

## The Role of Delocalization in Benzene

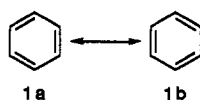
Eric D. Glendening,<sup>1,†</sup> Rüdiger Faust,<sup>1,‡</sup> Andrew Streitwieser,<sup>\*,1</sup>  
K. Peter C. Vollhardt,<sup>\*,1</sup> and Frank Weinhold<sup>\*,1</sup>*Contribution from the Department of Chemistry, University of California—Berkeley, Berkeley, California 94720, Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720, and Theoretical Chemistry Institute and Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706*

Received February 16, 1993\*

**Abstract:** The influence of  $\pi$  delocalization on the geometry of benzene is examined at the ab initio SCF level of theory. We find that benzene favors a bond alternating geometry when its canonical  $\pi$  MOs are replaced by three localized ethylenic orbitals, revealing that delocalization is in part responsible for the equilibrium symmetric structure. In apparent contrast, a  $\sigma$ - $\pi$  energy partitioning analysis suggests that the benzene  $\sigma$  framework is responsible for the symmetric structure, the  $\pi$  system preferring a distorted geometry. Shaik et al. have therefore concluded that delocalization is not an important symmetrizing force in this molecule. We show, however, that the  $\pi$  energy component contains a sizable and strongly geometry dependent contribution from the localized (Kekulé) wave function. Thus, it appears to be misleading to judge the nature of delocalization based on a  $\sigma$ - $\pi$  partition. We conclude that delocalization effects act to strongly stabilize symmetric benzene in essential accord with the concepts of classical resonance theory.

## Introduction

One of the early successes and a cornerstone of modern molecular orbital (MO) theory is its ability to predict the stabilizing effect of  $\pi$  electronic delocalization in benzene.<sup>1</sup> Although this effect is generally accepted by the chemical community, the relationship between  $\pi$  delocalization and the geometry of benzene remains an issue of some debate.<sup>2-6</sup> It has generally been argued, based on a valence bond picture,<sup>7</sup> that resonance mixing of the Kekulé structures **1a**, **1b**



leads to the symmetric (equilibrium) structure with CC bond

<sup>1</sup> University of California—Berkeley and Lawrence Berkeley Laboratory.

<sup>†</sup> University of Wisconsin—Madison.

<sup>‡</sup> Present address: Molecular Science Research Center, Pacific Northwest Laboratory, Battelle Blvd., MS K1-90, Richland, WA 99352.

<sup>\*</sup> Present address: Laboratorium für Organische Chemie, ETH-Zentrum, Universitätsstrasse 16, CH-8092 Zürich, Switzerland.

\* Abstract published in *Advance ACS Abstracts*, August 15, 1993.

(1) (a) Hückel, E. *Z. Phys.* **1931**, *70*, 204-286. (b) Hückel, E. *Grundzüge der Theorie ungesättigter und aromatischer Verbindungen*; Chemie: Berlin, 1938.

(2) (a) Shaik, S. S.; Bar, R. *Nouv. J. Chim.* **1984**, *8*, 411. (b) Shaik, S. S.; Hiberty, P. C.; Ohanessian, G.; Lefour, J.-M. *Nouv. J. Chim.* **1985**, *9*, 385. (c) Hiberty, P. C.; Shaik, S. S.; Lefour, J.-M.; Ohanessian, G. *J. Org. Chem.* **1985**, *50*, 4657. (d) Shaik, S. S.; Hiberty, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 3089. (e) Shaik, S. S.; Hiberty, P. C.; Lefour, J.-M.; Ohanessian, G. *J. Am. Chem. Soc.* **1987**, *109*, 363. (f) Shaik, S. S.; Hiberty, P. C.; Ohanessian, G.; Lefour, J.-M. *J. Phys. Chem.* **1988**, *92*, 5086. (g) Ohanessian, G.; Hiberty, P. C.; Lefour, J.-M.; Flament, J.-P.; Shaik, S. S. *Inorg. Chem.* **1988**, *27*, 2219. (h) Hiberty, P. C. In *Topics in Current Chemistry*; Gutman, I., Cyrin, S. J., Eds.; Springer: New York, 1990; Vol. 153, p 27.

(3) Jug, K.; Köster, A. M. *J. Am. Chem. Soc.* **1990**, *112*, 6772.

(4) Stanger, A.; Vollhardt, K. P. C. *J. Org. Chem.* **1988**, *53*, 4889.

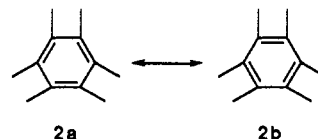
(5) Also see: (a) Longuet-Higgins, H. C.; Salem, L. *Proc. R. Soc. (London)* **1959**, *251*, 172. (b) Berry, R. S. *J. Chem. Phys.* **1961**, *35*, 29. (c) Berry, R. S. *J. Chem. Phys.* **1961**, *35*, 2253. (d) Epiotis, N. D. *Pure Appl. Chem.* **1983**, *55*, 229. (e) Epiotis, N. D. *Nouv. J. Chim.* **1984**, *8*, 11.

(6) (a) Baird, N. C. *J. Org. Chem.* **1986**, *51*, 3907. (b) Wiberg, K. B.; Nakaji, D.; Breneman, C. M. *J. Am. Chem. Soc.* **1989**, *111*, 4178. (c) Aihara, J. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1956. A rebuttal to Baird's criticism appears in: (d) Hiberty, P. C.; Shaik, S. S.; Ohanessian, G.; Lefour, J.-M. *J. Org. Chem.* **1986**, *51*, 3908.

