Geometrical and Electronic Features of the Benzene Ring in Benzocycloalkenes and Related Compounds

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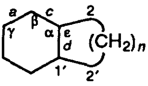
The fusion of a small, strained ring on a benzene molecule causes remarkable perturbations on the geometry of the latter molecule, perturbations which reduce with increasing number of atoms in the fused ring and become negligible as fusion involves rings larger than five-membered ones. The Cambridge structural database was searched for the experimental geometrical features of compounds containing from three- to ten-membered cycloalkene rings condensed with benzene. MO *ab initio* calculations at the 3-21G level were employed for studying the calculated features, *i.e.* geometries, total energies, enthalpies of formation, strain energies and π-electron distribution, in compounds containing cycloalkenes (from three- to five-membered rings) and related rings with further unsaturation, and in systems related to benzocyclopropene with a heteroatom (oxygen) or a positively charged carbon. The effect of the additional strain, generated in the molecule by the fusion of the two rings, on molecular geometry and π-electron distribution is discussed. Strain, which is highest when a three-membered ring is annellated to the benzene molecule, seems to be the main factor responsible for the geometrical perturbations of these molecules, whereas the π-electron distribution is mainly determined by interactions between the electrons of the atoms or groups at the functions of the annellated ring and those of the benzene π-orbitals.

The fusion of a small, strained ring with a benzene molecule induces structural and chemical properties in the new compound which can, in a number of cases, be evidenced experimentally. As regards the geometrical structure, it has been recognized[1,2] in benzocyclopropene that the bond common to the benzene and cyclopropene rings and the two adjacent bonds are shortened with respect to their length in benzene. Nevertheless, these differences tend to become quite negligible, at the limit of being detectable, when the fusion occurs with larger cycloalkenes.[3] Often, the presence of substituents on the fused ring does not facilitate extrapolation of the geometrical features of the unsubstituted molecule from the experimental results of a substituted derivative.[4] More evident is the deformation of the internal bond angles, as pointed out by Allen[5] in an analysis based on the X-ray crystal structure data.



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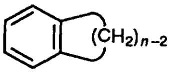
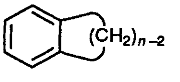


1a



1b

As regards the chemical point of view, Mills and Nixon[6] reported almost sixty years ago that aromatic electrophilic substitution in benzocycloalkenes (**1**; n = 5,6) is favoured in the β position. These authors postulated that the fusion of a small ring compound on a benzene molecule causes a partial π-bond localization, which, in terms of the theory of aromaticity current at that time, is equivalent to postulating a higher weight of a Kekulé structure over the other, as depicted in **1a** and **1b**. Much work has been done since then in order to prove or disprove that this partial bond fixation occurs in benzocycloalkenes. Experimental studies employing NMR,[7] UV spectroscopy[4] and X-ray structural data[5] showed that in these systems the benzene ring is sensitive to anellation, but no clear answers to the problem of bond fixation were achieved.

Theoretical VB calculations have recently shown[8] that in benzocyclopropene (**1**; n = 3) and benzocyclobutene (**1**; n = 4) the weights of the Kekulé structures are indeed different and in the sense originally indicated by Mills and Nixon (**1a** < **1b**). The geometric distortions induced by the strained ring at the σ-bond level is mainly responsible for this effect in benzocyclobutene and hyperconjugation of the CH_2 group contributes significantly to the partial bond fixation in the benzene ring of benzocyclopropene. Double-bond alternation in the benzene ring of benzocyclobutenes[3] and biphenylene[9] has also been rationalized on the basis of hybridization arguments and the parallel effect on the σ- and π-system has been stressed.

In chemical systems like those depicted by **1**, the effects of annellation on the properties of the benzene ring thus seem fairly well investigated and the explanations at the electronic level appear convincing.

Less well documented, both as regards the geometrical structure and the chemical and electronic properties, is the behaviour of molecules obtained by fusion of a strained ring different from a cycloalkene to the benzene molecule. We therefore deemed it interesting to examine molecules structurally related to benzocyclopropene, but containing either a heteroatom or a positively charged carbon, and molecules containing a dienic unsaturation in systems related to **1** with n = 4 and 5. From a comparative study of these molecules with respect to cycloalkenes we expected to obtain further insight into the electronic effects which characterize the geometrical structure of the benzene ring condensed with strained rings, and into its possible loss of aromaticity in the light of theories hitherto advanced to explain the physical and chemical behaviour of these kinds of molecules.

