hydration sites of adjacent residues on the two strands. Because of helical periodicity, such a situation leads to a regular hydration network called the hydration spine.[31] It is expected that this hydration spin contributes in an important way to the stabilization of the unusual properties of dA·dT polymers, and the evaluation of that factor will be the aim of further studies.

Acknowledgment. We thank G. S. Manning and D. L. Beveridge for continuing discussions and helpful comments on the theoretical treatment of the ionic environment on the modelling of nucleic acids. We also thank P. Koehl (IBMC, Strasbourg) and G. Wipff (Universitê Louis Pasteur, Strasbourg) for computer programs, and C. Gross, M. F. Janot, B. Speckel, and C. Tugene at the Centre de Calcul (Strasbourg–Cronenbourg) for help with the IBM 3090 system.

Registry No. Poly(dA)·poly(dT), 24939-09-1.

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(31) Drew, H. R.; Dickerson, R. E. *J. Mol. Biol.* **1981**, *151*, 535–556. Chuprina, V. P. *Nucleic Acids Res.* **1987**, *15*, 293–311. Westhof, E. *Annu. Rev. Biophys. Chem.* **1988**, *17*, 125–144.

Is the Mills–Nixon Effect Real?

Amnon Stanger

Contribution from the Department of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel.
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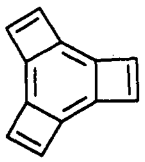
Abstract: The long debated issue of the Mills–Nixon effect is reexamined. If benzene's hydrogens are bent as if to form small rings, pure strain is imposed on the aromatic system. The result of this strain is fixation of benzene's bonds according to the Mills–Nixon postulation. It was found (eq 1) that ΔR is proportional to $\sin^2 \alpha$, where ΔR is the difference between the long and the short bonds in the alternated benzene and α is the deviation from the natural bond angle (120°). However, the 3-21G-optimized geometries for **2** and **3** show that these systems are much more delocalized (i.e., ΔR is much smaller) than is expected from the bent benzene model. The "effective" bond angles (i.e., the angles that should have caused the observed ΔR) of these molecules were calculated by using the ΔR values from the 3-21G-optimized geometries and the relationship found between the bending angle and ΔR (eq 1). Thus, 3-21G angles are 86.2 and 93.6° for **2** and **3**, respectively, whereas the "effective" angles (eq 1) are 92.0 and 108.1°, respectively. This difference was attributed to the formation of "banana bonds" in these systems. Comparison of the 3-21G results and the effective bond angles with the literature X-ray structures and electron-density-deformation analyses for benzenes annelated to three- and four-membered rings shows excellent agreement. It is concluded that when strain is imposed on a benzene the system responds by localizing its bonds in the Mills–Nixon manner. However, when small rings are annelated, the Mills–Nixon effect diminishes due to the formation of "banana bonds". Thus, special conditions must be fulfilled in order to observe the effect. Some predictions as to the geometries and electron densities of yet unstudied systems are given.



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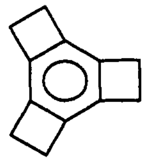

3

Introduction

The Mills–Nixon effect is a long debated issue.[1] Originally, it was suggested to explain reactivities and selectivities of benzenes annelated to small rings.[1a] However, during the years the subject evolved, and today it is known as the effect causing an aromatic moiety to localize its bonds (e.g., alternating arrangement of single and double bonds instead of the usual symmetric arrangement) due to strain imposed by small annelated ring(s) and hence to change the system's structure and reactivity. Some chemists claim that the effect is real[1c–f,i–k] whereas others suggest that it is an artifact of theoretical approximations, and higher level calculations show that the effect is not real.[1b,h,g] Experimentally, no evidence that unambiguously demonstrates the effect has been found, although it was looked for.[2]

Our interest in the issue began with the synthesis and structure determination of **1** by Diercks and Vollhardt.[3] The central ring of the molecule shows pronounced bond fixation (i.e., alternating C–C bond lengths of ca. 1.494 and 1.335 Å), whereas the outer rings are almost completely delocalized. The authors suggested that the reason for the bond localization in the central ring is the aromaticity–antiaromaticity interplay. The delocalization of the central ring would cause strong cyclobutadienic (antiaromatic) character in the four-membered rings. Thus, the authors assumed that the loss of aromaticity in one ring is energetically favorable as compared to the formation of three cyclobutadienes. On the other hand, the three four-membered rings form small angles with

