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The Role of Delocalization in Benzene

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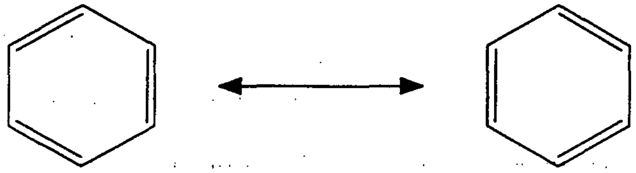
Abstract. The influence of π delocalization on the geometry of benzene is examined at the ab initio SCF level of theory. We find that benzene favors a bond alternating geometry when its canonical π MOs are replaced by three localized ethylenic orbitals, revealing that delocalization is in part responsible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

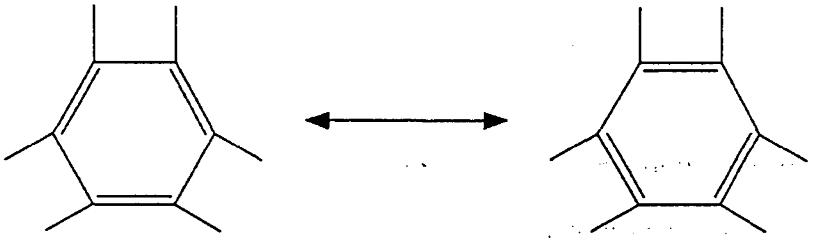
Introduction. One of the early successes and a cornerstone of modern molecular orbital (MO) theory is its ability to predict the stabilizing effect of π electronic delocalization in benzene.[1] Although this effect is generally accepted by the chemical community, the relationship between π delocalization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



1a **1b**

leads to the symmetric (equilibrium) structure with CC bond lengths (~1.40 Å) intermediate between those of idealized single and double bonds. Hence, the structure of benzene and the stabilizing effect of π delocalization appear to be directly related. Recent theoretical studies[2-5] have, however, challenged this view, suggesting instead that the σ system, rather than the π, is entirely responsible for the symmetric structure.

Support for this alternative viewpoint generally originates from the analysis of σ and π energy components of SCF-MO wavefunctions. Shaik, Hiberty, and coworkers[2] demonstrated that the π component is stabilized by distorting benzene to a bond alternating "cyclohexatriene" geometry and thereby concluded that π delocalization is *not* a driving force in this molecule but is instead "a byproduct of the σ-imposed geometric symmetry." Jug and Köster[3] evaluated energy components for benzene and several heterocyclic aromatic species, finding that the π component favors bond alternating geometries in each case. Stanger and Vollhardt[4] examined benzene with HCC bond angles distorted in a pairwise fashion to 90° in **2** (D_{3h} symmetry),



2a **2b**

a highly strained structure that exhibits significant CC bond alternation in the sense of **2a**. Their analysis also revealed that the π 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 wavefunction is constructed by replacing benzene's three delocalized π orbitals by a set of non-resonating, ethylenic π orbitals. Using a simple π-electron wavefunction and empirical CC stretching force constants, Mulliken and Parr[8] 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^{-1} 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 symmetric geometry while preventing the π system to delocalize. Thus their analysis suggested, at a qualitative level, that π delocalization is at least in part responsible for the equilibrium geometry. More recently, Kollmar[9] reexamined benzene at the ab initio level, calculating that the localized wavefunction favors a bond alternating structure by 30 kcal mol^{-1}, thereby supporting the conclusions of Mulliken and Parr.

In this paper, we present a comparison study of benzene using both localized orbital and σ-π energy partitioning methods in an effort to gain insight into the nature of π 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

$$d = R_1 - R_2 \tag{1}$$

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.[2e] The geometry $d_{SH} = 0$ 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 nuclear repulsions contribution 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°).