Results and Discussion

Experimental X-Ray Crystal Data.—The search for the literature X-ray data was carried out in the 1988 release of the Cambridge structural database.[10] The criterion used for the search was to consider only the analyses with $R \leqslant 0.07$ of compounds containing the monocycloalkene moieties **1** with n = 3–10, with no substituents at the benzene ring and no interaction with metal centres. The averaged values of Table 1

Table 1 Averaged structural data relative to monocycloalkenobenzenes[a]

	Bond length /Å				Bond angle /°					
n^b	*a*	*b*	*c*	*d*	α	β	γ	ε	δ	N^c
3	1.384(4)	1.388(6)	1.379(6)	1.355(4)	124.0(2)	113.0(3)	123.0(4)	61.8(5)	173.4(12)	1
4	1.396(3)	1.389(4)	1.386(2)	1.383(4)	122.6(2)	115.2(2)	122.2(2)	93.4(2)	143.8(1)	23
5	1.386(1)	1.384(1)	1.388(1)	1.393(1)	120.6(6)	118.6(2)	120.8(2)	110.4(1)	128.9(4)	127
6	1.390(1)	1.383(1)	1.392(1)	1.399(1)	120.0(1)	119.6(1)	120.4(1)	115.9(1)	124.0(1)	379
7	1.387(3)	1.379(2)	1.392(2)	1.401(1)	119.7(1)	120.0(1)	120.2(1)	116.2(2)	124.1(2)	73
8	1.390(2)	1.379(3)	1.394(1)	1.397(2)	119.6(1)	120.3(1)	120.2(2)	117.4(2)	123.0(1)	50
9	1.389(2)	1.380(1)	1.390(1)	1.399(1)	119.9(1)	119.7(1)	120.4(1)	114.8(1)	125.3(1)	78
10	1.390(2)	1.382(2)	1.392(1)	1.403(1)	119.8(1)	119.8(1)	120.3(1)	115.2(1)	125.0(1)	86

[a] Averaged from structural data reported in the literature.[5] Esds are given in parentheses. [b] Number of CH_2 groups is $n - 2$. [c] Number of compounds considered in the average.

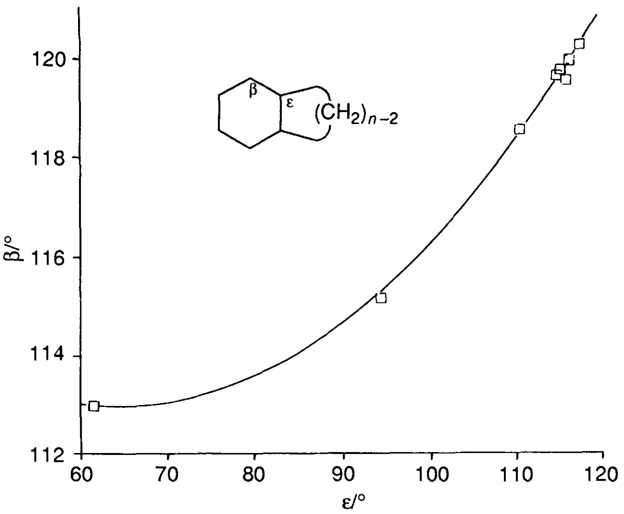


Fig. 1 The $\beta = \beta(\varepsilon)$ relationship for monocycloalkenobenzenes with no substituents at the benzene ring. The continuous curve has been calculated by the least-squares equation: $\beta = 123.8(3) - 0.336(8)\varepsilon + 0.002\,61(4)\varepsilon^2$; $r^2 = 1.000$

