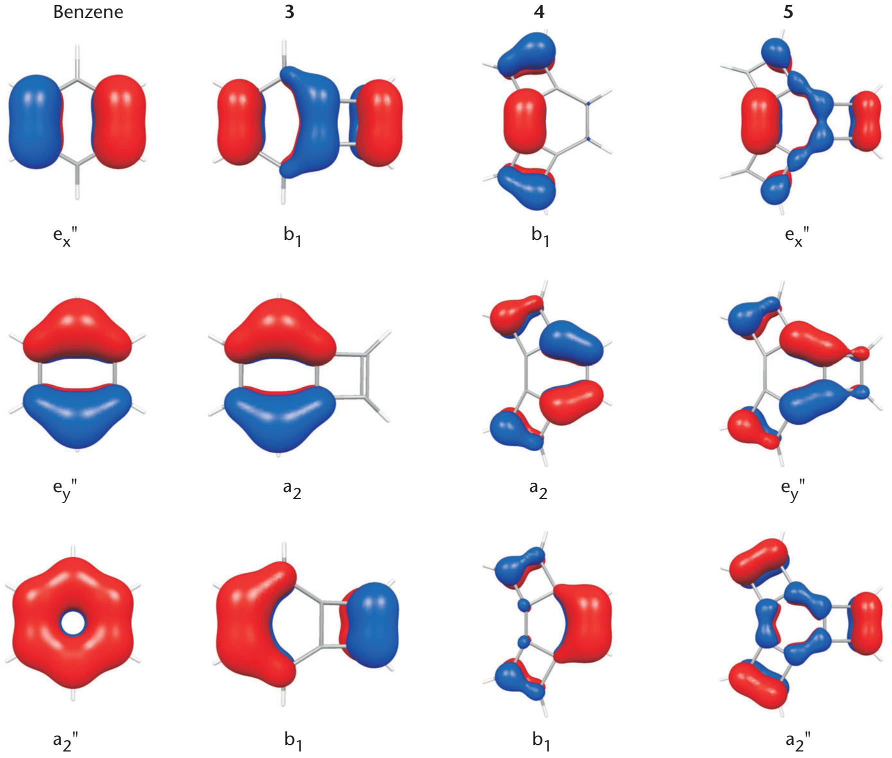


FIG. 2
The three filled π MOs of benzene and the three highest energy filled π MOs of **3**–**5**. The MOs were computed with a bond length of $R = 1.397$ Å for all the C–C bonds in the benzene rings of **3**–**5**. The representation of the D_{3h} or C_{2v} point group to which each MO belongs is shown under it

how annelation causes the a_2 MOs of **3** and **4** to evolve from e_y" MO of benzene and to culminate in the e_y" MO of **5**.

For example, Fig. 2 shows that mono-annelation of benzene has no detectable effect on the e_y" MO, because the filled π MO of the annelating etheno group in **3** has the wrong symmetry to interact with this MO of benzene. The filled e_y" MO of benzene can interact with the π* MO of the etheno group in **3**. However, the energy diffeence between these MOs (2β in Hückel theory) is apparently large enough and the coefficients of the benzene e_y" MO at the annelated ring carbons of **3** are small enough (1/2√3 in Hückel theory) that there is no discernable contribution of π* of the etheno group to the a_2 MO of **3**, at least at the level of contouring at which the MOs are plotted in Fig. 2.

Unlike the mono-annelation of benzene to form **3**, Fig. 2 shows that the bis-annelation to form **4** results in a major modification of the e_y" MO of benzene. An antibonding interaction with the out-of-phase combination of the two bonding π MOs of the etheno groups transforms the delocalized e_y" MO in benzene into the more localized a_2 combination of two π bonds in **4**.

Fig. 3 shows that this transformation of the benzene e_y" orbital is brought about by mixing into it the unfilled benzene orbital, e_y"*. This mixing occurs due to a bonding interaction between the e_y"* benzene MO and the out-of-phase combination of the filled π orbitals of the two annelating etheno groups. Inspection of Fig. 3 shows that the same type of mixing also occurs between the benzene e_x"* orbital and both the single etheno π orbital in **3** and the pair of etheno π orbitals in **4**.

Simple Hückel calculations show that mixing of the pair of benzene e"* MOs with the two etheno π bonds in **4** provides twice the stabilization energy as the mixing of the e_x"* MO with the single etheno π bond in **3**. Similarly, mixing of the pair of benzene e″* MOs with the three etheno π bonds in **5** provides three times the stabilization energy as the mixing of the e_x"* MO with the single etheno π bond in **3**. Therefore, the mixing between the e"* benzene orbitals and the π bonds in **3–5** is not the source of the cooperative effects on $-\Delta E_0$ that are seen in Table III.

