structure is close to the experimental value (1.399 Å[4]) for benzene, and that for the longer bonds in the alternating structure is close to that found for the long CC bonds in butadiene (1.463 Å[4]) and hexatriene (1.458 Å[4]). We note in passing that a purely single $C(sp^2)–C(sp^2)$ bond, i.e., one across which no conjugation occurs, is longer still—about 1.512 Å.[5]

The value of 1.34 Å chosen by Hiberty and co-workers for the shorter bond in the alternating structure is similar to the experimental distance for the purely double bond in ethylene (1.337 Å[4]) and to the terminal double bonds in butadiene (1.344 Å[4]) and 1,3,5-hexatriene (1.337 Å[4]). However, all the "double" bonds in the asymmetrically distorted "Kekulé" structure for benzene are conjugated from *both* sides rather than from none or one. Thus the appropriate choice for the shorter distances in the Kekulé structure is the average length for *internal* C=C bonds in conjugated polyenes. MO calculations generally predict that such linkages are longer than are terminal double bonds.[5] The only experimental value available is that of 1.368 Å for the 3,4-bond in 1,3,5-hexatriene.[4]

Although an increase from 1.340 to 1.368 Å makes little difference to the total energy of a C=C unit (since $dE_{total}/dR \approx 0$ near the equilibrium distance R), this is *not* true for the σ and π *components* of the energy. Since the C=C length is displaced substantially from the optimum value of about 1.512 Å[5] for the σ component, E_σ varies rapidly with R in the 1.34–1.368-Å region. According to a Morse function potential with parameters established by Dewar and deLlano,[5] the energy of the σ component of each CC bond is 5.2 kcal mol^{-1} worse at the shorter distance of 1.340 Å than when it is stretched by 0.028 Å. Indeed, if E_σ for the symmetric and asymmetric structures are computed by Dewar and deLlano's Morse potential,[5] the symmetric structure is indeed found to be preferred, by 14.5 kcal mol^{-1}, if $R_{C=C}$ = 1.34 Å, whereas the asymmetric (alternating) Kekulé structure is preferred, by 1.1 kcal mol^{-1}, for $R_{C=C}$ = 1.368 Å. Use of other $R_{C=C}$ values in the range of the latter, i.e., from 1.36 to 1.38 Å, similarly all yield $\Delta E_\sigma \approx 0$ between the two structures. (The estimate of 14.5 kcal mol^{-1} for the structure with $R_{C=C}$ = 1.34 Å agrees well with that of about 17 kcal mol^{-1} obtained in ab initio calculations by Hiberty and co-workers, particularly since their calculations did not include electron correlation effects for the σ bond framework.) For the allyl radical, use of their bond lengths and the Morse function yields ΔE_σ = +4.8 kcal mol^{-1}, in good agreement with their ab initio values of 5.68 (STO-3G basis set) and 4.80 kcal mol^{-1} (6-311G basis set). If $R_{C=C}$ is stretched to the more appropriate value, ΔE_σ = –0.4 kcal mol^{-1}.

Since $\Delta E_{total} > 0$ but $\Delta E_\sigma \approx 0$ for the asymmetric distortion in both benzene and allyl, it follows that $\Delta E_\pi > 0$, i.e., that the π electron energy for the symmetric form is lower than that for the asymmetric; thus the traditional view, that E_π is the driving force for equalization of CC bond lengths, is recovered intact!

The magnitude of ΔE_{total} and thus also of ΔE_π is rather small compared to most estimates of the "resonance" energies of benzene and allyl. However it must be realized that most of the extraordinary conjugation of the double bonds in benzene occurs even if the bond *lengths* are artificially distorted and alternated. The aromaticity and delocalization of π electrons in benzene is only slightly damped, rather than destroyed completely, when it is forced to adopt bond lengths appropriate to polyenes. Ab initio estimates of ΔE_σ, ΔE_π, and ΔE_{total}, obtained by using the method of Hiberty and co-workers, would be of great interest here.

Hiberty and co-workers support their case with the statement that "... even at the Hückel level (with variable β) it can be shown that an hexagonal π-system prefers to distort to a localized structure".[2] I should like to point out that this conclusion follows *only* if the increase in the resonance integral β upon contraction to double bond length equals or exceeds the decrease in β assumed when the other three bonds are lengthened to the single bond distance. However, as discussed out above, bond elongation exceeds bond contraction (due to the character of the σ bond energy function); for the bond distances recommended herein, β decreases more for the single bonds than it increases for the double, and consequently the symmetrical structure is *preferred* even at the Hückel level.

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[4] See the summary in: Kao, J.; Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 975.

[5] Dewar, M. J. S.; deLlano, C. *J. Am. Chem. Soc.* **1969**, *91*, 789.

