Notes

Bond Localization in Annelated Benzenes: An Additivity Scheme

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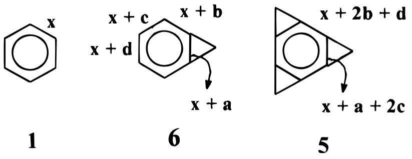
Introduction

Intensive research is going on to trap the elusive cyclohexatriene, one of the resonance structures of benzene.[1] The idea of annelation of strained rings to localize the bonds in benzene has been around for a long time. During the days of the oscillation model for benzene (**1**), Mills and Nixon[2] suggested that the two principal Kekule structures could be trapped by small ring annelation. Despite the failure of the oscillation model and the subsequent rejection of the MN effect, the possibility of synthesizing annelated benzenes with significantly different C−C bond lengths continues to fascinate chemists. There has been two different approaches to this problem. One method is based on the annelation by antiaromatic cyclobutadiene rings, pioneered by Vollhardt.[1d,3] The attempt to avoid antiaromaticity following the conjugation leads to the localization of the π bonds in benzene, so that the canonical structures with cyclobutadienoid rings contribute minimally. Several molecules have been synthesized in this category.[4] For example, [4]phenylene[5] **2**, where the bond lengths of the central benzene ring differ by 15.2 pm, has the maximum bond length alternation known so far. A different strategy has been adopted by Siegel,[6] who used annelation by strained nonconjugating bicyclic systems. The recent structural study of strained bicyclic systems such as bicyclo[2.1.1]hexene[7] **(3)** and oxanorbornadiene[8] have shown that substantial bond length variations can be realized even without extension of conjugation in benzene and other related systems such as [14]annulenes.[9] There have been many earlier attempts to induce bond length variations in benzene by annelating strained rings.[10] Tricyclobutabenzene, **4**, for example, gave a difference in C−C bond lengths of 2.3 pm.[10] On the other hand tricyclopropabenzene, **5**, is calculated to give no bond length alternation, though all bonds were shortened.[11] This is surprising because monocyclopropabenzene,[12] **6**, had shown a large variation of bond lengths compared to monocyclobutabenzene,[13] **7**. In most of the annelated systems we have observed systematic variation in bond lengths on going from monoannelation to triannelation. Here we analyze and explain the variations brought by the annelation of nonconjugating strained rings and show that these are additive. The additive nature of bond length variations is demonstrated for experimentally known structures. An internally consistent set of values is obtained for structures calculated at the Hartree−Fock level using the 6-31G* basis set.[14]

Scheme 1



Results and Discussion

The extent of C−C bond length variations in benzene on annelation of a ring can be expressed in relation to the parent benzene. For example, the annelated bond, C_1-C_2, in cyclopropabenzene, **6**, is shortened by 5.0 pm, from the reference bond length 138.4 pm (X-ray) (Table 1) of benzene. Similarly, the C_2-C_3 bond decreases by 2.1 pm. These and other changes (a−d) are characteristic of cyclopropane annelation, Scheme 1 . Sets of a−d values obtained for different rings are given in Table 2.

These variations are found to be additive in multiannelated molecules. For example, cyclopropane and cyclobutane in **8** are trans to each other. The C_1-C_2 bond annelated to cyclopropane should decrease by 5.0 pm, (138.4 − 5.0). But the C_1-C_2 bond is also trans to the

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(1) (a) Frank, N. L.; Siegel, J. S. *Advances in Theoretically Interesting Molecules;* JAI Press Inc.: New York; Vol. 3. (b) Siegel, J. S. *Angew. Chem., Int. Ed. Engl.* **1994**, *33,* 1721. (c) Mo, O.; Tanez, M.; Maksic, M. E.; Maksic, Z. B. *J. Org. Chem.* **1995**, *60,* 1638, and references therein. (d) Boese, R.; Matzger, A. J.; Mohler, D. L.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34,* 1478, and references therein.