As shown in Fig. 2, transformation of the e_y" MO of benzene into the a_2 MO of **4** is accompanied by desymmetrization of the bonding π orbitals of the etheno groups. The a_2 MO of **4** is largely confined to AOs on only two of the four carbons of the benzene ring to which the etheno groups are annelated. Therefore, in order to minimize the antibonding interaction of the etheno π orbitals with the benzene ring orbitals in the a_2 MO of **4**, it is energetically advantageous for the π orbitals of the etheno groups to desymmetrize, so that the etheno π orbitals have more density on the etheno carbons that are attached to the carbons of the benzene ring on which the a_2 MO in **4** has no density. Fig. 2 shows that similar desymmetrization of the etheno π orbitals of **4** occurs in the b_1 MOs.

Fig. 4 demonstrates that desymmetrization of the π bonds of the annelating etheno groups in **4** is accomplished by mixing the π* orbitals of the etheno groups into the a_2 and b_1 wave functions for **4**. Mixing occurs between the π* orbitals of the etheno groups and both the bonding e" and antibonding e"* orbitals of the benzene ring.

Simple Hückel calculations reveal that the interactions of the π* orbitals of the two etheno groups in **4** and the three etheno groups in **5** with the bonding e" orbitals of benzene contribute to the stabilization energies of these two molecules by, respectively, twice and three times as much as the interaction of a single π* orbital with e_y'' contributes to the stabilization energy of **3**. Consequently, the mixing between the e" benzene orbitals

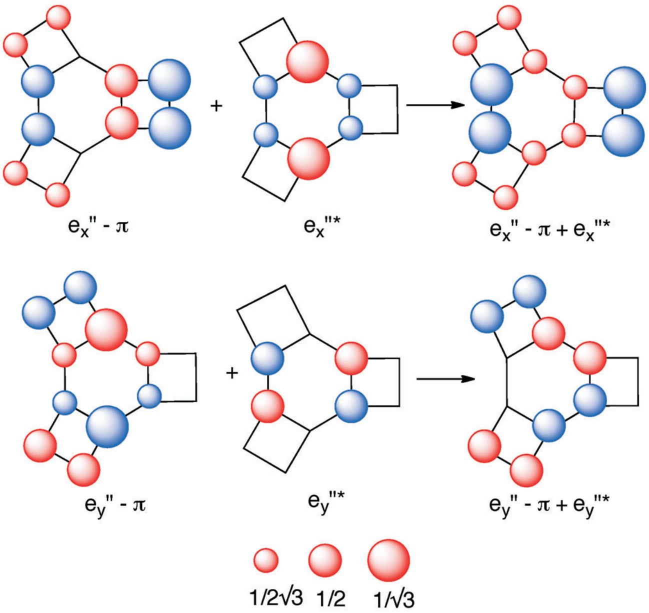


Fig. 3

Schematic representation of the effect in **5** of mixing between the degenerate, benzene, antibonding, π MOs (e"*) and the e" combinations of the bonding π orbitals of the three annelating etheno groups. As in Fig. 2, the π orbitals of the annelating etheno groups are shown as being mixed out-of-phase with the degenerate, benzene, bonding, π MOs (e"). The effect of these orbital interactions in **3** and **4** can be seen by deleting the contributions from the π orbitals of the appropriate etheno groups to the e" MOs of **5** and the π* orbitals of the etheno groups in **3**–**5** is not the source of the co-operative effects on $-\Delta E_0$ that are seen in Table III.

However, as discussed above, the antibonding $e_y''^*$ benzene orbital is also present in the a_2 MO for **4**, mixed into this MO by a bonding interaction between $e_y''^*$ and the π orbitals of the etheno groups. As shown in Fig. 5, the pair of etheno π* orbitals in **4** can interact in a stabilizing way with $e_y''^*$. Fig. 5 also shows that the pair of etheno π* orbitals in the b_1 MO of **4** interact even more strongly with the antibonding $e_x''^*$ benzene orbital.

Interactions between the e"* benzene MOs and π* MO of the annelating etheno groups do not stabilize **3**. The π orbital of the lone etheno group in **3** does mix with the $e_x''^*$ benzene MO, but the π* orbital of the etheno