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(1) (a) Mills, W. H.; Nixon, I. G. *J. Chem. Soc.* **1930**, 2510. (b) Longust-Higgins, H. L.; Coulson, C. A. *Trans. Faraday Soc.* **1946**, *42*, 756. (c) Chung, C. S.; Cooper, M. A.; Manatt, S. L. *Tetrahedron* **1971**, *27*, 701. (d) Halton, B.; Halton, M. P. *Tetrahedron* **1973**, *29*, 1717. (e) Mahanti, M. K. *Indian J. Chem.* **1980**, *19B*, 149. (f) Hiberty, P. C.; Ohanessian, G.; Delbecq, F. *J. Am. Chem. Soc.* **1985**, *107*, 3095. (g) Apeloig, Y.; Arad, D.; Halton, B.; Randell, C. J. *J. Am. Chem. Soc.* **1986**, *108*, 4932. (h) Apeloig, Y.; Arad, D. *J. Am. Chem. Soc.* **1986**, *108*, 3241. (i) Dewar, M. J. S.; Holloway, U. K. *J. Chem. Soc., Chem. Commun.* **1984**, 1188. This paper presents MNDO calculations of tricyclopropabenzene (**6**) and finds a strong Mills–Nixon effect. However, MNDO tends to overemphesize bond fixation, as is evident from our calculations of **2** and **3** (unpublished). See also ref 1h. (j) Eckert-Maksič, M.; HodoščCek, M.; Kovaček, D.; Mitič, D.; Maksič, Z. B.; Poljanec, K. *J. Mol. Struct.* **1990**, *206*, 89 and references therein. (k) Maksič, Z. B. Manuscripts in preparation.

(2) For example: Mitchell, R. H.; Slowey, P. D.; Kamada, T.; Williams, R. V.; Garratt, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 2431 and ref 4 therein.

(3) Diercks, R.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 3150.

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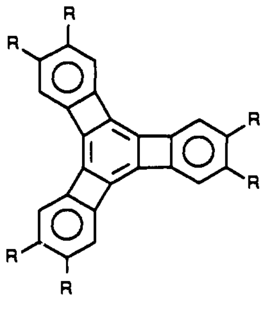


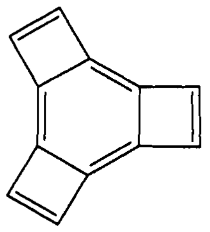
1 a: R=H; b: R=TMS

the central benzene ring (ca. 88.3°),[3] so that it is possible that the Mills–Nixon effect is responsible for the observed bond localization.

About six years ago, Shaik and his collaborators reopened the question of the essence of aromaticity,[4] and the issue has been debated since.[5] They claimed that the D_{6h} symmetry of benzene is a result of the σ skeleton preference, whereas the π frame is more stable as a cyclohexatriene. Following their arguments, one cannot rationalize the structure of **1** by aromaticity–antiaromaticity arguments. In light of the Shaik's understanding of aromaticity and of our earlier results concerning this issue,[5c] we decided to study the relative importance of aromatic vs Mills–Nixon effects in the determination of the geometry of strained benzenoid molecules.

Results and Discussion

First, it was attempted to distinguish between aromaticity and strain effects in **1**. Thus, **2** was chosen as a model for the actual molecule, which is too large for reasonable level calculations. In fact, **2** should enhance the two possible effects as compared to **1** because the four-membered rings do not share their π electrons with other benzene rings (as in **1**), and thus, the aromaticity–antiaromaticity effect should be more pronounced in the model. On the other hand, since in **2** the angles of the annelated four-membered rings are smaller than those in **1**, the strain will also be more pronounced. Figure 1 shows the main geometrical parameters and the total electronic population (Mulliken analysis) between adjacent atoms (D_{3h} symmetry assumed). The bonds exocyclic to the annelated small rings are short (1.309 Å), and the endocyclic bonds are long (1.523 Å). The bonds' populations are in accordance with the geometrical parameters. Thus, the long C–C endocyclic bond is populated by 0.2665 electrons (comparable to the single cyclobutenoic bond with 0.2817 electrons) whereas the short exocyclic bond is populated by 0.5684 electrons, comparable to the cyclobutenoic double bond with 0.6511 electrons. It is thus clear that **2** serves as a good model for **1**.