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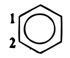
cyclobutane, so it is elongated by 1.5 pm (Table 2). The net effect is that the bond length is brought to 133.9 pm (138.4 − 5.0 + 1.5). This is identical to the X-ray value of 133.9 pm (Table 1). Similarly the C_4-C_5 bond length comes to 139.7 pm (138.4 + 0.7 + 0.6) compared to 139.9 pm obtained from X-ray studies (Table 1). When cyclopropane and cyclobutane are annelated asymmetrically as in **9**, all the bond lengths can be predicted by the bond increment scheme (BIS) (Table 1). Standard deviation of the difference between BIS (X-ray) and X-ray bond lengths is 0.43 pm. The corresponding value for BIS-(HF/6-31G*) and HF/6-31G* bond lengths is 0.32 pm. In general, the maximum deviation of the BIS bond lengths from the observed ones is less than 1 pm.



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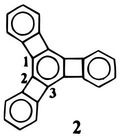

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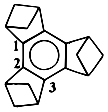

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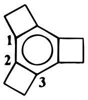

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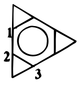

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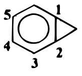

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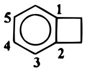

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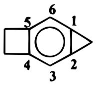

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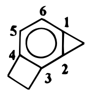

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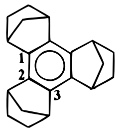

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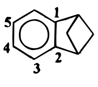

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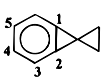

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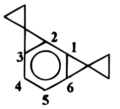

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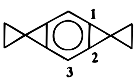

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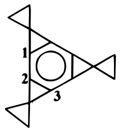

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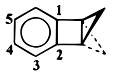

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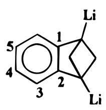

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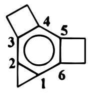

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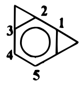

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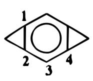

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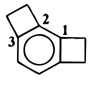

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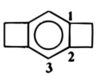

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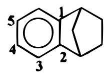

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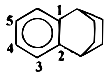

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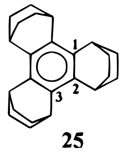

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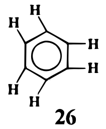

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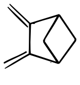

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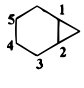

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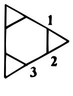

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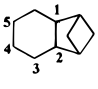

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Equal bond lengths observed in tris-cyclopropabenzene, **5**, can now be understood from the BIS. The C_1-C_2 bond length would be 136.0 pm (138.6 − 5.4 + 1.4 + 1.4), and the C_2-C_3 bond length 136.3 pm (138.6 − 1.6 − 1.6 + 0.9).** Since annelation of cyclopropane does not induce alternating bond lengths (Table 2), large variations cannot be realized on tris-annelation. The large localization observed in **3** is a result of alternating signs (−ve., +ve., −ve., and +ve.) of a−d parameters in **11**. The effect of spiropentane annelation to benzene has also been studied (**12**−**15**) (Table 3) which follows the BIS. The success of BIS over a large number of known and calculated molecules shows that the bond length variations in the annelated benzenes are additive.

Table 1. Experimental Bond Lengths of Annelated Benzenes from X-ray Studies along with Bond Increment Scheme (BIS) Values and Theoretical Values at the HF/6-31G* Level along with BIS Values