The second distortion, d_{SV}, was that examined by Stanger and Vollhardt.[4] 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° to highly strained 90° (**2**) with all other internal coordinates optimized. To some degree, such distortion resembles annelation of benzene by small strained rings.[4,10,11] As demonstrated previously,[11,12] decreasing the HCC angles induces bond alternation within the ring due to rehybridization of the carbon centers. For $\angle$HCC = 90°, 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[13] or GAMESS[14] at the SCF level of theory with the split-valence 6-31G* basis.[15,16]

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 π delocalization in benzene can be studied by comparing the properties of its delocalized SCF wavefunction with those of a hypothetically localized (Kekulé) system. The latter is constructed by replacing the three canonical π MOs of the delocalized wavefunction with a set of non-resonating, ethylenic orbitals. This is the approach previously taken by Mulliken and Parr[8] and Kollmar.[9]

Computationally, localizing the benzene wavefunction is a three step procedure: (i) transformation of the π MOs to an orthogonal set of symmetry-equivalent atomic hybrids, (ii) construction of the localized π orbitals from the in-phase combination of adjacent hybrids, and (iii) substitution of the localized orbitals into the SCF wavefunction. Step (i) is well-defined for minimal basis sets, i.e. those having only one p_π function per carbon. But for an extended basis, such as 6-31G*, with two or more such functions per carbon, the transformation is not straightforward. Natural bond orbital analysis[17] assists here by calculating the $2p_\pi$ hybrids of maximum orbital occupancy (that is, the set of hybrids that best reflects the π 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 σ orbitals but effectively mixes part of the virtual π space into the set of occupied π orbitals. As a result, the energy of the localized system, $E^{(loc)}$, is greater than the variational SCF energy, E_0,

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

raised in energy by an amount equivalent to the so-called "vertical delocalization energy," $E_\pi^{(deloc)}$.[18] Since π 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^{-1}). Although this energy is significantly stronger than suggested by thermochemical measures (-36 kcal mol^{-1}),[19] it compares more favorably to spectroscopic values.[20] A Hückel MO treatment of the $^1B_{1u}$-$^1A_{1g}$ (lowest π–π^*) 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^{-1}, 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 wavefunction. The two higher energy curves 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^{-1}) is only diminished by a factor of two from that of equilibrium benzene. This result is consistent with an analysis of the resonance contributions of **1a** and **1b**.[21] 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 wavefunction is minimized near d_{SH} = ±0.23 Å (R_{CC} = ~1.29, 1.52 Å), thereby demonstrating that in the absence of delocalization, benzene favors bond alternation. Indeed, the energy at this geometry is nearly 60 kcal mol^{-1} less than at $d_{SH} = 0$. Thus, in contrast to the contentions of Shaik, Hiberty, et al.,[2] 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 wavefunction in this case favors a geometry near d_{SV} = ±0.02 Å (R_{CC} = ~1.38, 1.40 Å; ∠HCC = 115°).

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 distorted HCC bond angles (∠HCC = 114.9°). The energy of the localized wavefunction is 63 kcal mol^{-1} 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,[2] Jug and Köster,[3] and Stanger and Vollhardt.[4] These methods decompose the total energy, E_0, into separate σ and π electronic components and a nuclear repulsions term

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

Although the symmetric (σ) and antisymmetric (π) 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 σ–π partitioning, several schemes have been proposed.

Previous applications of these schemes have been generally limited to the analysis of single configuration, restricted Hartree-Fock wavefunctions.[22] At this level of theory, the total energy is given by

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

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

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

Shaik, Hiberty, et al.[2e] extended their analysis to configuration interaction (CI) wavefunctions but this will not be considered here.

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

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

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

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_{SH} distortion along which V^{nn} remains constant.

Jug and Köster (JK)[3] proposed an alternative approach, evenly distributing the interaction terms between E_σ and E_π and partitioning V^{nn} according to the formal number of σ and π electrons on each atomic center. The resulting energy components have a relatively simple form

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

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

Expressions for the V_σ^{nn} and V_π^{nn} are given in ref 3. This method avoids separate consideration of the nuclear repulsions component (as in eq 3) by incorporating its contribution directly into the σ and π 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)[4] took the most straightforward approach, calculating E_π as a simple sum of orbital energies

$$E_\pi^{(SV)} = \sum_i^\pi \varepsilon_i \tag{8}$$

in direct analogy to a Walsh-type analysis.[23] All other energy contributions, including the π-type core Hamiltonian terms of eqs 6b and 7b, were assigned to the σ 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_{SH} distortion coordinate, E_π 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 π system favors bond alternating geometries and to thereby question the role of delocalization. Note that the magnitude of the variation in E_π 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^{-1} at the most distorted geometry relative to the symmetric structure.

