ion-pairing by a mass-action effect and thus also to decrease $E_1 - E_2$. We explored this point further by measuring the DC polarogram of anthraquinone in T3–TBATFB. This substrate is more sensitive to ion-pairing effects than are hydrocarbons, because of the higher electronegativity of oxygen over carbon and the consequent higher charge carried by the two oxygen atoms in the dianion.[1] The spacing between the first and second polarographic waves was found to be 0.48 V, which may be compared with a spacing of 0.65 V for anthraquinone in DMF containing 0.1 M tetrabutylammonium iodide (TBAI).[1] The difference between the two solvents, while real, is relatively small.

The only point at which ordinary electrochemical experimentation in T3–TBATFB was found to produce results significantly different from those in DMF was in the effects of added proton donors upon the voltammetry of PAH's in the respective solvents. Addition of increasing amounts of proton donors to such solutions is known to produce a gradual increase in the height of the first wave, with corresponding decrease in the height of the second wave, until at high proton donor concentration the first wave has doubled in height and the second has disappeared.[1-3] This behavior is caused by protonation of the radical anion **2** to afford neutral radical **4**, whose reduction potential is well negative of E_1, so that **4** is reduced as soon as it is formed. In the case of 9,10-diphenylanthracene in DMF with phenol as proton donor, a phenol:hydrocarbon ratio of ca. 20:1 is required (for 1 mM hydrocarbon) to effect a 50% increase in the height of the first wave and a ratio of between 50 and 200:1 to double the height of this wave.[12] In T3–TBATFB, however, 1:1 and 10:1 phenol:hydrocarbon ratios, respectively, sufficed to create the same effects upon wave height. Thus phenol appears to be a noticeably better proton donor in T3–TBATFB than it is in DMF. We presume that this is because DMF is the better hydrogen-bond acceptor and that therefore phenol, being hydrogen-bonded to DMF, is not as good a proton donor in this solvent. It is already well-known that water is a very poor proton donor in DMF and Me_2SO, to which it is very tightly hydrogen-bonded, and that it is a much better proton donor in acetonitrile, a poorer hydrogen-bond acceptor.[13]

Finally, we note that the reduction potentials of unsaturated hydrocarbons are very similar in DMF and THF,[14] in contrast to reported[15] results for alkyl halides, sulfonates, and unsaturated carbonyl compounds.

Experimental Section

Toluene was distilled from sodium immediately before use. Tetrabutylammonium tetrafluoroborate was prepared by the metathetic reaction between tetrabutylammonium iodide and tetrafluoroboric acid.[16] (Toluene)$_3$–tetrabutylammonium tetrafluoroborate was prepared by stirring the salt with an excess of toluene.[6] It was found necessary to keep solutions of the "hydrocarbon electrolyte" covered with a thin layer of toluene during voltammetry in order to prevent slow evaporation of solvent and consequent precipitation of the toluene-free salt. Cyclic voltammetry and polarography were carried out in a Brinkmann cell, Model EA874/875-20. The reference electrode consisted of a silver wire immersed in a 0.1 M solution of silver nitrate in acetonitrile, contained in a length of heavy-walled Teflon-brand tubing sealed at one end with a short length in porous Vycor. The potential of this electrode is +0.35 V vs. SCE.

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Registry No. T3, 429-42-5; TBATFB, 108-88-3; pyrene, 129-00-0; perylene, 198-55-0; 9,10-diphenylanthracene, 1499-10-1; anthraquinone, 84-65-1; phenol, 108-95-2.

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[12] Santhanam, K. S. V.; Bard, A. J. *J. Am. Chem. Soc.* **1966**, *88*, 2669.

[13] Jezorek, J. R.; Mark, H. B., Jr. *J. Phys. Chem.* **1970**, *74*, 1627.

[14] Table I and A. J. Fry, unpublished observations.

[15] Lipshutz, B. H.; Wilhelm, R. S.; Nugent, S. T.; Little, R. D.; Baizer, M. M. *J. Org. Chem.* **1983**, *48*, 3306.

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Communications

On the Driving Force for the Symmetric Structure of Benzene and the Allyl Radical: σ or π?[1]

Summary: The conclusion of Hiberty and co-workers that the symmetric structures of benzene and the allyl radical are preferred to those with alternating bonds because of the σ bond energy is shown to be critically dependent upon the choice of the C=C length in the alternating structure. Use of a more appropriate value reverses their controversial conclusions.

Sir: Recently Hiberty and co-workers have argued that the symmetric structures of benzene and the allyl radical are superior to those with alternating bonds because of the energetic preferences of the σ bonds and that in fact the π system itself prefers an asymmetric structure.[2,3] In this paper I show that their arguments rest critically on a questionable assumption concerning the bond distances for the alternating structure and that if more appropriate values are used, their conclusions are reversed and the traditional view—that the symmetrical structure is due to π electrons—is recovered.

Hiberty and co-workers compare the σ and π energies of benzene with all bond lengths chosen as 1.400 Å to a structure with bonds of alternating lengths of 1.34 and 1.4627 Å. They find that the σ energy is better in the symmetrical structure by about 17 kcal mol^{-1}, that the π energy is worse by about 11 kcal mol^{-1}, and that overall the symmetric is preferred by about 6 kcal mol^{-1}. They do not discuss the choice of bond distances assumed for their structures, but clearly that for the symmetrical

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[1] Research supported by the Natural Sciences and Engineering Research Council of Canada.

[2] Hiberty, P. C.; Shaik, S. S.; Lefour, J.-M.; Ohanessian, G. *J. Org. Chem.* **1985**, *50*, 4657.

[3] Shaik, S. S.; Hiberty, P. C.; Lefour, J.-M.; Ohanessian, G. *Nouv. J. Chim.* **1985**, *9*, 385.

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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 $\Delta E_\sigma = +4.8$ 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, $\Delta E_\sigma = -0.4$ 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.

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

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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.

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