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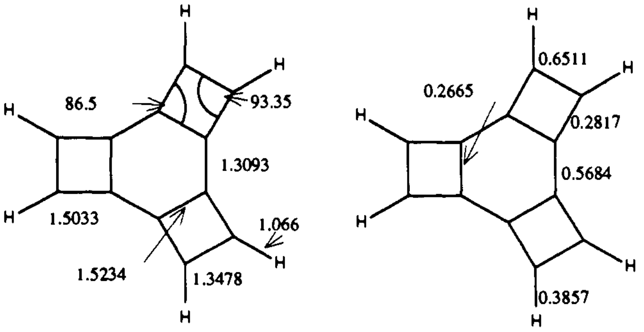
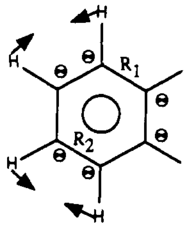


Figure 1. 3-21G geometries and bond populations of **2**.

Table I. 3-21G Geometries and Bond Populations of Bent Benzenes



Θ, deg	R_1, Å	R_2, Å	R_1 pop, e	R_2 pop, e
120.0	1.3845	1.3845	0.4715	0.4715
110.0	1.3656	1.4108	0.4839	0.4554
100.0	1.3456	1.4588	0.5018	0.4294
90.0	1.3188	1.5615	0.5554	0.3803

Table II. Geometrical Parameters of "90° Benzene" at Various Theoretical Levels

theoretical level	R_1, Å	R_2, Å
MP2/3-21G	1.3463	1.5790
HF/6-31G*	1.3288	1.5290

Table III. Hybridization of the Carbons in the Bent Benzenes (NBO) and Bond Length Differences

Θ, deg	sp^n(R_1)	sp^n(R_2)	ΔR, Å
120.0	1.88	1.88	0.0
110.0	1.72	2.06	0.0452
100.0	1.56	2.35	0.1132
90.0	1.37	3.00	0.2427

The next step was to eliminate one of the possible influencing factors, i.e., either strain or π electrons, in order to study the influence of only one of them. Thus, to study the influence of pure strain, a system that does not contain outer π electrons was investigated. This was done by optimizing the structure of benzene while bending the hydrogens in such a way as if to form small rings (i.e., the only constrains were the bending angle (Θ) (see Table I) and the D_{3h} symmetry). The basis set for the hydrogens was kept relatively small (i.e., only s orbitals) in order to minimize electronic flexibility, so that the system will respond to "pure" strain. Table I shows the results.

According to these results, it is clear that strain alone is sufficient to cause bond fixation in benzene. In addition, one can see that the process is "well-behaved"; i.e., the electronic population decreases as the bond length increases and vise versa.

In order to verify that these results are not artifacts of an insufficient theoretical level, the structure of the "90° benzene" was optimized with inclusion of electron correlation (at MP2 level) and with a larger polarized basis set. The results are given in Table II.

As expected, the absolute values of the geometrical parameters are changed at different theoretical levels, but the "90° benzene"