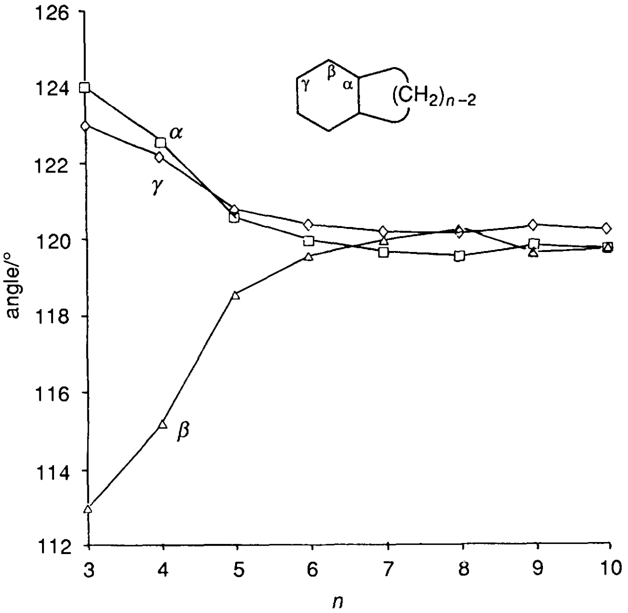


Fig. 2 Variations of the α, β and γ benzene angles with increasing number, *n*, of carbon atoms in the fused ring

were calculated assuming a local *m* symmetry for the alkenobenzene moiety. Error estimates for the mean parameters ($\bar{x}$) are given by $\sigma(\bar{x}) = [\Sigma(\bar{x} - x_i)^2/n(n - 1)]^{\frac{1}{2}}$ for *n* observations x_i ($i = 1,n$).

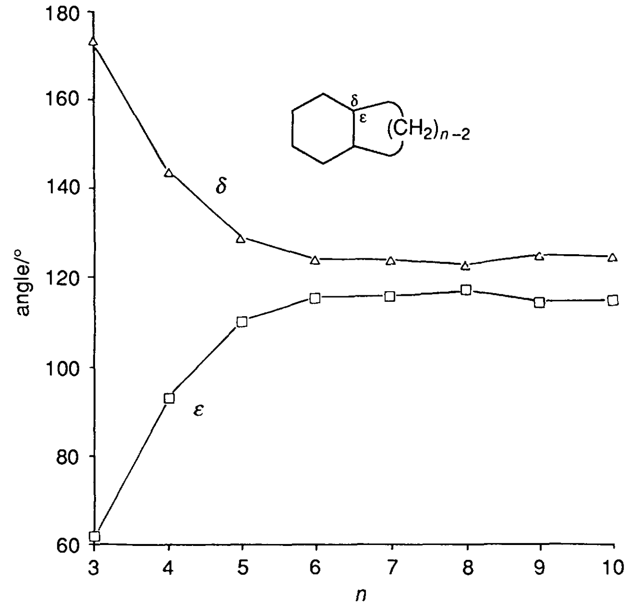


Fig. 3 Variation of the ε and δ angles with increasing number, *n*, of carbon atoms in the fused ring

Only one derivative of benzocyclopropene with no substituents at the benzene ring has been studied by X-ray methods: this is (diphenylmethylene)cyclopropabenzene.[11] Using the data from this analysis it appears that the $\beta = \beta(\varepsilon)$ relationship (β angle as a function of angle ε, Fig. 1) is not simply linear as Allen[5] found by using for benzocyclopropene the only data at that time available which were from benzene-substituted derivatives (*i.e.* 2,5-diphenylbenzocyclopropene-1,1-dicarboxylate[2] and 1,1-dichloro-2,5-diphenylbenzocyclopropene[12]). This finding indicates that neglecting anharmonicity in the energy-minimisation model proposed by Allen, is too great an approximation when the deformations are as high as those present in benzocyclopropene.

From Figs. 2 and 3, which show how the angular deformations reduce with increasing number, *n*, of atoms in the fused alkene ring, it appears that when $n > 5$ no significant deformation is observed. Less relevant and not significant are the variations observed in the benzene bond longths, even if some systematic trends seem to be present.