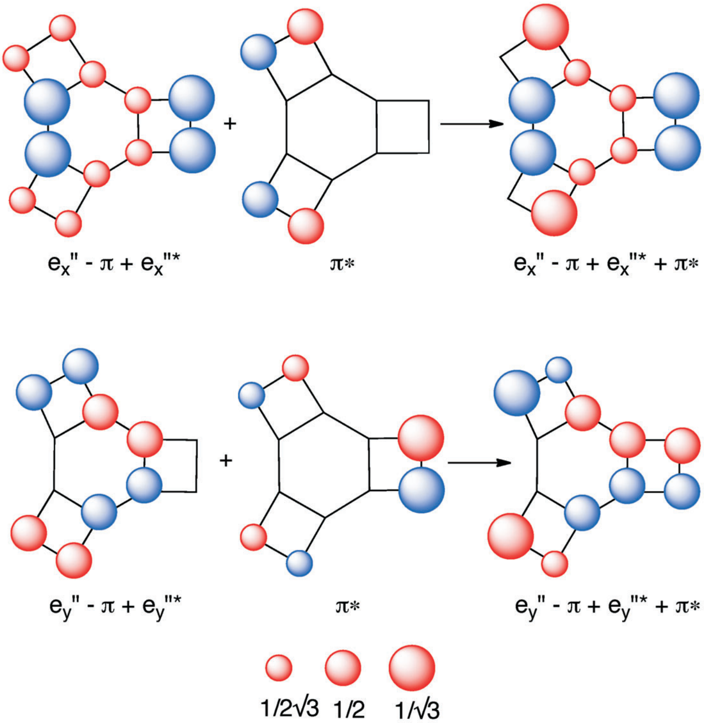


FIG. 4

Schematic representation of the effect in **5** of mixing of the MOs on the right hand side of Fig. 3 with the e" combinations of the antibonding π* orbitals of the three annelating etheno groups. The effect of these orbital interactions in **4** can be seen by deleting the contributions from the π and π* orbitals of the unique etheno group to the e" MOs of **5** group has the wrong symmetry to mix with e_x"*. Although the π* orbital of the etheno group in **3** can mix with the e_y"* orbital of the benzene ring, the filled π orbtial of the etheno group has the wrong symmetry to mix the e_y"* orbital into the a_2 MO of **3**.

Consequently, **4** is stabilized by orbital interactions of a type that do not occur in **3**. It is due to the stabilizing effect of the interactions between the e"* and the π* orbitals in **4** that we attribute the difference of 6.1 kcal/mol between $-\Delta E_0$ in **4** and twice $-\Delta E_0$ in **3**.

Actually, just looking at the a_2 MOs for **3** and **4** in Fig. 2 shows that the bis-annelated molecule is stabilized by an effect – desymmetrization of the π bonding orbitals of the etheno groups in response to the desymmetrization of the benene e_y" orbital – that is absent from the MOs of the mono-annelated molecule. As already discussed, the benzene e_y" orbital is desymmetrized in the a_2 MO of **4** by the presence of the e_y"* orbital, which is

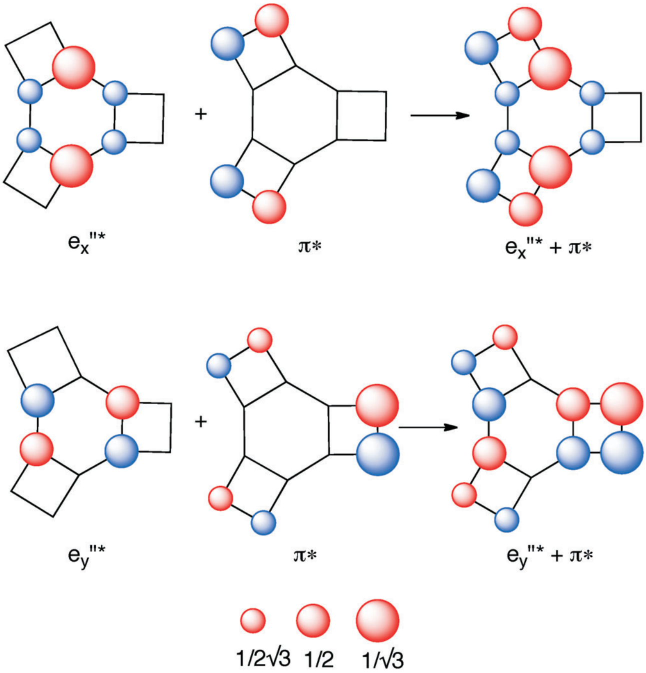


FIG. 5

Schematic depiction of the stabilizing interactions between the e" symmetry combinations of the π* MOs of the three annelating etheno groups in **5** and the degenerate, antibonding e"* MOs of the benzene ring. These orbital interactions in **4** can be seen by deleting the contributions from the π* orbital of the unique etheno group mixed into the a_2 MO of **4** by the stabilizing interaction e_y"* with the pair of bonding π orbitals of the annelating etheno groups. The π bonds of the annelating etheno group are desymmetrized in the a_2 MO of **4** by the presence of the etheno π* orbitals, which are mixed into the a_2 MO of **4** by their stabilizing interaction with the benzene e_y" MO.

The cooperative nature of the desymmetrizations of the e_y" orbital of the benzene ring and the π orbitals of the etheno groups in the a_2 MO of **4** is due to the bonding interaction, shown in Fig. 5, between the e_y"* orbital and the a_2 combination of etheno π* orbitals. This stabilizing, cooperative interaction is responsible for the fact that, as shown in Table III, $-\Delta E_0$ for bis-annelation of benzene, with $R = 1.397$Å, is 16.1 kcal/mol more favorable than twice $-\Delta E_0$ for mono-annelation.