structure		expt	bis (expt)	HF/6-31G*	bis (6-31G*)
1[a]	C_1-C_2	138.4	138.4	138.6	138.6
3[b]	C_1-C_2	143.8	–	144.0	144.1
	C_2-C_3	134.9	–	134.4	133.7
4	C_1-C_2	141.3	142.3	139.1	139.4
	C_2-C_3	139.0	140.1	137.8	137.9
7	C_1-C_2	134.9	134.9	133.5	133.8
	C_2-C_3	138.5	137.9	137.8	137.7
	C_3-C_4	140.5	138.8	139.3	139.2
	C_4-C_5	139.9	140.3	138.9	138.9
8	C_1-C_2	135.1	135.0	133.9	133.9
	C_2-C_3	136.3	136.4	136.7	136.2
	C3−C4	139.3	139.4	139.0	139.4
	C4−C5	138.4	139.1	138.5	138.7
	C5−C6	140.1	140.3	140.7	140.7
	C6−C1	136.8	137.8	137.6	137.6
10	C1−C2	141.7	–	141.6	141.7
	C2−C3	137.9	–	136.4	136.3
18	C1−C2	136.3	136.6	134.5	134.6
	C2−C3	137.2	137.9	136.9	136.7
	C3−C4	141.1	141.0	139.7	140.0
	C4−C5	138.5	137.9	137.8	138.2
21	C1−C2	139.9	140.6	138.6	138.6
	C2−C3	139.4	140.1	138.5	138.5
	C4−C5	138.2	140.0	138.3	138.7
	C5−C6	141.3	141.6	140.0	138.6
22	C1−C2	140.2	140.7	138.6	138.7
	C2−C3	138.5	138.7	137.3	137.0
25	C_1-C_2	140.8	–	140.6	140.4
	C_2-C_3	137.9	–	138.0	137.6

[a] This work. [b] Structures **3**, **4**, **7**, **8**, **9**, **17**, **20**, **21**, and **24** are taken form ref 1a.

Table 2. Bond Length Increments in Benzene Annelated by Different Rings.[a] These Values Are Obtained by Subtracting the Bond Lengths From the Standard Benzene Value of 138.4 pm, for X-ray and 138.6 pm for HF/6-31G* Geometries. Negative Sign Indicates Shortening and Positive Sign Indicates Lengthening from the Standard Values

rings	a	b	c	d
cyclopropane	−5.0 (−5.4)[b]	−2.1 (−1.6)[b]	0.3 (1.4)[b]	0.6 (0.9)[b]
cyclobutane	0.7 (−0.6)[b]	0.1 (−0.8)[b]	1.6 (0.7)[b]	1.5 (0.6)[b]
[2.1.1]hexane[b]	1.7	−2.0	1.9	−0.9
[2.2.1]hexane[b]	1.1	−1.0	1.0	−0.3
[2.2.2]hexane[b]	1.0	−0.4	0.4	−0.2
spiropentane[b]	−4.0	−0.17	1.6	0.6

[a] The bond lengths data for **6**, **7**, **11**, **12**, **23**, and **24** are not given in the Tables 1 or 3. The same can be generated by adding corresponding a−d to 138.4 pm for X-ray and 138.6 pm for HF/6-31G* values. [b] Corresponds to HF/6-31G* values.

One of the earlier attempts to explain the bond length variations on annelation by small rings considered the angularly constrained benzene as a model.[15] When the CCH angle is 90.0°, **26**, the C−C bond lengths differed by as much as 20 pm. The lack of corresponding difference in **4** is attributed to cyclobutane banana bonds. We find that the dramatic bond length differences observed in the model, **26**, are not from the small CCH angle, but from the H---H repulsive interactions operating at that short distance. These are removed on going to **4**, where H---H repulsive interactions are eliminated by forming the C−C bonds, so that there is little bond length alternation. A similar repulsive force is also the key in causing the significant C−C bond length variations in benzene annelated by [2.1.1]hexane **3**. Here the repulsion is between the bridgehead carbons which elongates the ipso bond. Earlier, in an attempt to explain the differences in reactivity between bicylco[2.1.1]hexane, **27**, and 2,3-bismethylenebicyclo[2.1.1]hexane, **28**, Jorgensen and Borden[16] considered the interaction of ethylene and butadiene with the cyclobutane ring. This