(7) See, e.g.: (a) Wheland, G. *Resonance in Organic Chemistry*; Wiley: New York, 1955. (b) Coulson, C. A. *Valence*, 2nd ed.; Oxford: New York, 1961; p 237.

lengths ( $\sim 1.40$  Å) intermediate between those of idealized single and double bonds. Hence, the structure of benzene and the stabilizing effect of  $\pi$  delocalization appear to be directly related. Recent theoretical studies<sup>2-5</sup> have, however, challenged this view, suggesting instead that the  $\sigma$  system, rather than the  $\pi$ , is entirely responsible for the symmetric structure.

Support for this alternative viewpoint generally originates from the analysis of  $\sigma$  and  $\pi$  energy components of SCF-MO wave functions. Shaik, Hiberty, and co-workers<sup>2</sup> demonstrated that the  $\pi$  component is stabilized by distorting benzene to a bond alternating "cyclohexatriene" geometry and thereby concluded that  $\pi$  delocalization is *not* a driving force in this molecule but is instead "a byproduct of the  $\sigma$ -imposed geometric symmetry". Jug and Köster<sup>3</sup> evaluated energy components for benzene and several heterocyclic aromatic species, finding that the  $\pi$  component favors bond alternating geometries in each case. Stanger and Vollhardt<sup>4</sup> examined benzene with HCC bond angles distorted in a pairwise fashion to  $90^\circ$  in **2** ( $D_{3h}$  symmetry),



a highly strained structure that exhibits significant CC bond alternation in the sense of **2a**. Their analysis also revealed that the  $\pi$  component of **2** is stabilized relative to that of the symmetric  $D_{6h}$  structure.

In contrast, localized orbital analysis generally supports the traditional, resonance-based view. In this analysis, a localized wave function is constructed by replacing benzene's three delocalized  $\pi$  orbitals by a set of non-resonating, ethylenic  $\pi$  orbitals. Using a simple  $\pi$ -electron wave function and empirical CC stretching force constants, Mulliken and Parr<sup>8</sup> estimated that in the absence of delocalization benzene favors a geometry with alternating CC bond lengths ( $R_{CC} = 1.34, 1.54$  Å) by roughly 37 kcal mol<sup>-1</sup> over the symmetric structure ( $R_{CC} = 1.39$  Å). This energy difference was termed the "compression energy", corresponding to the energy required to distort an idealized Kekulé structure with alternating single and double bond lengths to a

(8) Mulliken, R. S.; Parr, R. G. *J. Chem. Phys.* **1951**, *19*, 1271.

**Table I.** Benzene Geometries and Energies along the  $d_{SH}$  Distortion Coordinate<sup>a</sup>

$d_{SH}$	$R_{CC}$ (long)	$R_{CC}$ (short)	$E_0$	$E^{(loc)}$	$E_{\pi}^{(SH)}$	$E_{\pi}^{(JK)}$	$E_{\pi}^{(SV)}$
0.000 0	1.400 0	1.40	-230.701 88	-230.473 53	-6.358 65	-9.303 36	-1.148 7
0.040 3	1.420 3	1.38	-230.700 94	-230.501 79	-6.360 67	-9.309 15	-1.149 8
0.081 1	1.441 1	1.36	-230.698 02	-230.524 80	-6.366 72	-9.326 40	-1.153 0
0.122 4	1.462 4	1.34	-230.692 84	-230.542 45	-6.376 69	-9.354 35	-1.158 4
0.164 4	1.484 4	1.32	-230.685 06	-230.554 64	-6.390 33	-9.391 74	-1.165 8
0.207 0	1.507 0	1.30	-230.674 21	-230.561 21	-6.407 32	-9.437 14	-1.174 5
0.250 2	1.530 2	1.28	-230.659 84	-230.562 02	-6.427 35	-9.489 13	-1.185 0
0.294 1	1.554 1	1.26	-230.641 42	-230.556 83	-6.450 09	-9.546 49	-1.196 6
0.338 8	1.578 8	1.24	-230.618 44	-230.545 39	-6.475 27	-9.608 14	-1.209 4

<sup>a</sup> Distances in Å, energies in au.**Table II.** Benzene Geometries and Energies along the  $d_{SV}$  Distortion Coordinate<sup>a</sup>

$d_{SV}$	$R_{CC}$ (long)	$R_{CC}$ (short)	$\angle HCC$	$E_0$	$E^{(loc)}$	$E_{\pi}^{(SH)}$	$E_{\pi}^{(JK)}$	$E_{\pi}^{(SV)}$
0.000 0	1.386 2	1.386 2	120	-230.703 14	-230.468 67	-6.409 80	-9.295 06	-1.159 2
0.037 6	1.407 8	1.370 2	110	-230.679 51	-230.469 39	-6.406 04	-9.302 23	-1.160 2
0.093 9	1.446 8	1.352 9	100	-230.605 39	-230.431 00	-6.389 64	-9.332 44	-1.162 8
0.200 2	1.529 0	1.328 8	90	-230.473 74	-230.354 97	-6.344 13	-9.427 09	-1.168 3

<sup>a</sup> Distances in Å, angles in deg, energies in au.

symmetric geometry while preventing the  $\pi$  system from delocalizing. Thus their analysis suggested, at a qualitative level, that  $\pi$  delocalization is at least in part responsible for the equilibrium geometry. More recently, Kollmar<sup>9</sup> reexamined benzene at the ab initio level, calculating that the localized wave function favors a bond alternating structure by 30 kcal mol<sup>-1</sup>, thereby supporting the conclusions of Mulliken and Parr.