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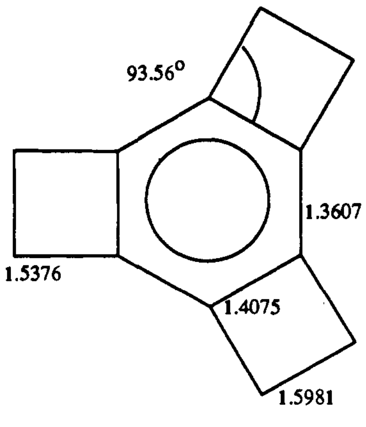
(4) (a) Shaik, S. S.; Hiberty, P. C.; Ohanessian, G.; Lefour, J.-M. *J. Phys. Chem.* **1988**, *92*, 5068. (b) Shaik, S. S.; Hiberty, P. C.; Ohanessian, G.; Lefour, J.-M. *J. Am. Chem. Soc.* **1987**, *109*, 363. (c) Shaik, S. S.; Hiberty, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 3089. (d) Hiberty, P. C.; Shaik, S. S.; Lefour, J.-M.; Ohanessian, G. *J. Org. Chem.* **1985**, *50*, 4657. (e) Shaik, S. S.; Bar, R. *Nouv. J. Chim.* **1984**, *8*, 411. (f) Shaik, S. S.; Hiberty, P. C.; Ohanessian, G. Lefour, J.-M. *Ibid.* **1985**, *9*, 385.

(5) For opposing views, see for example: (a) Baird, N. C. *J. Org. Chem.* **1986**, *51*, 3907. (b) Weinhold, F.; Glendening, E. D. "How Important is Resonance in Organic Chemistry?". We are thankful to Professor Weinhold for making the manuscript available to us prior to publication. For papers agreeing with Shaik's views, see: (c) Stanger, A.; Vollhardt, K. P. C. *J. Org. Chem.* **1988**, *53*, 4879 and references therein.



(a) Bond lengths in Å.

Figure 2. 3-21G geometry of 3. Bond lengths in Å.

is bond-fixed even at high calculational levels. Note also that inclusion of electron correlation does not change much the difference between the long and the short bonds (0.243 Å in 3-21G vs 0.233 Å in MP2/3-21G) whereas a more flexible basis set somewhat decreases this difference (0.200 Å in 6-31G*).

Forcing the C–C–H angle (Θ) to values other than 120° changes the hybridization[6] of the carbons, and natural bond orbital (NBO)[7] analysis (Table III) shows this effect.

As expected, the bonds lengthen as the p character in the hybridization increases and vice versa. A semiquantitative correlation between the bending angle and the localization of the bent benzene's bonds is described in the following paragraph.

The overlap between the two hybrids should decrease as the bond lengths increase. Since these depend on the relative amount of p character in the hybrid and because of the D_{3h} symmetry of the molecules, the hybridization of the carbons in a bond are identical, there should be a correlation between Δp^n and ΔR. Indeed, a linear correlation (slope = 0.14987; intercept = -3.14×10^{-3}; correlation coefficient = 0.999652) is found for ΔR as a function of $n_{\text{long}} - n_{\text{short}}$, where n is the amount of p in the hybridization.[8]

Table III suggests that the bending angle is correlated to a change in the hybridization, and this change correlates to ΔR. Thus, a quantitative correlation between the deviation from the natural bond angle (α, where $\alpha = 120° - \Theta$) and ΔR should exist. It was found that eq 1 describes this correlation, with a correlation

$$\Delta R = A \sin^2 \alpha + B \qquad (1)$$

coefficient of 0.9976 and $A = 0.94140$ and $B = 6.81 \times 10^{-3}$. Thus, imposing strain on benzene in the fashion described (i.e., on the σ frame, orthogonally to the π orbitals) results in fixation of the benzene's bonds.

These results suggest that all strained aromatic systems should show bond fixation. As a test case, the structure of tricyclobutabenzene (3) was calculated. Surprisingly, the optimized structure is almost totally symmetric (Figure 2). Although the angles of the annelated small rings with the benzene are still small (93.6°), the difference between the short and the long bonds is only 0.047 Å (i.e., less than in the 100° benzene). How could the absence of the Mills–Nixon effect in 3 be understood in light of the above results?

Table IV. ΔR and Θ from 3-21G and from Equation 1 for **2** and **3**[a]

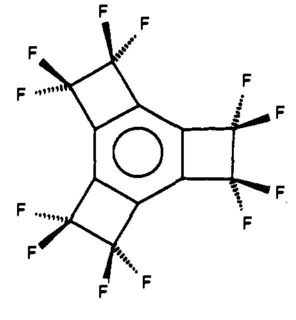
	ΔR		Θ	
	3-21G	eq 1	3-21G	eq 1
2	0.2141	0.2883	86.85	92.01
3	0.0468	0.1934	93.56	108.11

[a] ΔR in Å, Θ in degrees.