Adding a third annelating etheno group to **4**, to make **5**, increases the stabilization provided by mixing of the e"* MOs of the benzene ring with the π* MOs of the etheno groups. As can be seen by inspection of Fig. 2, of the benzene contribution to the e_y" MO of **5** appears to be the same as that in the a_2 MO of **4**. The reason is that the bonding π orbital of the additional etheno group in **5** has the wrong symmetry to mix with the e_y"* orbital of the benzene ring; so the contribtion of the benzene e_y"* orbital to the a_2 MO of **4** and to the e_y" MO of **5** is essentially the same. However, the third etheno group does contributes a π* orbital to the e_y" MO of **5**; and, as shown in Fig. 5, this π* orbital interacts in a strongly stabilizing fashion with the e_y"* orbital of the benzene ring.

The π* orbital of the third etheno group does not have the right symmetry to contribute to the e_x" MO of **5**, but the π MO of the third etheno group does. The contribution of this π orbital results in more of the e_x"* benzene orbital being mixed into the e_x" MO of **5** than appears in the a_2 MO of **4**. Thus, on going from **4** to **5**, the stabilizing interactions between the e_x"* and the π* orbitals of two of the etheno groups are enhanced by increasing the contribution of the benzene e_x"* orbital to the e_x" MO of **5**.

Origin of the cooperativity in the values of ΔE_{geom}. The values in Table III of $-\Delta E_{\text{geom}} = 9.1$ kcal/mol for **4** and $-\Delta E_{\text{geom}} = 17.3$ kcal/mol for **5** are, respectively, 4.3 and 8.2 times the value of $-\Delta E_{\text{geom}} = 2.1$ kcal/mol for **3**. Based on additivity, values of $-\Delta E_{\text{geom}} = 4.2$ kcal/mol for **4** and $-\Delta E_{\text{geom}} = 6.3$ kcal/mol for **5** would be expected. Thus, the $-\Delta E_{\text{geom}}$ values for **4** and **5** show clear signs of cooperativity between the two annelating etheno groups in the former and the three annelating etheno groups in the latter molecule.

We have previously derived a mathematical formula[19] that successfully predicts the sizes of the cooperative effects of the radical-stabilizing substituents on the Cope rearrangements of phenyl-substituted 1,5-hexadienes[18].

The mathematical model is based on the effects of substituents on the interallylic distance in each transition structure and the effects of the interallylic distance in each transition structure on the sizes of the substituent effects[19]. Because the interallylic distance depends on the number of stabilizing substituents, and the stabilization energy depends on both the interallylic distance and the number of substituents, the net substituent stabilization energy in the Cope rearrangement increases as the square of the number of stabilizing substituents.

The derivation of a formula, similar to that in ref.[19], but for the effect of the number of substituents (n) on the energy lowering (ΔE_{geom}) upon allowing for C–C bond length alternation in the benzene rings of **3–5** is given in the Appendix to this paper. However, the qualitative reason why cooperative substituent effects are seen in the values of ΔE_{geom} in Table III for **3–5** is the same as the qualitative reason why cooperative substituent effects occur in the Cope rearrangement. The amount of bond length alternation in **3–5** depends on, n, the number of etheno annelating groups, and the size of ΔE_{geom} depends on both the amount of bond length alternation and the number of etheno annelating groups. Therefore, the model predicts that ΔE_{geom} in **3–5** should be proportional to n^2.

The simple model that is developed in the Appendix for ΔE_{geom} utilizes a single asymmetric distortion coordinate. However, as already noted, the optimized geometries of **3–5** in Table I involve two types of distortions of the benzenoid C–C bond lengths from the value of $R = 1.397$ Å in benzene – a small increase in the average lengths of the C–C bonds, plus a bond-alternation distortion that increases the lengths of three C–C bonds in the benzene ring and shortens the lengths of three other ring bonds.

Unfortunately, the C_{2v} symmetry of **3** and **4** means that the increases and decreases in the C–C bond lengths in the benzene rings of these two molecules are not the same for all of the C–C bonds. Consequently, a simple model that is based on the averages of these distortions is less likely to be successful in accurately describing the cooperative effects of bond length alternation in **3–5** than the same type of model is in describing the substituent effects in the Cope rearrangement. In that reaction, changes in the interallylic bond length really do characterize adequately changes in the transition state geometries[18,19].

The increase in the average length of the C–C bonds on going from benzene to **3**, from 1.397 to 1.400 Å, has a negligible effect on ΔE_{geom}. The 0.017 and 0.030 Å increases in the average lengths of the C–C bonds in **4** and **5** raises the energies of these two molecules by 0.4 and 0.3 kcal/mol, respectively. These small energy increases also increase the values of

$-\Delta E_{geom}$ for these two molecules by the same amounts, to the values shown in parentheses in Table III.