In this paper, we present a comparison study of benzene using both localized orbital and  $\sigma$ - $\pi$  energy partitioning methods in an effort to gain insight into the nature of  $\pi$  delocalization and its role with regard to geometry. The relationship between the localized orbital and energy partitioning methods is analyzed.

### Benzene Distortions

Two distortions of the benzene geometry are considered in this work. Although the details of these distortions differ somewhat, both lead to alternating CC bond lengths ( $R_1$ ,  $R_2$ ) around the ring. We use the quantity  $d$

$$d = R_1 - R_2 \quad (1)$$

as a measure of the degree of alternation in the structure,  $d = 0$  thereby referring to the equilibrium geometry with equivalent bond lengths.

The first distortion, denoted  $d_{SH}$ , was previously investigated by Shaik, Hiberty, et al.<sup>2e</sup> The geometry, denoted  $d_{SH} = 0$  corresponds to the symmetrical benzene structure with  $R_{CC} = 1.40$  Å. The geometries  $d_{SH} \neq 0$  arise from variations in  $R_1$ ,  $R_2$  within the constraint that the contribution of the nuclear repulsion to the total energy remains constant, equal to that of the  $d_{SH} = 0$  geometry. Clearly, this requirement leads to bond alternation; the  $R_1$  bond length necessarily lengthens, for example, to compensate for increased nuclear repulsion as  $R_2$  shortens. The most distorted geometry investigated along  $d_{SH}$  has alternating bond lengths of 1.240 and 1.579 Å ( $d_{SH} = 0.339$  Å). All other internal coordinates are constrained to standard values ( $R_{CH} = 1.08$  Å,  $\angle HCC = 120^\circ$ ).

The second distortion,  $d_{SV}$ , was that examined by Stanger and Vollhardt.<sup>4</sup> In this case,  $d_{SV} = 0$  corresponds to the RHF/6-31G\* optimized benzene geometry. The  $d_{SV} \neq 0$  geometries result from decreasing the HCC bond angles in a pairwise fashion from their optimal value of  $120^\circ$  to highly strained  $90^\circ$  (2) with all other internal coordinates optimized. To some degree, such distortion resembles annelation of benzene by small strained

rings.<sup>4,10,11</sup> As demonstrated previously,<sup>11,12</sup> decreasing the HCC angles induces bond alternation within the ring due to rehybridization of the carbon centers. For  $\angle HCC = 90^\circ$ , for example, the optimized geometry has CC bond lengths of 1.329 and 1.529 Å ( $d_{SV} = 0.200$  Å).

All calculations reported here were performed by GAUSSIAN 90<sup>13</sup> or GAMESS<sup>14</sup> at the SCF level of theory with the split-valence 6-31G\* basis.<sup>15,16</sup> Geometries and energy components for the localized orbital and energy partitioning analyses are given in Tables I ( $d_{SH}$ ) and II ( $d_{SV}$ ).

### Localized Orbital Analysis

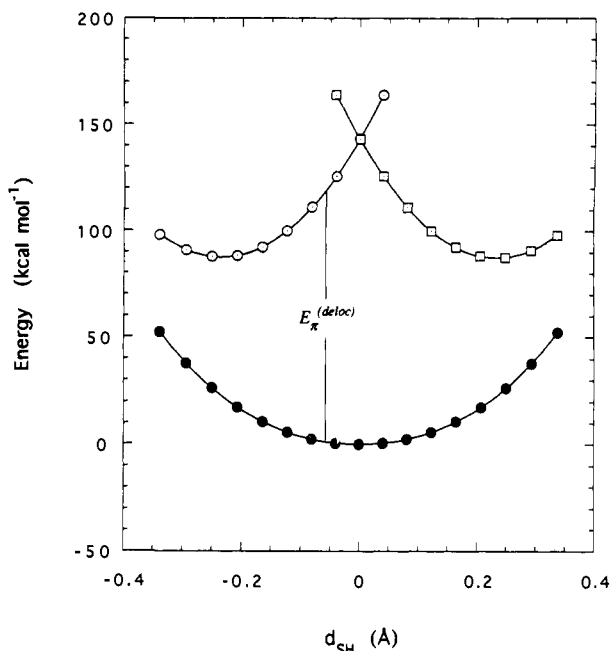
The nature of  $\pi$  delocalization in benzene can be studied by comparing the properties of its delocalized SCF wave function with those of a hypothetically localized (Kekulé) system. The latter is constructed by replacing the three canonical  $\pi$  MOs of the delocalized wave function with a set of non-resonating, ethylenic orbitals. This is the approach previously taken by Mulliken and Parr<sup>8</sup> and Kollmar.<sup>9</sup>

Computationally, localizing the benzene wave function is a three-step procedure: (i) transformation of the  $\pi$  MOs to an orthogonal set of symmetry-equivalent atomic hybrids, (ii) construction of the localized  $\pi$  orbitals from the in-phase combination of adjacent hybrids, and (iii) substitution of the localized orbitals into the SCF wave function. Step i is well-defined for minimal basis sets, i.e. those having only one  $p_{\pi}$  function per carbon. But for an extended basis, such as 6-31G\*, with two or more such functions per carbon, the transformation is not

(9) Kollmar, H. *J. Am. Chem. Soc.* **1979**, *101*, 4832.(10) Faust, R.; Glendening, E. D.; Streitwieser, A.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1992**, *114*, 8263.(11) Stanger, A. *J. Am. Chem. Soc.* **1991**, *113*, 8277.(12) Apeloig, Y.; Arad, D. *J. Am. Chem. Soc.* **1986**, *108*, 3241.