The behavior of E_π along d_{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[4] concluded that their analysis of the d_{SV} distortion supported the views of Shaik and Hiberty, who limited their investigations to d_{SH}. It is important to realize, however, that while the behavior of $E_\pi^{(SV)}$ along d_{SV} and of $E_\pi^{(SH)}$ along d_{SH} are 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 π component favors bond alternating geometries. A Hückel MO treatment of benzene distortion with variable resonance integral β also reveals that the π system favors the asymmetric geometry.[24] Nevertheless, we contend that delocalization strongly stabilizes symmetric benzene, regardless of the behavior of E_π, 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 Shaik-Hiberty analysis (eq 6) to the energy $E^{(loc)}$ of the localized wavefunctions

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

We use this method, rather than that of Jug-Köster or Stanger-Vollhardt, because it affords a simplification resulting from the assignment of all σ-π interaction terms to the π component. Since the localization procedure has no influence on the form of the σ

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

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

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

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

A priori, there is no reason to anticipate that the geometry dependence of $E_\pi^{(SH)}$ should be fully associated with the π 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 σ and π energy components due to the manner in which the σ-π 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 to 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 energy of the three ethylenic π 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 $E_\pi^{(SH)}$ for ethylene is shown in Figure 6.[25] Since the π system of this molecule is localized ($E_\pi^{(deloc)}$=0), the curve plotted in this Figure corresponds to $E_\pi^{(loc)}$. Clearly, $E_\pi^{(SH)}$ has a sizable bond length dependence even for fully localized π systems. The tendency for $E_\pi^{(SH)}$ to favor short bond lengths is similar to the behavior of the *electronic* energy of the H_2 molecule which decreases asymptotically to that of the helium atom as the HH distance approaches the united atom limit. It appears therefore rather problematic to judge the role of delocalization based on the geometry dependence of E_π.

To summarize, localized orbital analysis of benzene reveals that π delocalization strongly stabilizes the symmetric benzene geometry. A geometry with alternating CC bond lengths is favored when the canonical π MOs of the SCF wavefunction 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 concepts but in conflict with recent suggestions of Shaik, Hiberty, et al..[2,26] We have shown that the π energy component of the Shaik-Hiberty analysis contains a geometry dependent contribution from the localized benzene wavefunction that potentially obscures delocalization effects. Therefore, it appears that a σ–π energy partitioning analysis cannot be employed without reservation to address to role of delocalization in benzene.

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(25) Note that V^{nn} 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 C^{+6} nuclei) whose separation distance is allowed to vary to counterbalance changes in V^{nn} as the ethylene CC bond length decreases. Such a model system would then satisfy the V^{nn}=constant constraint of Shaik-Hiberty partitioning without changing any detail of the electronic behavior shown in Figure 6.

(26) A review article (Ref 27) by Hiberty, Shaik, and coworkers appeared about the time this manuscript was submitted for publication. Whereas these authors previously concluded that π delocalization does not play an important role in benzene (see, e.g., Refs 2d, 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.

Figure Captions

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.

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.

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

Figure 4. Geometry dependence of the total energy E_0 (filled circles) and the π 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 wavefunctions showing $E_\pi^{(SH)}$ (squares), $E_\pi^{(loc)}$ (circles), and $E_\pi^{(deloc)}$ (pluses).

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.

Table I. Benzene Geometries and Energies along the d_{SH} Distortion Coordinate[a]