We now make use of two mathematical results from the Appendix. According to Eq. (*A-6*), the amount of asymmetric distortion, ΔR, that minimizes $\Delta E_{geom} = \Delta E - \Delta E_0$ should be proportional to n, the number of annelating etheno groups. The optimal values of ΔR from Table I are 0.032 Å for **3**, 0.068 Å for **4**, and 0.089 Å for **5**. The ratios of the ΔR values are 1:2.1:2.8, in reasonable agreement with the expected ratios of 1:2:3. We conjecture that the reason ΔR for **5** is a little lower than predicted by Eq. (*A-6*) is that, around $\Delta R = 0.089$ Å, an unsubstituted benzene ring is more resistant to further shortening of three bonds than is predicted by the quadratic potential function that is assumed in the derivation in the Appendix.

According to Eq. (*A-7*) of the Appendix, the values of ΔE_{geom} in **3–5** should be proportional to n^2, the square of the number of annelating double bonds. The values of $-\Delta E_{geom}$ in Table III are 2.1 kcal/mol for **3** and (using the values in parentheses) 9.5 kcal/mol for **4** and 17.6 kcal/mol for **5**. The ratios are 1:4.5:8.4, which can be compared with the expected ratios of 1:4:9. The agreement between the ratios of the B3LYP values and those expected from Eq. (*A-7*) are probably as good as can be expected, given the facts that (i) the asymmetric distortions of the individual bond lengths in **3** and **4** cannot actually be represented by a single parameter, and (ii) a quadratic potential function probably underestimates the energy required for large asymmetric distortions of the bond lengths in unsubstituted benzene.

SUMMARY AND CONCLUSIONS

The energies, ΔE, for annelation of benzene by one, two, and three etheno groups, to form **3–5**, show strong cooperative effects. Cooperative effects are seen in both the annelation energies, ΔE_0, at the optimized D_{6h} geometry of unsubstituted benzene ($R = 1.397$ Å) and also in the energies, ΔE_{geom}, for asymmetric distortion of the C–C bond lengths to the bond-alternated equilibrium geometries of the annelated benzene molecules.

We have attributed the cooperativity seen in the values of ΔE_0 in Table I to a synergistic bonding interaction between the e"* orbitals of the benzene ring and the π* orbitals of the annelating etheno groups. Although interactions between unfilled orbitals ordinarily have no effect on ground state properties, the e"* orbitals of the benzene ring are mixed into the bonding π MOs of **3–5** by stabilizing interactions with the bonding π orbitals of the annelating etheno groups; and the π* orbitals of the etheno group are mixed into the bonding MOs of **3**–**5** by stabilizing interactions with the bonding e" orbitals of the benzene ring.

Since the contributions to the π MOs of **3**–**5** of both the e"* orbitals of the benzene ring and the π* orbitals of the etheno group increase with *n*, the number of annelating etheno groups, the cooperativity in the values of ΔE_0 should come from a term in the annelation energies that depends on n^2. Writing

$$\Delta E_0 = n\Delta E_1 + n^2\Delta E_2 \tag{7}$$

and substituting the values of $-\Delta E_0$ = 12.8 kcal/mol for **3** ($n = 1$) and $-\Delta E_0$ = 31.7 kcal/mol for **4** ($n = 2$) gives $-\Delta E_1$ = 9.8 kcal/mol and $-\Delta E_2$ = 3.0 kcal/mol. Using these values in Eq. (*7*) to compute $-\Delta E_0$ for **5** ($n = 3$) gives $-\Delta E_0$ = 56.4 kcal/mol, in excellent agreement with the value of $-\Delta E_0$ = 56.6 kcal/mol for **5** in Table III.

Although the excellent fit that Eq. (*7*) gives to the $-\Delta E_0$ values in Table III is consistent with our model for a synergistic interaction between e"* and π* as being the source of cooperativity seen in the $-\Delta E_0$ values, it is certainly possible that other effects might give $-\Delta E_0$ values that are consistent with Eq. (*7*). However, there are indications in the optimized geometries of **3**–**5** of the predicted increase in the contributions of the e"* and π* orbitals to the filled MOs of **3**–**5** with increasing numbers of annelating etheno groups.

As already noted, Table I shows values of $R' = R_{avg} - 1.397$ Å that increase non-linearly with *n*. A simple explanation is that the contribution of the antibonding benzene e"* MO to the filled MOs of **3**–**5** increases with increasing *n*. Similarly, the increases in the lengths of the C–C bonds in the annelating etheno groups, from 1.352 Å in **3** to 1.375 Å in **5**, can be attributed to increases in the contributions of the π* orbitals with increasing *n*. The combined effect of the increases in the contributions of both e"* and π* with increasing *n* would be to increase the π bonding between the ring and the etheno bridges and, thus, shorten the C–C bonds connecting them. Indeed, as already noted, these C–C bond lengths decrease from 1.525 Å in **3** to 1.473 Å in **5**.