(13) GAUSSIAN 90. Rev., F.; Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A.; Gaussian, Inc.: Pittsburgh, PA, 1990.

(14) GAMESS. Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Jensen, J. H.; Koseki, S.; Gordon, M. S.; Nguyen, K. A.; Windus, T. L.; Elbert, S. T. *QCPE Bull.* **1990**, *10*, 52. We thank Dr. Mike Schmidt for providing a copy of this program.(15) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *66*, 217.(16) For a discussion of the computational methods, see: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986, and references therein.



**Figure 1.** Behavior of the total energy  $E_0$  (filled circles) and the energies  $E^{(loc)}$  of the Kekulé structures **1a** (circles) and **1b** (squares) along the  $d_{SH}$  distortion coordinate.

straightforward. Natural bond orbital analysis<sup>17</sup> assists here by calculating the  $2p_{\pi}$  hybrids of maximum orbital occupancy (that is, the set of hybrids that best reflects the  $\pi$  electron distribution). For benzene, this occupancy is nearly one (0.997) electron per hybrid with the residual electron density occupying extra-valence  $3p_{\pi}$  and  $3d_{\pi}$  basis functions. Note that the localization procedure has absolutely no influence on the form of the  $\sigma$  orbitals but effectively mixes part of the virtual  $\pi$  space into the set of occupied  $\pi$  orbitals. As a result, the energy of the localized system,  $E^{(loc)}$ , is greater than the variational SCF energy,  $E_0$ ,

$$E_0 = E^{(loc)} + E_{\pi}^{(deloc)} \quad (2)$$

raised in energy by an amount equivalent to the so-called "vertical delocalization energy",  $E_{\pi}^{(deloc)}$ .<sup>18</sup> Since  $\pi$  delocalization stabilizes the system, we adopt the convention here that  $E_{\pi}^{(deloc)}$  is a negative quantity.

At its equilibrium geometry, benzene is strongly stabilized by delocalization ( $E_{\pi}^{(deloc)} = -147$  kcal mol<sup>-1</sup>). Although this energy is significantly stronger than suggested by thermochemical measures ( $-36$  kcal mol<sup>-1</sup>),<sup>19</sup> it compares more favorably to spectroscopic values.<sup>20</sup> A Hückel MO treatment of the  ${}^1B_{1u} \rightarrow {}^1A_{1g}$  (lowest  $\pi \rightarrow \pi^*$ ) electronic transition predicts an excitation energy of  $|2\beta|$ , a quantity equivalent to the delocalization energy. The corresponding UV absorption band appears at 207 nm or roughly  $-138$  kcal mol<sup>-1</sup>, an energy somewhat weaker than our calculated value due in part to electronic relaxation of the  ${}^1B_{1u}$  excited state.

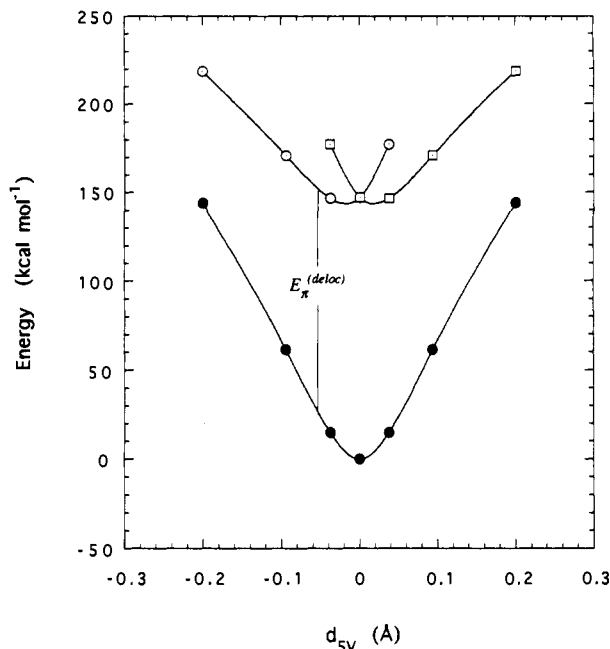
Localized orbital analysis for benzene geometries along  $d_{SH}$  is shown in Figure 1. The lowest curve shows the energy  $E_0$  of the delocalized SCF wave function. The two higher energy curves

(17) (a) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211. (b) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (c) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *QCPE Bull.* **1990**, *10*, 58. The natural bond orbital program is readily available in the GAUSSIAN package (Link 607).

(18) We use the terms "vertical delocalization energy" and "delocalization energy" interchangeably. These terms are equivalent to the QMRE of Shaik, Hiberty, et al. (ref 2e).

(19) Streitwieser, A., Jr. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961.

(20) (a) Parmenter, C. S. *Adv. Chem. Phys.* **1972**, *22*, 365. (b) Karplus, M.; Porter, R. N. *Atoms and Molecules*; Benjamin/Cummings: Menlo Park, 1970; p 375.



**Figure 2.** Behavior of the total energy  $E_0$  (filled circles) and the energies  $E^{(loc)}$  of the Kekulé structures **2a** (circles) and **2b** (squares) along the  $d_{SV}$  distortion coordinate.

represent respectively the energies  $E^{(loc)}$  of the two localized Kekulé structures that are degenerate at the symmetric geometry ( $d_{SH} = 0$ ). For a specified geometry  $d_{SH}$ , the delocalization energy corresponds to the separation between the  $E_0$  and  $E^{(loc)}$  curves.