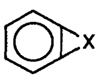
Calculations of Molecular Properties.—The molecules chosen for this study are **2**–**4**. They were examined with a theoretical approach, in the frame of *ab initio* MO calculations. The standard GAUSSIAN-86 package[13] was employed on a CRAY-X-MP48 supercomputer and full-geometry relaxation was performed with a built-in gradient procedure in the software employed. The 3-21G level was adopted, even though

Table 2 Selected parameters relative to the calculated geometries for compounds **2**–**4** at the 3-21G level

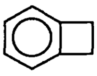
	Bond lengths/Å				Bond angles/°				
Compound	*a*	*b*	*c*	*d*	α	β	γ	ε	Other geometrical parameters
2a	1.406	1.390	1.362	1.337	124.7	113.1	122.2	63.9	C(1)–C(2) 1.517; C(1)–C(2)–C′(1) 52.3
2b	1.363	1.460	1.404	1.380	124.8	111.3	123.9	59.7	C(1)–C(2) 1.365; C(1)–C(2)–C′(1) 60.7
2c	1.438	1.375	1.340	1.311	127.4	109.7	122.9	64.2	C(1)–O 1.503; C(1)–O–C′(1) 51.7
3a	1.396	1.387	1.371	1.386	122.2	116.2	121.5	94.0	C(1)–C(2) 1.538; C(2)–C′(2) 1.599; C(1)–C(2)–C′(2) 86.0
3b	1.438	1.358	1.340	1.426	127.6	115.7	121.7	88.4	C(1)–C(2) 1.546; C(2)–C′(2) 1.337; C(1)–C(2)–C′(2) 91.7
4a[a]	1.385	1.386	1.382	1.384	120.4	119.3	120.3	111.9	C(2)–C(2) 1.518; C(1)–C(2)–C(3) 104.6
4b	1.391	1.385	1.375	1.397	120.6	118.8	220.6	108.2	C(1)–C(2) 1.521; C′(1)–C′(2) 1.478; C′(2)–C(3) 1.328; C(1)–C′(1)–C′(2) 108.2; C′(1)–C′(2)–C(3) 109.8

[a] The calculated ground state of this molecule is nearly planar.

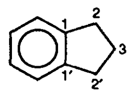
some criticism on this basis set has been advanced[3] in view of the deficiency in properly reproducing a number of C–C bond distances. The choice was principally dictated by the necessity of also tackling at the same level large molecules like **4a** and **4b** and performing full-geometry relaxation in a reasonable computing time. Furthermore, the bond distances overestimated at the 3-21G level differ[3] by 0.01–0.02 Å from those obtained with the larger 6-31G basis set: this difference seemed to us an acceptable limit in view of the comparisons we intended to carry out between the compounds considered here.



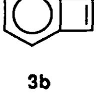
2 a X = CH$_2$
b X = CH$^+$
c X = O



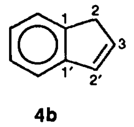
3a



4a



3b



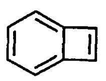
4b

The most significant calculated geometrical parameters are reported in Table 2. For compounds **2a** and **3a** the results do not differ significantly from those reported in previous papers.[3,14] A comparison with the results of X-ray analysis shows that for compounds **2a**, **3a** and **4a** the agreement is satisfactory since the trend of calculated and experimental values (Tables 1 and 2) is quite close. For compound **4a** the calculated ground-state structure is very near to complete planarity and the puckering of the cyclopentene ring close to zero. Rotational analysis[15] of the electronic spectrum of this molecule shows sequence bands of the puckering vibrations of the CH$_2$ group which are likely to be accommodated with a W-shaped potential, probably similar to that of cyclopentene. The 3-21G level does not reproduce such a type of potential and, at this stage, it is difficult to assess whether this is due to a failure of this level of calculation, or if the W-shaped potential is characterized in indane by a very low inversion barrier, smaller than that of cyclopentene.

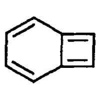
For compound **2a** the molecular geometry obtained from experimental results is from one compound only and so is not reliable enough for carrying out a detailed comparison with the single calculated bond lengths: nevertheless, it clearly appears that the bond-length reduction of *c* and exceptionally *d*, with respect to benzene, is also reproduced by the calculated values. For bond *b* the calculated reduction is underestimated.