There really can be no question that the contribution of the e"* benzene MO increases on going from **3** to **5**. The changes in the e" π orbitals, seen in Fig. 2, show that the pair of degenerate, D_{6h}, benzene π MOs evolve in **5** into a pair of degenerate D_{3h} π MOs for three localized double bonds. As shown in Fig. 3, mixing of the benzene antibonding e"* MOs into the benzene bonding e" MOs is what creates this localization of the double bonds in the benzene ring of **5**.

The MOs for the three localized double bonds in the benzene ring of **5** in Fig. 2, computed with all the C–C bond lengths fixed at $R = 1.397$ Å, leave no doubt that interactions between the π bonds of the benzene ring and the π bonds of the annelating etheno groups are responsible for the bond-alternated equilibrium geometry of **5**. Even the nodeless a_2" MO of **5** is localized into three double bonds by the contributions of 3d AOs to the 2p AOs on the ring carbons.

The methodology used in this paper for the study of **3**–**5** can also be used to attempt to establish whether the bond alternated geometry of **2** [3a–3c] is due to some sort of σ strain effect, or to an electronic preference of the annelating cyclobutano groups to be bridged by butadieno, rather than by etheno π orbitals[10,12]. Calculations should reveal whether in **2**, as in **5**, the π bonds in the benzene ring are largely localized, even at a geometry with the benzene C–C bond lengths constrained to be equal.

An interesting question is whether calculations on **2** and on related molecules, containing fewer cyclobutano annelating groups, will reveal the cooperative effects on ΔE_0 and ΔE_{geom} that we have found in **3**–**5**. We have attributed the cooperative effects seen in ΔE_0 for **3**–**5** to orbital mixing that involves the π* orbitals of the etheno groups. Although a 1,3-cyclobutano group does have a high-lying filled MO that resembles the π orbital of etheno, a 1,3-cyclobutano group lacks the low-lying unfilled equivalent of the π* orbital of ethylene[8,10]. Therefore, if calculations on **2** and on related molecules, containing one or two cyclobutano annelating groups, fail to find cooperative effects on the calculated values of ΔE_0, this finding will provide indirect support for our explanation of the cooperative effects on ΔE_0 that our calculations have found in **3**–**5**.

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APPENDIX

We assume that ΔE_{geom}, the energy lowering on allowing the C–C bond lengths in **3**–**5** to undergo asymmetric distortion by an amount, ΔR, to their fully optimized lengths, is comprised of two terms. The first is the energy cost of this distortion of the C–C bond lengths in unsubstitiuted benzene (ΔE_{dist}). The second is the stabilization of such a distortion that is contributed by the annelated double bonds ($\Delta E_{\mathrm{subst}}$). The net stabilization energy is the sum of ΔE_{dist} and $\Delta E_{\mathrm{subst}}$.

$$\Delta E_{\mathrm{geom}} = \Delta E_{\mathrm{dist}} + \Delta E_{\mathrm{subst}} \tag{A-1}$$

We further assume, for simplicity, that ΔE_{dist} is quadratic in ΔR.

$$\Delta E_{\mathrm{dist}} = k_{\mathrm{dist}}(\Delta R)^2/2 \tag{A-2}$$

Whether an asymmetric distortion increases or decreases the energy depends on the sign of ΔR, i.e., on which bonds lengthen and which shorten. Therefore, we assume that $\Delta E_{\mathrm{subst}}$ is linearly dependent on ΔR and also on the number, n, of etheno substituents. Thus,

$$\Delta E_{\mathrm{subst}} = -nk_{\mathrm{subst}}R\ . \tag{A-3}$$

Combining Eqs (*A-1*), (*A-2*), and (*A-3*),

$$\Delta E_{\mathrm{geom}} = k_{\mathrm{dist}}(\Delta R)^2/2 - nk_{\mathrm{subst}}\Delta R\ . \tag{A-4}$$

Differentiating Eq. (*A-4*) with respect to ΔR and using the fact that, at equilibrium,

$$\mathrm{d}\Delta E_{\mathrm{geom}}/\mathrm{d}\Delta R = 0 = k_{\mathrm{dist}}\Delta R - nk_{\mathrm{subst}} \tag{A-5}$$

gives

$$\Delta R = nk_{\mathrm{subst}}/k_{\mathrm{dist}}\ . \tag{A-6}$$

Substituting Eq. (*A-6*) in Eq. (*A-4*),

$$\Delta E_{\mathrm{geom}} = n^2k^2{}_{\mathrm{subst}}/2k_{\mathrm{dist}} - n^2k^2{}_{\mathrm{subst}}/k_{\mathrm{dist}} = -n^2k^2{}_{\mathrm{subst}}/2k_{\mathrm{dist}}\ . \tag{A-7}$$

According to Eq. (*A-6*), ΔR for **3–5** should increase linearly with n, the number of annelating etheno groups; and, according to Eq. (*A-7*), $-\Delta E_{\mathrm{geom}}$ for **4** ($n = 2$) and **5** ($n = 3$) should be, respectively, 4 times and 9 larger than $-\Delta E_{\mathrm{geom}}$ for **3**.