As anticipated, the delocalization energy is most stabilizing at the symmetric geometry and monotonically weakens as the carbon framework is increasingly distorted away from equilibrium. However, it is particularly noteworthy that delocalization strongly stabilizes *all* geometries, even highly distorted ones. For instance, consider the  $d_{SH} = 0.207$  Å ( $R_{CC} = 1.300, 1.507$  Å) geometry, one that resembles an idealized cyclohexatriene structure of alternating single and double CC bond lengths. Although one might judge resonance effects to be negligible based on geometry, localized orbital analysis suggests that the delocalization energy ( $E_{\pi}^{(deloc)} = -71$  kcal mol<sup>-1</sup>) is only diminished by a factor of 2 from that of equilibrium benzene. This result is consistent with an analysis of the resonance contributions of **1a** and **1b**.<sup>21</sup> Their weights shift from 50:50 at the symmetric geometry to 76:20 at  $d_{SH} = 0.21$  Å, revealing that the contribution of the lesser Kekulé form remains sizable in highly distorted geometries.

Figure 1 also shows that the energy  $E^{(loc)}$  of the localized wave function is minimized near  $d_{SH} = \pm 0.23$  Å ( $R_{CC} = \sim 1.29, 1.51$  Å), thereby demonstrating that in the absence of delocalization, benzene favors bond alternation. Indeed, the energy at this geometry is nearly 60 kcal mol<sup>-1</sup> less than at  $d_{SH} = 0$ . Thus, in contrast to the contentions of Shaik, Hiberty, et al.,<sup>2</sup> our analysis suggests that delocalization is an important symmetrizing force in the benzene molecule and is at least in part responsible for the equilibrium structure.

Similar conclusions result from the analysis of the  $d_{SV}$  distortion (Figure 2). Here, however, the effect of localization on geometry is somewhat less dramatic due to the unfavorable bending of the HCC bond angles. The localized wave function in this case favors a geometry near  $d_{SV} = \pm 0.02$  Å ( $R_{CC} = \sim 1.38, 1.40$  Å;  $\angle HCC = 115^\circ$ ).

To investigate the effect of localization further, we performed a *full* geometry optimization of benzene ( $D_{3h}$  symmetry constraints imposed) with respect to  $E^{(loc)}$ . The resulting structure exhibits significant bond alternation ( $R_{CC} = 1.307, 1.565$  Å) with slightly

(21) Glendening, E. D. Ph.D. Thesis, University of Wisconsin, Madison, WI, 1991. Also see ref 10.

distorted HCC bond angles ( $\angle\text{HCC} = 114.9^\circ$ ). The energy of the localized wave function is 63 kcal mol<sup>-1</sup> less at this geometry than at the symmetric geometry, a large energy difference that must be overcome by delocalization in order to stabilize the latter geometry.

### Energy Partitioning Analysis

An alternative approach for analyzing benzene is based on the energy partitioning schemes of Shaik and Hiberty,<sup>2</sup> Jug and Köster,<sup>3</sup> and Stanger and Vollhardt.<sup>4</sup> These methods decompose the total energy,  $E_0$ , into separate  $\sigma$  and  $\pi$  electronic components and a nuclear repulsions term

$$E_0 = E_\sigma + E_\pi + V^{nn} \quad (3)$$

Although the symmetric ( $\sigma$ ) and antisymmetric ( $\pi$ ) character of the canonical benzene MOs is easily identified, the Coulomb and exchange interactions of electrons occupying orbitals of differing symmetry prevent the unique separation of the energy into symmetry components. Despite the arbitrary nature of any  $\sigma$ - $\pi$  partitioning, several schemes have been proposed.

Previous applications of these schemes have been generally limited to the analysis of single configuration, restricted Hartree-Fock wave functions.<sup>22</sup> At this level of theory, the total energy is given by

$$E_0 = \sum_i (h_{ii} + \epsilon_i) + V^{nn} \quad (4)$$

where  $h_{ii}$  is the core Hamiltonian contribution (electron kinetic energy and nuclear attraction terms) and  $\epsilon_i$  is the orbital energy of the  $i$ th MO, often expressed in terms of the familiar Coulomb  $J_{ij}$  and exchange  $K_{ij}$  integrals

$$\epsilon_i = h_{ii} + \sum_j (2J_{ij} - K_{ij}) \quad (5)$$

Shaik, Hiberty, et al.<sup>2c</sup> extended their analysis to configuration interaction (CI) wave functions, but this will not be considered here. The fundamental problem arises in apportioning the  $\sigma, \pi$  interaction terms. Such apportioning is avoided by the  $\pi$ -delocalization analysis of the preceding section.

The approach of Shaik and Hiberty (SH) assigns all  $\sigma, \pi$  interaction terms (Coulomb and exchange integrals of the form  $J_{\sigma\pi}, K_{\sigma\pi}$ ) to the  $\pi$  component. Thus, their energy components can be expressed in the following form

$$E_\sigma^{(SH)} = \sum_i (h_{ii} + \epsilon_i) - \sum_i \sum_j^\pi (2J_{ij} - K_{ij}) \quad (6a)$$

$$E_\pi^{(SH)} = \sum_i (h_{ii} + \epsilon_i) + \sum_i \sum_j^\pi (2J_{ij} - K_{ij}) \quad (6b)$$

where the summations are restricted to MOs of the specified symmetry type. Note that eq 6 accounts only for the electronic energy of the system so that nuclear repulsions ( $V^{nn}$ ) must be considered separately when analyzing the total energy. This led Shaik and Hiberty to investigate the  $d_{\text{SH}}$  distortion along which  $V^{nn}$  remains constant.