For compound **2c** no experimental molecular structure seems to be available. The calculated effect of annellation is qualitatively similar to that observed in **2a**, with stronger reduction of the bond lengths of *c* and *d*. For the benzocyclopropene molecule the VB treatment has shown[8] that structures of type **1b** have a higher weight than those of type **1a**. The control of π-bond localizations and, partly, of molecular geometry, is mostly given by orbital interactions.[8] The interaction between the $\pi^*_{CH_2}$ antibonding orbital and the π-orbital of an adjacent double bond has a destabilizing effect which, for overlapping reasons, is higher when one ethylene bond interacts as in structure **1a** than when it interacts as in **1b**. The same reasoning should apply to **2c**, where a doubly occupied p-orbital of oxygen is responsible for interaction with an ethylene occupied π-orbital. On the basis of a simple qualitative reasoning, destabilization of the ethylene occupied orbital should be expected to occur to a greater extent than when a CH$_2$ group is involved, owing to the greater ability of the oxygen lone pair to repel the electrons of the ethylene bond. Bond alternation of the type represented by **1b** is in fact present and appears particularly relevant in bonds *a* and *c*.

In **2b** an empty p-orbital interacts with the ethylene π-orbital: stabilization of the ethylene π MO orbital should occur and structure **1a** appears to be favoured over **1b**. The calculated bond distances are in agreement with this kind of picture of the π-electron distribution. The presence of bent bonds in small strained rings should be at the origin of the shortening of bond distances as well, especially as regards bond *d*, since the molecule tries to increase the overlap between twisted orbitals.[16] In compound **3a** the higher weight of the structures of type **1b** is favoured[8] primarily as a consequence of the geometric distortion induced by the annellated strained ring at the σ-bond level. In compound **3b** bond alternation is rather pronounced and of the type **1b**. In this case, it is very likely that the molecule tends to avoid the electronic structure of the anti-aromatic cyclobutadiene, as should occur in the case of structure **1a**. In biphenylene,[4,9,17] the potential anti-aromaticity constraint induced by the four-membered ring is alleviated by significant bond alternation in the benzene rings: X-ray analysis[17] provides evidence for shortening of the benzene bonds exocyclic to the small ring. The experimental results obtained for compounds **3b** by flow NMR resonance[18] indicate that this molecule has polyalkene character, and a prevalent **3b(II)** structure was tentatively assigned. Furthermore, in compound **3b**, the short C(2)–C(2′) and long C(1)–C(2), calculated bond distances suggest that between the two possible structures **3b(I)** and **3b(II)**, the latter is less representative in describing the electronic structure of this molecule. This conclusion is in better agreement with the structure obtained from the X-ray analysis of a highly substituted benzocyclobutadiene[19] than with the assignment made from the NMR results.[18] Theoretical studies[20] at the semiempirical level (MNDO and MINDO/3) reached the same conclusion.



3b(I)



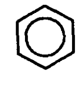
3b(II)

Calculated bond distances and bond angles in the sixmembered ring of compound **4a** are close to those of a benzene molecule, and the perturbation induced by annellation is small. Bond alternation is slightly more pronounced in compound **4b** and in favour of structure **1b**. Since π-conjugation should occur in the latter molecule, the double bond of the five-membered ring should impose a certain degree of localization on the electrons of the aromatic ring. In other words, conjugation should be more efficient when an *s-trans* arrangement of the π-bonds is present, and this should make structure **1b** slightly preferred. This effect seems, however, rather small. A correct description of the relative weight of resonance structures can be obtained only from VB calculations, and geometric distortion induced by annellation does not represent unambiguously π-electron localization.

Enthalpy of Formation and Strain in Annellated Systems of Benzene.—The perturbations induced on the benzene ring at different levels (geometrical parameters, π-electron distribution and σ-bond rehybridization) are mostly ascribed to the strain induced by the annellated ring. The repulsion on the electrons of the formally localized bonds from atoms or groups forming the small ring also has an effect, but to a lesser extent. This mechanism is more efficient[8] in benzocyclopropene than in benzocyclobutene, and stronger for an oxygen atom than for a CH_2 group. While this effect should mainly perturb the distribution of the π-electron system, the resulting geometrical structure of the molecule should be principally imposed by strain. This quantity is thus considered mainly responsible for the geometrical features, which may be known or require future experimental investigation. Hitherto, it seems quite desirable to quantify, even at an approximate level, the strain energy of compounds **2**–**4**. For compound **2a** this has been achieved[21] by employing experimental enthalpy changes in a chemical reaction and a value of 68 kcal mol^{-1} was estimated (by assuming no loss of aromaticity of the benzene ring). This value is higher than the strain of cyclopropene itself[22] (52.6 kcal mol^{-1}).