[6] The use of bond parameters appropriate to conjugated but nonaromatic systems was pioneered by Dewar, who employed C=C and C–C bond energies appropriate to long polyenes, which therefore refer to internal bonds, in his definition of resonance energy. See ref 5.

[7] **Added Note:** It is gratifying to see, in the last paragraph of the accompanying reply by Hiberty et al. that the role of π electron delocalization in promoting aromaticity now is emphasized—viz., their statement that ".... [the] π tendency for bond alternation .... is weaker in aromatic systems than it is in open chains ....". With regard to their point that the π energy of the symmetric, 1.40-Å structure of a benzene molecule is unstable with respect to an asymmetric distortion, it is worth noting that the π system presumably also is unstable with respect to a symmetric distortion which contracts all CC lengths (since the optimum CC distance for purely π bonds is very short). It would be interesting to investigate the asymmetric distortion properties of benzene at CC distances that are optimum for the π energy, since one can argue that such a reference structure is the appropriate one for these comparisons.

The π-Distortive Propensities in Benzene and the Allyl Radical. A Reply to a Criticism

Summary: The criticism in the preceding paper is answered. To prove instability of a structure toward a localizing distortion mode it is sufficient to identify one such distortion mode that lowers the energy of the delocalized structure. Aromaticity and π-distortive propensity in C_6H_6 are unrelated properties that coexist in harmony and must be explored by different means.

Sir: In recent papers[1] we have used an avoided - crossing model to predict that the symmetric π-components of benzene and the allyl radical are unstable toward localizing distortions. The predictions were verified by ab initio techniques,[2] and it was shown that the symmetric structures of benzene and allyl are imposed by their σ-frames which oppose the π-propensities. These conclusions are criticized by Baird[3] who argues that if one uses "realistic"

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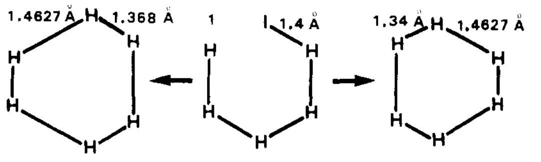
[1] (a) Shaik, S. S.; Bar, R. *Nouv. J. Chim.* **1984**, *8*, 411. (b) Shaik, S. S.; Hiberty, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 3089. (c) See also similar theoretical predictions in: Epiotis, N. D. *Nouv. J. Chim.* **1984**, *8*, 11; *Pure Appl. Chem.* **1983**, *55*, 229.

[2] (a) Hiberty, P. C.; Shaik, S. S.; Lefour, J.-M.; Ohanessian, G. *J. Org. Chem.* **1985**, *50*, 4657. (b) Shaik, S. S.; Hiberty, P. C.; Ohanessian, G.; Lefour, J.-M. *Nouv. J. Chim.* **1985**, *9*, 385. (c) Borden presented (Borden, W. T. Presented at the 185th National Meeting of the American Chemical Society Seattle, WA, March 1983; paper PHYS 57) 3-21G/MCSCF results, on the allyl radical, that are in qualitative agreement with those in ref 2b.

bond lengths for the localized structures, then the traditional views on benzene and allyl radical can be recovered intact. The present paper is a reply to Baird's criticism.

The key argument in ref 3 is as follows. If instead of the asymmetric localizing distortion in our study[2] ($\Delta r \simeq \pm 0.06$ Å), one employs a more "appropriate" distortion, then the π-energy of benzene and the allyl radical can be shown to *increase* upon distortion. This, according to ref 3, recovers the status of the π-component as the driving force for the symmetric structures of benzene and the allyl radical.

It is entirely true that one can take an *unstable* structure and show that it is stable toward some distortion. But to use this result as evidence for the stability of the structure would be incorrect. This can be illustrated by a simple thought experiment. Let us use, as an example, the symmetric hexagonal H_6 (**1a**) that is isoelectronic and isostructural with the π-component of benzene. This H_6 species is extremely unstable (~120 kcal/mol) relative to its localized constituents (3 H_2).[1b] We are starting then with the a priori knowledge that the delocalized structure **1a** possesses a distortive propensity.



E_{rel} = 3.9 kcal/mol E_{rel} = 0.0 E_{rel} = −6.5 kcal/mol

1c **1a** **1b**

Applying, on **1a**, the localizing distortion used in our study[2a] generates **1b** and results in a ~6.5 kcal/mol energy lowering, at the STO-3G level. This result confirms the a priori knowledge that the delocalized structure **1a** is unstable toward a localizing distortion. On the other hand, the distortion recommended in ref 3 (**1a** → **1c**) raises the energy by ~3.9 kcal/mol and, thus, belies the above a priori knowledge. The point is clear then: it is sufficient to find *one* localizing distortion mode that lowers the energy of the delocalized structure, in order to *prove* that the structure is *unstable* toward localization and structural relaxation. The findings in our study[2] constitute then a positive proof that the π-components of benzene and the allyl radical prefer to distort to their localized constituents.