Jug and Köster (JK)<sup>3</sup> proposed an alternative approach, evenly distributing the interaction terms between  $E_\sigma$  and  $E_\pi$  and partitioning  $V^{nn}$  according to the formal number of  $\sigma$  and  $\pi$  electrons on each atomic center. The resulting energy components have a relatively simple form

$$E_\sigma^{(JK)} = \sum_i (h_{ii} + \epsilon_i) + V_\sigma^{nn} \quad (7a)$$

$$E_\pi^{(JK)} = \sum_i (h_{ii} + \epsilon_i) + V_\pi^{nn} \quad (7b)$$

Expressions for the  $V_\sigma^{nn}$  and  $V_\pi^{nn}$  are given in ref 3. This method

(22) Szabo, A.; Ostlund, N. S. *Modern Quantum Chemistry*; McGraw-Hill: New York, 1982; pp 131-152.

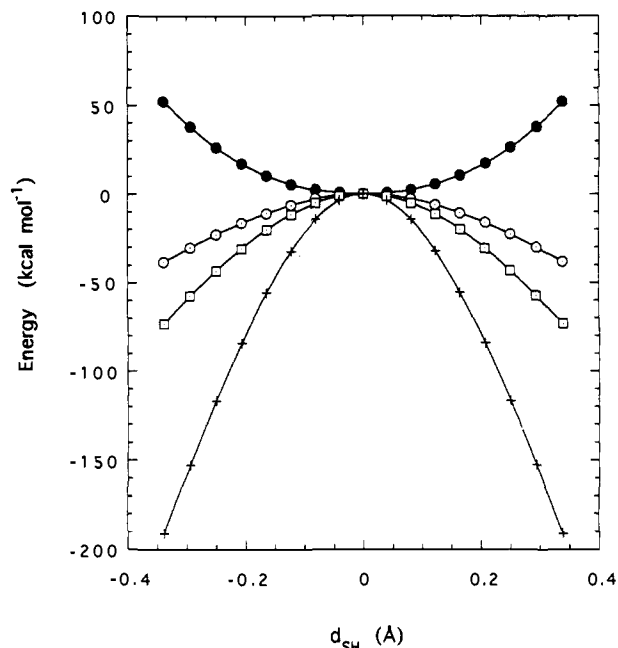


Figure 3. Geometry dependence of the total energy  $E_0$  (filled circles) and the  $\pi$  energy components  $E_\pi^{(SV)}$  (circles),  $E_\pi^{(SH)}$  (squares), and  $E_\pi^{(JK)}$  (pluses) along the  $d_{\text{SH}}$  distortion coordinate.

avoids separate consideration of the nuclear repulsions component (as in eq 3) by incorporating its contribution directly into the  $\sigma$  and  $\pi$  components. However, an important point of criticism is that delocalization is a purely electronic effect that may potentially be obscured by nuclear repulsions.

Finally, Stanger and Vollhardt (SV)<sup>4</sup> took the most straightforward approach, calculating  $E_\pi$  as a simple sum of orbital energies

$$E_\pi^{(SV)} = \sum_i^\pi \epsilon_i \quad (8)$$

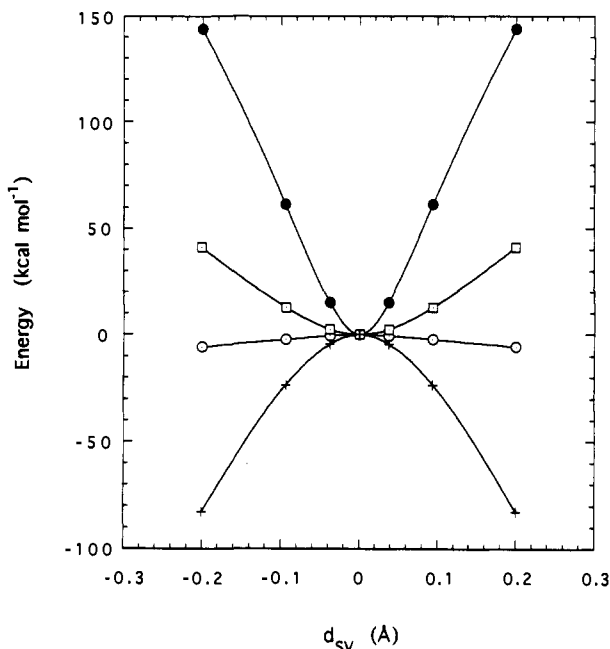
in direct analogy to a Walsh-type analysis.<sup>23</sup> All other energy contributions, including the  $\pi$ -type core Hamiltonian terms of eqs 6b and 7b, were assigned to the  $\sigma$  system. As a result, this method can be judged inferior to those of SH and JK, but it is considered here for comparison with previous work.

Along the  $d_{\text{SH}}$  distortion coordinate,  $E_\pi$  is maximized at the symmetric geometry for each of the partitioning methods considered (Figure 3). This behavior led Shaik, Hiberty, et al. to suggest that the  $\pi$  system favors bond alternating geometries and to thereby question the role of delocalization. Note that the magnitude of the variation in  $E_\pi$  depends critically on the partitioning scheme employed. For example, this component is stabilized by 38 ( $E_\pi^{(SV)}$ ), 73 ( $E_\pi^{(SH)}$ ), and 191 ( $E_\pi^{(JK)}$ ) kcal mol<sup>-1</sup> at the most distorted geometry relative to the symmetric structure.