Equation 1 describes the effect of pure strain on the geometry of a benzene.[9] However, when more flexibility is allowed (see for example Table II, 6-31G* results), the system compensates the strain in some way. Since carbons are more flexible than hydrogens (because they have more valence orbitals and more basis functions within the same basis set), the flexibility of the system (i.e., 2 and 3 as compared to the bent benzene) increases. What would the geometry of 2 and 3 be if the effect of the four-membered rings would have been pure strain? The use of eq 1 gives the answer. Table IV shows ΔR's calculated by eq 1 when the 3-21G Θ's are used and the Θ's calculated by eq 1 when 3-21G ΔR's are used.

The comparison clarifies the picture. If the 3-21G Θ's are used in eq 1, the ΔR's calculated are 0.074 and 0.147 Å larger than the respective 3-21G values for 2 and 3. A different way to look at it is to use the 3-21G values of ΔR in eq 1 for the calculation of the "effective Θ's", which are found to be 5.2 and 14.6° larger than the 3-21G values for 2 and 3, respectively. Thus, it is clear that when flexibility is allowed the system introduces an additional factor that compensates for some of the strain and therefore decreases the bond alternation in these molecules. Please also note that although 2 has the aromatic–antiaromatic factor in addition to strain, it alternates less than what could be expected from the benzene model (which has no π electrons that could bring in antiaromatic effects) and that the effect of substituting the hydrogens by carbons is smaller for sp^2 than for sp^3 carbons. In light of these results, we suggest that *the higher flexibility of the carbons* (*as compared to hydrogens*) *manifests itself by forming "banana bonds"*. Thus, although Θ is expected to be ca. 87 and 93.5° for 2 and 3, respectively, the maximum electron-density path should form respective bond angles of 92 and 108°.

How do these conclusions compare to available experimental data? The X-ray structure of **1b**[3] shows that Θ is ca. 88.3°,[10] but no electron-density-deformation study was carried out as yet. Another related experimental result is the structure of **3a**, which was published in two different papers. Thummel et al.[11a] found



3a

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(6) The concept of rehybridization was introduced to explain the reactivity of strained aromatic compounds. Streitwieser, A.; Zigler, G. R.; Mowery, P. C.; Lewis, A.; Lawler, R. G. *J. Am. Chem. Soc.* **1968**, *90*, 1357. However, the authors do not conclude bond fixation (i.e., Mills–Nixon effect) as a result of the rehybridization.

(7) Reed, A. E.; Curtis, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(8) Each bond length (R_1 and R_2) shows a good correlation to n. For R_1: intercept = 1.14353, slope = 0.12869, correlation coefficient = 0.999103. For R_2: intercept = 1.08505, slope = 0.15881, correlation coefficient = 0.999917.

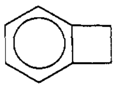
(9) (a) A reviewer suggested that the C–H bonds in the strained benzene model should also be curved, and I agree that this might indeed be the case. However, due to the smaller flexibility of the hydrogens (see text) within the basis set limitations, the curvature of C–H bonds must be much smaller than the curvature of C–C bonds. Thus, even if the C–H bonds in the bent benzene are somewhat curved, they are taken as a reference for the "pure" strain in this study, and the other systems (which are more flexible) are compared to this model. (b) This study uses the basis set limitations (inflexibility) in order to study pure strain. We do not suggest that real systems behave accordingly. However, due to the nature of the model, we are able to separate the strain from the other factors.

(10) Due to crystal packing forces, the structure of **1b** is not completely planar (see ref 5). Thus, the measured Θ's are 88.10–88.69°.