REFERENCES AND NOTES

1. For a brief review see: Bachrach S. M.: *Computational Organic Chemistry*, pp. 97–103. John Wiley & Sons, Inc. Hoboken, New Jersey 2007.
2. Diercks R., Vollhardt K. P. C.: *J. Am. Chem. Soc.* **1986**, *108*, 3150.

3. a) Burgi H. B., Baldridge K. K., Hardcastle K., Frank N. L., Ganzel P., Siegel J. S., Ziller J.: *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1454; b) Frank N. L., Baldridge K. K., Siegel J. S.: *J. Am. Chem. Soc.* **1995**, *117*, 2102; c) This type of localization of the double bonds in **2** was first predicted computationally by: Baldridge K. K., Siegel J. S.: *J. Am. Chem. Soc.* **1992**, *114*, 9583; d) The same type of localization of the double bonds in cyclooctatetraene, tetrakis-annelated with four 1,3-cyclobutano groups, was predicted by: Baldridge K. K., Siegel J. S.: *J. Am. Chem. Soc.* **2001**, *123*, 1755; e) This prediction too was subsequently confirmed experimentally by: Matsura A., Komatsu K.: *J. Am. Chem. Soc.* **2001**, *123*, 1768; f) Komatsu and coworkers also found that, when one ring of naphthalene is annelated with two, 1,3-bridged, cyclobutano groups, the two partial double bonds in the annelated naphthalene ring lengthen: Uto T., Nishinaga T., Matsura A., Inoue R., Komatsu K.: *J. Am. Chem. Soc.* **2005**, *127*, 10162.
4. a) Faust R., Glendening E. D., Streitwieser A., Vollhardt K. P. C.: *J. Am. Chem. Soc.* **1992**, *114*, 8263; b) Bachrach S.: *J. Organomet. Chem.* **2002**, *643–644*, 39.
5. a) Stanger A.: *J. Am. Chem. Soc.* **1991**, *113*, 8277; b) Stanger A.: *J. Am. Chem. Soc.* **1998**, *120*, 12034; c) Stanger A., Tkachenko E.: *J. Comput. Chem.* **2001**, *22*, 1377; d) Alabugin I. V., Manoharan M.: *J. Comput. Chem.* **2007**, *28*, 373.
6. Benzene bond alternation, induced by annelation of saturated small rings, is usually called a Mills–Nixon effect. For a critical discussion of the Mills–Nixon effect see: Frank N. L., Siegel J. S. in: *Advances in Theoretically Interesting Molecules* (R. P. Thummel, Ed.), Vol. 3, p. 209. JAI Press, Greenwich (CT) 1995.
7. a) Shurki A., Shaik S.: *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2205; b) Shaik S., Shurki A., Danovich D., Hiberty P. C.: *Chem. Rev.* **2001**, *101*, 1501.
8. a) Hoffmann R., Davidson R. B.: *J. Am. Chem. Soc.* **1971**, *93*, 5699; b) Gleiter R., Kobayashi T.: *Helv. Chim. Acta* **1971**, *54*, 1081.
9. a) Meinwald J., Kaplan B. E.: *J. Am. Chem. Soc.* **1967**, *89*, 2611; b) Meinwald J., Uno F.: *J. Am. Chem. Soc.* **1968**, *90*, 800; c) Robin M. B., Basch H., Keubler N. A., Kaplan B. E., Meinwald J.: *J. Chem. Phys.* **1968**, *48*, 5037; d) Meinwald J., Tsuruta H.: *J. Am. Chem. Soc.* **1970**, *92*, 2579; e) Bischof P., Gleiter R., Kukla M. J., Paquette L.: *J. Electron Spectrosc. Relat. Phenom.* **1974**, *4*, 177.
10. a) Jorgensen W. L., Borden W. T.: *J. Am. Chem. Soc.* **1973**, *95*, 6649; b) See also, Jorgensen W. L., Borden W. T.: *Tetrahedron Lett.* **1975**, *16*, 223; c) Jorgensen W. L.: *J. Am. Chem. Soc.* **1975**, *97*, 3082.
11. a) Meinwald J., Schmidt D.: *J. Am. Chem. Soc.* **1969**, *91*, 5877; b) Meinwald J., Tsuruta H.: *J. Am. Chem. Soc.* **1969**, *91*, 5877; c) Zimmerman H. E., Robbins J. D., Schantl J.: *J. Am. Chem. Soc.* **1969**, *91*, 5878; d) Borden W. T., Gold A.: *J. Am. Chem. Soc.* **1973**, *95*, 3830; e) Borden W. T., Gold A., Young S. D.: *J. Org. Chem.* **1978**, *43*, 486; f) Consistent with the low temperature rearrangements of molecules containing cyclobutane rings that are 1,3-bridged by etheno groups[11a–11e] bicyclo[2.1.1]hex-2-ene appears to be thermodynamically destabilized, since it has been found to have an unusually high heat of hydration: Wiberg K. B., Wasserman D. J., Martin E. J., Murcko M. A.: *J. Am. Chem. Soc.* **1985**, *107*, 6019.
12. Nendel M., Houk K. N., Tolbert L. M., Vogel E., Jiao H., Schleyer P. von R.: *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 748.
13. Maksic Z. B., Eckert-Maksic M., Kovacek D., Margetic D.: *J. Mol. Struct.* **1992**, *260*, 241.
14. Becke A. D.: *J. Chem. Phys.* **1993**, *98*, 5648.
15. Lee C., Yang W., Parr R. G.: *Phys. Rev. B* **1988**, *37*, 785.