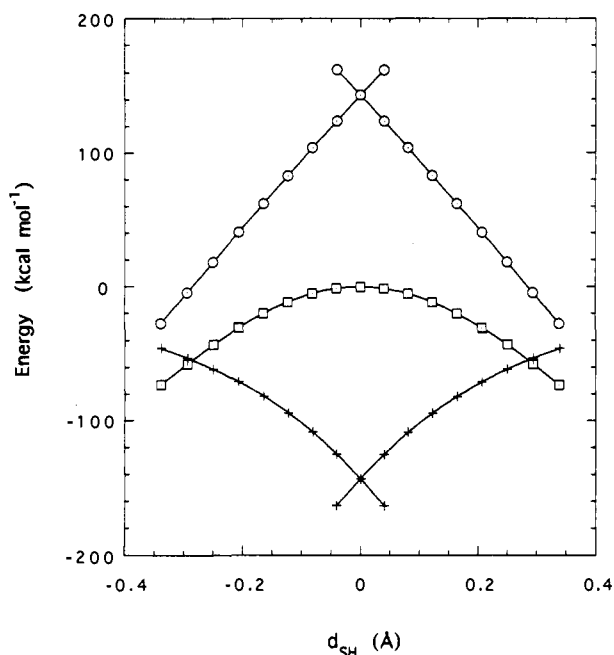
The behavior of  $E_\pi$  along  $d_{\text{SV}}$  differs somewhat for the three methods (Figure 4). Whereas  $E_\pi^{(JK)}$  and  $E_\pi^{(SV)}$  are again maximized at the symmetric geometry,  $E_\pi^{(SH)}$  is minimized. Stanger and Vollhardt<sup>4</sup> concluded that their analysis of the  $d_{\text{SV}}$  distortion supported the views of Shaik and Hiberty, who limited their investigations to  $d_{\text{SH}}$ . It is important to realize, however, that while the behavior of  $E_\pi^{(SV)}$  along  $d_{\text{SV}}$  and of  $E_\pi^{(SH)}$  along  $d_{\text{SH}}$  is similar, the more direct comparison of these components in Figure 4 reveals opposing trends.

Clearly, the conclusions derived from energy partitioning analysis depend critically on the method selected to decompose the energy and on the details of the geometry distortion. It is intriguing, however, that with only one exception, the  $\pi$  component

(23) Walsh, A. D. *J. Chem. Soc.* 1953, 2266.



**Figure 4.** Geometry dependence of the total energy  $E_0$  (filled circles) and the  $\pi$  energy components  $E_{\pi}^{(SV)}$  (circles),  $E_{\pi}^{(SH)}$  (squares), and  $E_{\pi}^{(JK)}$  (pluses) along the  $d_{sv}$  distortion coordinate.

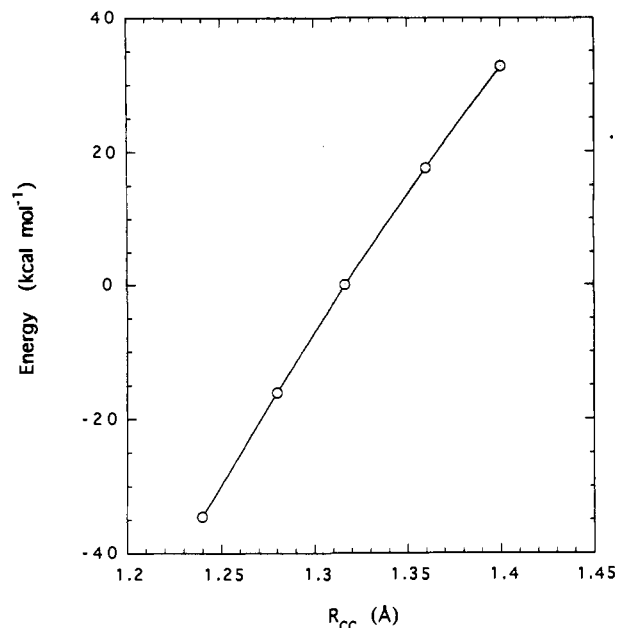


**Figure 5.** Shaik-Hiberty analysis (eq 6) of the localized benzene wave functions showing  $E_{\pi}^{(SH)}$  (squares),  $E_{\pi}^{(loc)}$  (circles), and  $E_{\pi}^{(deloc)}$  (pluses).

favors bond alternating geometries. A Hückel MO treatment of benzene distortion with variable resonance integral  $\beta$  also reveals that the  $\pi$  system favors the asymmetric geometry.<sup>24</sup> Nevertheless, we contend that delocalization strongly stabilizes symmetric benzene, regardless of the behavior of  $E_{\pi}$ , and that it can be misleading to judge the influence of delocalization based on such an energy partitioning scheme.

#### Comparison of Localized Orbital and Energy Partitioning Methods

The relationship between the localized orbital and energy partitioning analyses is examined most directly by applying the



**Figure 6.** Bond length dependence of  $E_{\pi}^{(SH)}$  for the ethylene molecule. Values are given relative to that of the optimized CC bond length (1.317 Å). All coordinates other than the CC bond length are fixed at their RHF/6-31G\* optimized values.