(11) (a) Thummel, R. P.; Korp, J. D.; Bernal, I.; Harlow, R. L.; Soulen, R. L. *J. Am. Chem. Soc.* **1977**, *99*, 6916. (b) Cobbledick, R. E.; Einstein, F. W. B. *Acta Crystallogr.* **1976**, *B32*, 1908.

that ΔR and Θ are 0.006 Å and 93.9°, respectively, whereas Cobbledick and Einstein[11b] suggested essentially the same respective values of 0.008 Å and 93.8°. However, the comparison between **3** and its perfluorinated analogue **3a** might be misleading because of the special effect fluorine has on small rings.[12]

To the best of our knowledge, the only directly related compounds that have had their structure and electron-density deformations studied are cyclobutabenzene (**4**) and 1,2:4,5-dicyclobutabenzene (**5**).[13] The agreement between the calculated and the experimental parameters is remarkable. Thus, the measured Θ for **4** and **5** is 93.5 and 93.4° whereas the maximum electron-density paths form angles of 106 and 107°, respectively. Please note that the respective Θ values for **3** (i.e., $\Theta_{3\text{-}21G}$ vs Θ_{eql}) are 93.6 and 108.1°!!!



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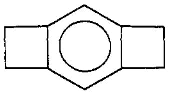

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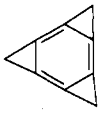
Other strained systems that can be used for comparison (although indirect) are cyclopropabenzenes. Apeloig, Karni, and Arad[14] have calculated the 3-21G structures of **6** and **7**. The calculated Θ's for the fused three-membered rings are 62.9 and 63.9° for **6** and **7**, respectively, and ΔR for **6** is 0.043 Å. The use of the last value in eq 1 yields an effective Θ of 108.7°. Tricyclopropabenzene (**6**) is yet unknown, but the X-ray structure and the electron density deformation of **7** were measured.[15] Θ was found to be 63.4°, whereas the maximum-density path forms an angle of ca. 109–110°. Considering the differences between **6** and **7**, the agreement between the theoretical analysis presented and the experimental results is also very good.



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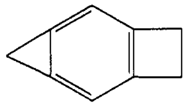

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Conclusions and Predictions

The answer to the title question is not simple. The Mills–Nixon effect is real in the sense that strain imposed on benzene in the way described causes localization of the bonds. However, when there are "real" (i.e., nonhydrogen) atoms at the strained positions, the systems compensate the imposed strain by forming "banana" bonds, and thus cyclobuta- and cyclopropabenzenes will not show the effect. In order to observe bond fixation in benzene, one has to build a system with a small Θ (<90°) so that the "effective" Θ (i.e., Θ calculated by eq 1) will remain less than 100°. This could be achieved by using sp^2 carbons at the strained positions. These, however, might participate in the π conjugation, and thus aromaticity effects could not be ruled out (as in **1**). Therefore, one needs an experimental system that has sp^2 carbons at strained conjugated positions that do not participate in the π conjugation. Systems like this can be prepared by using strained aromatic moieties as ligands on transition metals. It has been shown that the complexation of transition-metal fragments to a π system changes the properties of the noncomplexed conjugated aromatic part.[16] The change depends on the complexed metal fragment, and thus, by the choice of the appropriate metallic moiety (for example, η^6-Cr(CO)$_3$ vs η^4- or η^2-PtL$_2$), the effect of complexation should reverse. One metallic moiety type will eliminate the conjugation of the π electrons whereas the other type will force a nearly complete double bond, localized at a position conjugated to the aromatic ring. The comparison between these two types of complexes will allow an experimental answer as to the importance of the Mills–Nixon effect in controlling the structures of strained aromatic compounds. We are currently pursuing this approach.[17]

Two direct predictions are given here. The first concerns **1**. Its measured ΔR is 0.159 Å^3. Using this value in eq 1 predicts that the maximum electron density (the effective Θ) will form an angle of ca. 96° between the central and the annelated four-membered ring when the electron-density-deformation study is carried out.

The second prediction concerns **3**. It has been shown that 3-21G describes very well the geometry of strained aromatic compounds.[18] Thus it is predicted that both the structure and the electron-density deformation of **3** will follow the picture given here: i.e., the difference between the long and the short bonds is expected to be ca. 0.05 Å; the bond angle between the four-membered ring and benzene will be ca. 93–94°; and the maximum electron-density path will form the respective angle of ca. 108°. We are currently working on this point.[19]

Acknowledgment. Some of the calculations were carried out at the research group of Professor K. P. C. Vollhardt to whom I am grateful. I also thank Professors S. S. Shaik and Y. Apeloig for helpful discussions. The research was partly supported by the Israeli Absorption Office, by the E. & J. Bishop fund through the Technion Vice President for Research fund, and by the DOE in the USA.