Strain energies of molecules can be obtained from their enthalpies of formation, ΔH_f° (in the vapour phase and at a standard temperature) and those of unstrained models constructed according to standard additivity schemes (*i.e.* Franklin group equivalents[23]). Enthalpies of formation of compounds

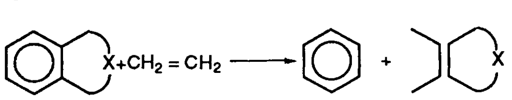
Table 3 Total molecular energies (a.u.) calculated at the 3-21G level, enthalpies of formation, ΔH_f° (kcal mol^{-1}) and strain energies, E_s (kcal mol^{-1}) for compounds **2**–**4**; data for reference compounds are also reported[a]

Compound	Total energy	ΔH_f° [b]	E_s [c]	ZPE[d]	ΔH (0–298 K)[e]	ΔE_s
2a	−266.952 832	90.7 (90.9) 87.1–87.5;[f] 80.2[g] 89.7[h]	71.6 (71.8) 68.0–68.4[f]	71.11	3.56	19 15[i]
2b	−266.118 839	281.6				
2c	−302.509 907	105.0 (104.8)	108.2 (108.0)	53.99	3.61	26
3a	−305.846 458	46.5	32.4			4
3b	−304.611 534	97;[j] 85.8[k]	53.1			29
4a	−344.718 370	16.3	7.1			1.2
4b	−343.535 285	39.5	1.5			−4.5
Reference compounds						
	−115.162 00[l]	66.2[m]	52.6[n]			
	−114.329 57[o]	256[m]				
	−150.728 612[p]	74 ± 3[q]	82 ± 3[q]			
	−154.030 72[o]	37.5[r] 33.2;[t] 36.4[t]	28.4[s]			
	−152.771 514[u]	102 ± 3[j] 92[j]	24[v]			
	−192.901 68[o]	7.87[w]	5.9			
	−191.717 08[o]	32.0[w]	6.0			
	−229.419 445	19.82[w]		68.28	3.10	
$CH_2{=}CH_2$	−77.600 99[x]	12.50[w]				

[a] When not otherwise specified entries refer to our calculations; 1 kcal mol^{-1} = 4.184 kJ mol^{-1}. [b] From the isodesmic reaction [eqn. (1)]: zero-point energies and temperature corrections to the enthalpy were not taken into account. For compounds **2a** and **2c** values corrected for these quantities are reported in parentheses. [c] Conventional strain energy referred to Franklin group equivalent scheme.[23] In parentheses values corrected for zero-point energies and temperature vibrational effects are reported. [d] Zero-point energies (kcal mol^{-1}). [e] Temperature corrections to the enthalpy in the interval 0–298 K (kcal mol^{-1}). [f] Ref. 21: from experimental data. [g] Theoretical estimate from MINDO/3.[14] [h] Theoretical estimate at MNDO level.[14] [i] From the data of ref. 21. [j] Employing a ΔH_f° for cyclobutadiene of 102 ± 3 kcal mol^{-1} estimated by us from 3-21G energies and through the isodesmic reactions: cyclobutadiene + $CH_3{-}CH_3 \longrightarrow CH_2{=}CH_2$ + cyclobutene; cyclobutadiene + cyclopropane ⟶ cyclobutene + cyclopropene. [k] By employing the ΔH_f° of cyclobutadiene from ref. 20. [l] Ref. 25. [m] Ref. 26. [n] Ref. 22. [o] Ref. 27. [p] Ref. 28. [q] Our estimate: ΔH_f° from molecular energies calculated at the 3-21G level and the isodesmic reactions: oxirene + $CH_3{-}CH_3 \longrightarrow$ oxirane + $CH_2{=}CH_2$; oxirene + cyclopropane ⟶ oxirane + cyclopropane. [r] Ref. 29. [s] Ref. 16. [t] Ref. 30. [u] Ref. 31. [v] Ref. 20. [w] Ref. 32. [x] Ref. 33.