Shaik-Hiberty analysis (eq 6) to the energy  $E^{(loc)}$  of the localized wave functions

$$E^{(loc)} = E_{\sigma}^{(loc)} + E_{\pi}^{(loc)} + V^{nn} \quad (9)$$

We use this method, rather than that of Jug-Köster or Stanger-Vollhardt, because it affords a simplification resulting from the assignment of all  $\sigma$ - $\pi$  interaction terms to the  $\pi$  component. Since the localization procedure has no influence on the form of the  $\sigma$  orbitals,  $E_{\sigma}^{(loc)}$  of eq 9 is equivalent to  $E_{\sigma}^{(SH)}$  of eq 6. Using this identity and substituting eq 9 into eq 2 gives

$$E_0 = E_{\sigma}^{(SH)} + E_{\pi}^{(loc)} + E_{\pi}^{(deloc)} + V^{nn} \quad (10)$$

which by comparison with eq 3 reveals that the  $\pi$  energy of the Shaik-Hiberty method has, in addition to the *entire* delocalization component, a contribution from the localized portion (non-resonating  $\pi$  orbitals) of the SCF wave function

$$E_{\pi}^{(SH)} = E_{\pi}^{(loc)} + E_{\pi}^{(deloc)} \quad (11)$$

A priori, there is no reason to anticipate that the geometry dependence of  $E_{\pi}^{(SH)}$  should be fully associated with the  $\pi$  delocalization term. Indeed, as shown below, we calculate an important contribution from  $E_{\pi}^{(loc)}$ . A similar analysis of the Jug-Köster and Stanger-Vollhardt schemes can be performed, but in these cases  $E_{\pi}^{(deloc)}$  contributes to both  $\sigma$  and  $\pi$  energy components due to the manner in which the  $\sigma$ - $\pi$  interaction terms are handled.

The energies of eq 11 are shown in Figure 5 for the  $d_{SH}$  distortion coordinate. The  $E_{\pi}^{(SH)}$  curve (squares) is identical with the corresponding curve of Figure 3 and the two  $E_{\pi}^{(deloc)}$  curves (pluses) are obtained from the data in Figure 1, the left (right) curve representing delocalization with respect to the Kekulé structure **1a** (**1b**). The  $E_{\pi}^{(loc)}$  data (circles) are obtained by difference.

Figure 5 reveals that  $E_{\pi}^{(SH)}$  contains an important contribution from  $E_{\pi}^{(loc)}$  that rapidly decreases with increasing distortion of the benzene ring, a trend that is not entirely unexpected. This contribution corresponds to the electronic energy of the three ethylenic  $\pi$  orbitals of the localized Kekulé structure, decreasing

as the carbon centers of these orbitals approach each other. For comparison, the CC bond length dependence of  $E_{\pi}^{(\text{SH})}$  for ethylene is shown in Figure 6.<sup>25</sup> Since the  $\pi$  system of this molecule is localized ( $E_{\pi}^{(\text{deloc})} = 0$ ), the curve plotted in this figure corresponds to  $E_{\pi}^{(\text{loc})}$ . Clearly,  $E_{\pi}^{(\text{SH})}$  has a sizable bond length dependence even for fully localized  $\pi$  systems. The tendency for  $E_{\pi}^{(\text{SH})}$  to favor short bond lengths is similar to the behavior of the electronic energy of the  $\text{H}_2$  molecule which decreases asymptotically to that of the helium atom as the HH distance approaches the unit atom limit. It appears therefore rather problematic to judge the role of delocalization based on the geometry dependence of  $E_{\pi}$ .

To summarize, localized orbital analysis of benzene reveals that  $\pi$  delocalization strongly stabilizes the symmetric benzene geometry. A geometry with alternating CC bond lengths is favored when the canonical  $\pi$  MOs of the SCF wave function are replaced by a set of localized orbitals. Hence, we conclude that delocalization provides an important symmetrizing force in this molecule, a viewpoint in accord with classical resonance theory

(25) Note that  $V^m$  varies significantly over the range of CC bond lengths shown in Figure 6. One might argue then that it is inappropriate to apply the Shaik-Hiberty partitioning to ethylene. However, we could have added to the ethylene analysis two remote bare nuclei (say, two  $\text{C}^{6+}$  nuclei) whose separation distance is allowed to vary to counterbalance changes in  $V^m$  as the ethylene CC bond length decreases. Such a model system would then satisfy the  $V^m = \text{constant}$  constraint of Shaik-Hiberty partitioning without changing any detail of the electronic behavior shown in Figure 6.

concepts but in conflict with recent suggestions of Shaik, Hiberty, et al.<sup>2,26</sup> We have shown that the  $\pi$  energy component of the Shaik-Hiberty analysis contains a geometry dependent contribution from the localized benzene wave function that potentially obscures delocalization effects. Therefore, it appears that a  $\sigma$ - $\pi$  energy partitioning analysis cannot be employed without reservation to address the role of delocalization in benzene.

**Acknowledgment.** This work was supported by the National Science Foundation (Grants 87-21134 and 92-02152) and the Director, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy (Contract DE-AC 03-76SF00098). Portions of this investigation were completed at the College of Chemistry Graphic Facility at the University of California—Berkeley (funded in part by National Institutes of Health Grant 8S0RR05651A). R.F. is grateful to the Fonds der Chemischen Industrie for providing a Kekulé fellowship (1989–1992).

(26) A review article by Hiberty, Shaik, and co-workers<sup>27</sup> appeared about the time this paper was submitted for publication. Whereas these authors previously concluded that  $\pi$  delocalization does not play an important role in benzene (see, e.g., refs 2d and 2e), they now write that delocalization "is a driving force which resists the localizing distortion and tends to impose the symmetric geometry."

(27) Hiberty, P. C.; Ohanessian, G.; Shaik, S. S.; Flament, J. P. *Pure Appl. Chem.* 1993, 65, 35.