16. Hariharan P. C., Pople J. A.: *Theor. Chim. Acta* **1973**, *28*, 213.
17. Frisch M. J., Trucks G. W., Schlegel H. B., Scuseria G. E., Robb M. A., Cheeseman J. R., Scalmani G., Barone V., Mennucci B., Petersson G. A., Nakatsuji H., Caricato M., Li X., Hratchian H. P., Izmaylov A. F., Bloino J., Zheng G., Sonnenberg J. L., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Vreven T., Montgomery J. A., Jr., Peralta J. E., Ogliaro F., Bearpark M., Heyd J. J., Brothers E., Kudin K. N., Staroverov V. N., Kobayashi R., Normand J., Raghavachari K., Rendell A., Burant J. C., Iyengar S. S., Tomasi J., Cossi M., Rega N., Millam N. J., Klene M., Knox J. E., Cross J. B., Bakken V., Adamo C., Jaramillo J., Gomperts R., Stratmann R. E., Yazyev O., Austin A. J., Cammi R., Pomelli C., Ochterski J. W., Martin R. L., Morokuma K., Zakrzewski V. G., Voth G. A., Salvador P., Dannenberg J. J., Dapprich S., Daniels A. D., Farkas O., Foresman J. B., Ortiz J. V., Cioslowski J., Fox D. J.: *Gaussian 09,* Revision A.02. Gaussian, Inc., Wallingford (CT) 2009.
18. Hrovat D. A., Chen J., Houk K. N., Borden W. T.: *J. Am. Chem. Soc.* **2000**, *122*, 7456.
19. Hrovat D. A., Borden W. T.: *J. Chem. Theory Comput.* **2005**, *1*, 87.
20. Rather than being cooperative, linear bis-annelation of benzene would be expected to be competitive; and our calculations confirm this to be the case. However, two valence isomers of nearly the same energy can be formed by linear bis-etheno annelation of benzene[21]. The C–C bond lengths in one of these isomers are those anticipated for a molecule containing two benzocyclobutadiene rings, in which symmetry prevents the type of bond localization that occurs in the benzene ring of **3**. The C–C bond lengths in the other valence isomer reveal that it has a [10]annulene periphery, perturbed by transannular bonds between C-1 and C-4 and C-6 and C-9. Our B3LYP/6-31G(d) calculations predict the latter isomer to be more stable than the former by 2.4 kcal/mol. The bis-annelation energy, calculated for forming the latter isomer, is $-\Delta E$ = 26.1 kcal/mol, which is 1.7 kcal/mol less than twice the benzene annelation energy of $-\Delta E$ = 14.9 kcal/mol for forming **3** and 14.7 kcal/mol less than $-\Delta E$ = 40.8 kcal/mol for angular bis-annelation of benzene to form **4**.
21. a) Schulman J. R., Disch R. L.: *J. Am. Chem. Soc.* **1993**, *115*, 11153; b) Boese R., Benet-Buchholz J., Stanger A., Tanaka K., Toda F.: *Chem. Commun.* **1999**, 319; c) Despotović I., Eckert-Maksić M., Maksić Z. B., Smith D. M.: *J. Phys. Chem. A* **2003**, *107*, 10396; d) Antol I., Eckert-Maksić M., Lischka H., Maksić Z. B.: *ChemPhysChem* **2004**, *5*, 975.
22. We could have constrained the lengths of the C=C bonds of the etheno groups and the C–C bonds joining them to the benzene rings in **4** and **5** to be the same as those in **3**. Our calculations show that, including the energy for the optimization of the these C–C bond lengths in ΔE_{geom} for **5**, would have increased the value of $-\Delta E_{\mathrm{geom}}$ in **5** by 3.5 kcal/mol and decreased the value of $-\Delta E_0$ by the same amount.
23. There is, of course, one more filled π MO in **3**, two more in **4**, and three more in **5**. In these MOs, which are not shown in Fig. 2, the interactions between the π orbitals of the benzene ring and the etheno bridges are bonding, so that these MOs do not contribute to the localization of the benzene ring π bonds, as do the MOs in Fig. 2.