Registry No. **2**, 69038-28-4; **3**, 60323-52-6; benzene, 71-43-2.

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(12) Fluorine has a large effect on the properties of small rings. Two representative examples are given. (a) Bis(trialkylphosphine)-nickel(COD) reacts with cyclopropabenzene to give the insertion or the dimerization products, depending on the phosphine (Mynott, R.; Neidlein, R.; Schwager, H.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 367. Neidlein, R.; Rufiñska, A.; Schwager, H.; Wilke, G. Ibid. 640). However, when 7,7-difluorocyclopropabenzene is used instead of cyclopropabenzene, the three-membered ring does not open up and only the propellane-type addition product is obtained (Schwager, H.; Krüger, C.; Neidlein, R.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 65). (b) For a theoretical investigation on the effect of fluorine as a cyclopropane substituent, see: Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3811 and references therein. (c) For a comprehensive review and data regarding the fluorine effect, see: Smart, B. E. *Mol. Struct. Energ.* **1986**, *3*, 141. (d) Even the authors of the paper presenting the structure of **3a** (ref 10a) are not sure that the comparison between **3** and **3a** is valid because of the same reason.

(13) Boese, R.; Bläser, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 304.

(14) Apeloig, Y.; Karni, M.; Arad, D. In *Strain and Its Implications in Organic Chemistry*; de Meijere, A., Blechert, S.; Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989; pp 457–462.

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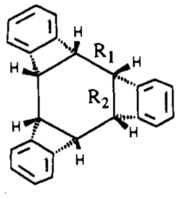
(16) For example: (a) Rogers, R. D.; Atwood, J. L.; Albright, T. A.; Lee, W. A.; Rausch, M. D. *Organometallics* **1984**, *3*, 263. (b) Mitchell, R. H.; Zhou, P.; Venugopalan, S.; Dingle, T. W. *J. Am. Chem. Soc.* **1990**, *112*, 7812. (c) Mitchell, R. H.; Venugopalan, S.; Zhou, P.; Dingle, T. W. *Tetrahedron Lett.* **1990**, *31*, 5281.

(17) (a) While this paper was in the reviewers' hands, a paper discussing **8** appeared. See: Mohler, D. L.; Vollhardt, K. P. C.; Wolff, S. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1151. The X-ray structure of the molecule reveals that the central ring's bonds are alternating in the same manner as in **1**, although the ring has no π electrons. Thus, R_1 = 1.511 Å and R_2 = 1.599 Å. Note that R_2 in **8** is even longer than the respective bond in cyclobutabenzene (1.576 Å)[12] and that ΔR for this molecule (with the saturated ring) is smaller than the respective ΔR for **1** (with the benzenoid ring). (b) See also ref 5c.



8

(18) For example: (a) Cyclopropabenzene: Experimental structure determination by Neidlein et al. (Neidlein, R.; Christen, D.; Poignée, V.; Boese, R.; Bläser, D.; Gieren, A.; Ruiz-Pérez, C.; Hübner, T. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 294) and 3-21G geometry calculated by Apeloig and Arad, ref 1h. (b) **7**: Experimental structure determination by Bläser et al.[14] and 3-21G geometry calculated by Apeloig et al.[13]

(19) For the preparation of **3**, see: (a) Nutakul, W.; Thummel, R. P.; Taggart, A. D. *J. Am. Chem. Soc.* **1979**, *101*, 770. (b) Heilbronner, E.; Kovač, B.; Nutakul, W.; Taggart, A. D.; Thummel, R. P. *J. Org. Chem.* **1981**, *46*, 5279. (c) Doecke, C. W.; Garrat, P. J.; Shahriari-Zavareh, H.; Zahler, R. *J. Org. Chem.* **1984**, *49*, 1412. The syntheses of the compound give extremely low yields and require many optimizations of conditions. We are currently developing a single-step process for the synthesis of this compound.