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Table 3. Theoretical Bond Lengths at HF/6-31G* along with BIS Values

structure		HF/6-31G*	BIS
5[a]	C_1-C_2	135.9	136.0
	C_2-C_3	135.6	136.3
13[b]	C_1-C_2	135.8	136.2
	C_2-C_3	135.5	135.2
	C_4-C_5	137.0	137.5
	C_5-C_6	142.2	141.8
14[b]	C_1-C_2	134.7	135.2
	C_2-C_3	138.6	138.5
15[b]	C_1-C_2	138.2	137.8
	C_2-C_3	134.7	135.8
16[b]	C_1-C_2	137.4	137.4
	C_2-C_3	137.9	137.9
	C_4-C_5	139.7	139.7
	C_5-C_6	139.2	139.2
17[b]	C_1-C_2	141.6	141.6
	C_2-C_3	136.7	136.7
	C_4-C_5	141.0	141.0
	C_5-C_6	137.3	137.3
19[b]	C_1-C_2	134.2	134.6
	C_2-C_3	136.0	135.4
	C_4-C_5	137.6	137.9
	C_5-C_6	141.6	141.4

[a] Structure **5** is taken form ref 1a. [b] This work.

filled−filled repulsive interaction is found to be the major destabilizing factor for **27** compared to **28**. The magnitude of this interaction in **11** is intermediate between those in **27** and **28**. So the extra stability of butadiene with cyclobutane is used to explain the elongation of the ipso bond in **11**; however, this is not the complete story. This interaction alone will not explain the variation of the annelated bond length as a function of the size of the bicyclic ring. If the repulsive interactions between bridgehead carbons is really operative, increasing the distance between them should result in the decrease of the bond length variations. This is indeed found to be true in going from **3** to **10** and **25**. One of the ways of eliminating the repulsions between the bridgehead carbons is to form a bond between the bridgeheads as in **16**, which will remove the repulsive interactions. Despite the high strain (455 kJ/mol for [2.1.1]propellane compared to 155 kJ/mol for [2.1.1]hexane), our calculations show that **16** has negligible variations in the C−C bond lengths (Table 3). This is similar to the small deviations found for cyclobutane annelations. Further support for this comes from calculations on the dilithio derivative **17** (of **11**) which has larger bridgehead C−C repulsions from the increased negative charge on the bridgehead carbons than that in **11.** Thus the largest variation observed by any monoannelation is seen in **17** (Table 3).

The annelated rings considered here perturb the σ framework of the benzene. If σ orbitals alone are responsible for the observed bond length alternation, how are the remote bonds getting affected? To understand the role of σ and π orbitals in bringing out the characteristic bond length variations, we have done a model study on cyclohexane where the six carbons are constrained to one plane. When cyclopropane is annelated, the nature of the variation in bond parameters in **29** is similar to that in **6** ($C_1-C_2 = 149.8$ pm, $C_2-C_3 = 151.8$ pm, $C_3-C_4 = 155.2$ pm, and $C_4-C_5 = 155.6$ pm; compared to the C_1-C_2 distances in planar cyclohexane 154.9 pm). Again, on triannelation of planar cyclohexane by cyclopropane no bond alternation is found, **30**. Annelation by [2.1.1]hexane ($C_1-C_2 = 157.0$ pm, $C_2-C_3 = 154.4$ pm, $C_3-C_4 = 155.1$ pm, and $C_4-C_5 = 155.0$ pm, **31**) showed similar patterns for the ipso and adjoining bond lengths as found in the corresponding benzene systems. As anticipated, the σ bonds do not transmit the effects beyond two bonds. The significant bond length variations found on remote bonds as in **6** and other monoannelated rings shows the importance of the transmission of the perturbation at C_1-C_2 to the rest of the ring by the conjugated π-system. This is carried over on multiannelation as well. These results are in agreement with the school of thought put forward by Shaik and coworkers that the equal bond lengths in benzene are due to the σ frame.[17] We also note that the bond length alternations calculated for annelated cyclohexane systems is further enhanced by the localizing nature of the π framework in the benzene skeleton.

In conclusion, the bond increment scheme presented here predicts the geometries of multiannelated benzenes from those of the monoannelated ones. The bond length variations or the lack of it is a result of this additivity. The nonbonded C---C repulsions at the bridge head positions of the bicyclic systems such as [2.1.1]hexane causes the C−C bond length variations. Studies on model planar cyclohexane indicate that small ring annelation effects the σ system, and the π system carries the perturbation to the rest of the benzene.

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Supporting Information Available: HF/6-31G* coordinates (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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