2–**4** in the vapour phase are not known experimentally, except for compound **2a**, for which an experimental estimate has been reported[21] (87.1–87.5 kcal mol^{-1}).

Calculated total molecular energies can be employed for obtaining an estimate of these values when they have not been determined experimentally. In comparing energies of different molecules calculated from single-determinant wavefunctions, large errors are introduced by the fact that electron correlation is not taken into account. These errors are largely cancelled by employing isodesmic reactions,[24] where the types and the number of bonds are the same in the molecules appearing on the two sides of the equation. The difference in the total energy of products and reactants is equated to the enthalpy of reaction and the enthalpy of formation of the molecule in question can be calculated involving compounds for which the enthalpies of formation are known. The isodesmic reaction we have employed is that represented by eqn. (1). The total molecular



(1)

energies are those calculated at the 3-21G level, with molecular geometry fully relaxed at the same level. These energies, together with the estimated enthalpies of formation for compounds **2**–**4**, are reported in Table 3. Enthalpies of formation and calculated total molecular energies for reference compounds are also collected in Table 3.

A further comment is worth making on the calculated enthalpies of formation and, as a result, on the strain energies derived from these quantities. A correct evaluation of the enthalpies of formation should refer to a common temperature value and the total molecular energies should be corrected[34] for the zero-point energy (E_{ZP}) and temperature effects ΔH (0–298 K) (if the comparisons are carried out at 298 K). For compounds **2**–**4** we have calculated the E_{ZP} values and ΔH (0–298 K) values: in Table 3 these are reported for compounds **2a** and **2c** together with the relative corrections to their enthalpies of formation.* Differences between corrected and uncorrected values are less than 0.5 kcal mol^{-1}, and can be considered negligible in view of the approximations involved in estimating enthalpies of formation and the large differences found for the values relative to the compounds examined.

The strain energy (E_s) values should provide an estimate of the additional strain resulting from the fusion of the benzene molecule and the small strained rings. The value we have obtained for compound **2a** is in reasonable agreement with previous experimental[21] and theoretical[14] estimates. Thus the fusion of cyclopropene on benzene gives rise to a molecule with an additional strain (ΔE_s) of 15–19 kcal mol^{-1}. In the same context, in the fusion with the oxirene ring the additional strain amounts to 26 kcal mol^{-1}, higher than that involved with cyclopropene. The additional strain is small and almost identical when cyclopentene and cyclopentadiene rings are involved in annellation with the benzene ring. The fusion with cyclobutene adds a small extra contribution but the effect is remarkable when cyclobutadiene is involved.

Conclusive comments on the effect of strain on the physical and chemical properties of these systems are as follows. For the two molecules most widely investigated in the past years, *i.e.* benzocyclopropene and benzocyclobutene, the strain energy is significantly different and the additional strain is particularly high for the former compound. The additional strain should thus be mainly responsible for the features which show clear differences in the two compounds, especially geometrical parameters, and bonds *c* and *d* in the first place. The effect of strain seems, on the other hand, to have a lower influence on the distribution of the π-electrons in the benzene ring. This emerges especially in the comparison between compounds **2** where the π-electron density alternation seems to depend mainly on the electronic perturbation induced by group X. The high additional strain estimated for compound **3b** seems mainly due to the attempt of the molecule to avoid the antiaromatic structure of cyclobutadiene by decreasing the weight of structures like **1a**; this is equivalent to a loss of π-electron delocalization (aromaticity). The cyclopentene ring does not originate significant additional strain and this is in agreement with the almost unperturbed geometrical parameters of the benzene ring in compound **4a**. The conjugative effect involving the unsaturated five-membered ring is probably responsible for the further small stabilization found for **4b** as shown by the distribution of the π-electron system and from the unperturbed molecular geometry which should indicate an insignificant presence of strain.

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* Zero-point energies and temperature corrections to the enthalpy were obtained from a theoretical complete vibrational anslysis of the molecules. For cyclopropene, oxirene and ethene molecular vibrations from literature sources were employed.

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