The key question is: how does one identify the crucial distortion mode with which to probe the instability of a given delocalized structure? According to the avoided-crossing model[1] the symmetric π-components of benzene and allyl radical may be viewed as "transition states" for the interconversion of two localized π-Kekulé structures (devoid of σ-bonds) in their equilibrium geometries.[4] Such a transition structure possesses only *one* asymmetric distortion along which the energy of the structure is lowered. This distortion is the reaction coordinate mode which is always antisymmetric[5] and electronically localizing.

The distortions that we used[2] to explore the π-distortive propensities in allyl and benzene are practically these unique reaction coordinate modes. All other distortion modes are not pertinent to the question because they are either perpendicular[5] to the reaction coordinate or contain a perpendicular component. If the latter is large, such modes will necessarily raise the energy and thereby belie the unstable nature of the investigated structure (e.g., **1a** → **1c**). The distortion recommended in ref 3 involves such a large perpendicular component[6] and therefore fails to predict the distortive propensity of H_6 in **1a**. For the same reason,[6] this distortion fails to predict the distortive propensities of the π-components of benzene.[2]

The similarity between H_6 and benzene has already been noted, at the semiempirical level, as we indicated earlier,[2a] by Salem and Longuet-Higgins[7] using Hückel theory with variable β. We may add that it is also true at the more reliable PPP level of theory, and Paldus[8] has noted that "clearly, at least at the semi-empirical hamiltonian level, the behavior of the π-electron part of cyclic polyenes will parallel that of the H_n systems. However, for the polyenic systems, the σ-energy will oppose the tendency of the π-electrons to dissipate."

It should lastly be noted that our results do not refute the concepts of aromaticity and allylic stability. In fact, it is possible to show that the special thermochemical stability of benzene, as well as allyl's barrier to rotation, exists *despite* the instability of their π-components toward a localizing distortion, and this will be done in detail in a forthcoming paper.[9] In brief, there exists, in both aromatic and open chain systems, a tendency of the σ-frame for bond equalization and a π-tendency for bond alternation. But the latter tendency is weaker in aromatic systems than it is in open chains, because the regular geometry favors the stabilizing mixture of Kekulé structures. As a consequence, the σ-frame, which is forced to have an alternated geometry in open chains, may relax itself in aromatic systems and equalize its bond lengths. So, the π-component of an aromatic molecule is indeed stabilized by aromaticity but not enough to make it stable, in itself, with respect to a localizing distortion. Thus, the thermochemical stabilities of benzene and allyl coexist in harmony with the π-distortive propensities. Different experimental criteria are required to probe these two different aspects of benzene and allyl radical. The spectroscopic data (vibrational spectra) that were used by Berry[10] to deduce the π-distortive propensity of benzene can serve as a starting point and a guide for experimental quantification of this distortive propensity.

Registry No. Benzene, 71-43-2; allyl radical, 1981-80-2.

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(3) Baird, N.C. *J. Org. Chem.*; preceding paper in this issue.

(4) It is important to note that the equilibrium bond length of a π_{CC} bond (devoid of a σ-bond) would be shorter than 1.34 Å (the equilibrium bond length of ethylene). For example, the σ_{LiLi} bond length is 2.7 Å while that for a π_{LiLi} bond is 2.2 Å.

(5) Totally symmetric distortions are always perpendicular to the reaction coordinate mode.

(6) The reaction coordinate mode for hexagonal structures has a B_{2u} symmetry. Such a distortion corresponds to compression of one bond and stretching of the other by an equal amount. The distortion in ref 3 involves shortening by ~0.03 Å and lengthening by ~0.06 Å. This distortion is approximately half B_{2u} and half A_{1g} (totally symmetric breathing mode). Thus the distortion involves ~50% of a perpendicular component.

(7) (a) Longuet-Higgins, H. C.; Salem, L. *Proc. R. Soc. London, A*, **1959**, *251*, 172. (b) Salem, L. *The Molecular Orbital Theory of Conjugated Systems*; W. A. Benjamin: Reading, MA, 1972; pp 103–106, 494–505.

(8) Paldus, J.; Chin, E. *Int. J. Quantum Chem.* **1983**, *24*, 373.

(9) Shaik, S. S.; Hiberty, P. C.; Ohanessian, G.; Lefour, J.-M., submitted for publication.

(10) Berry, R. S. *J. Chem. Phys.* **1961**, *35*, 29, 2253.

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