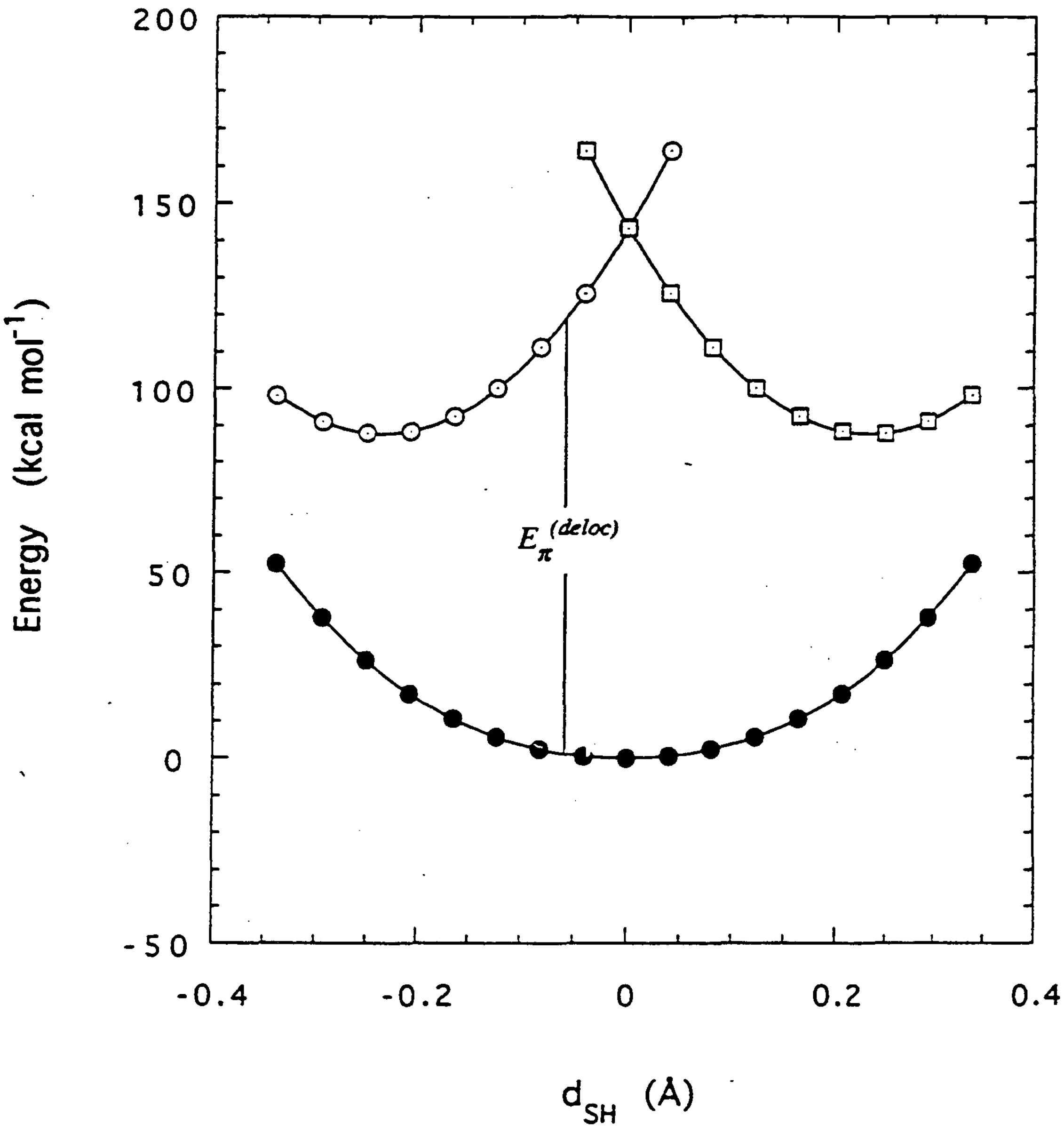
d_{SH}	R_{CC} (long)	R_{CC} (short)	E_0	$E^{(loc)}$	$E_\pi^{(SH)}$	$E_\pi^{(JK)}$	$E_\pi^{(SV)}$
0.0000	1.4000	1.40	-230.70188	-230.47353	-6.35865	-9.30336	-1.1487
0.0403	1.4203	1.38	-230.70094	-230.50179	-6.36067	-9.30915	-1.1498
0.0811	1.4411	1.36	-230.69802	-230.52480	-6.36672	-9.32640	-1.1530
0.1224	1.4624	1.34	-230.69284	-230.54245	-6.37669	-9.35435	-1.1584
0.1644	1.4844	1.32	-230.68506	-230.55464	-6.39033	-9.39174	-1.1658
0.2070	1.5070	1.30	-230.67421	-230.56121	-6.40732	-9.43714	-1.1745
0.2502	1.5302	1.28	-230.65984	-230.56202	-6.42735	-9.48913	-1.1850
0.2941	1.5541	1.26	-230.64142	-230.55683	-6.45009	-9.54649	-1.1966
0.3388	1.5788	1.24	-230.61844	-230.54539	-6.47527	-9.60814	-1.2094

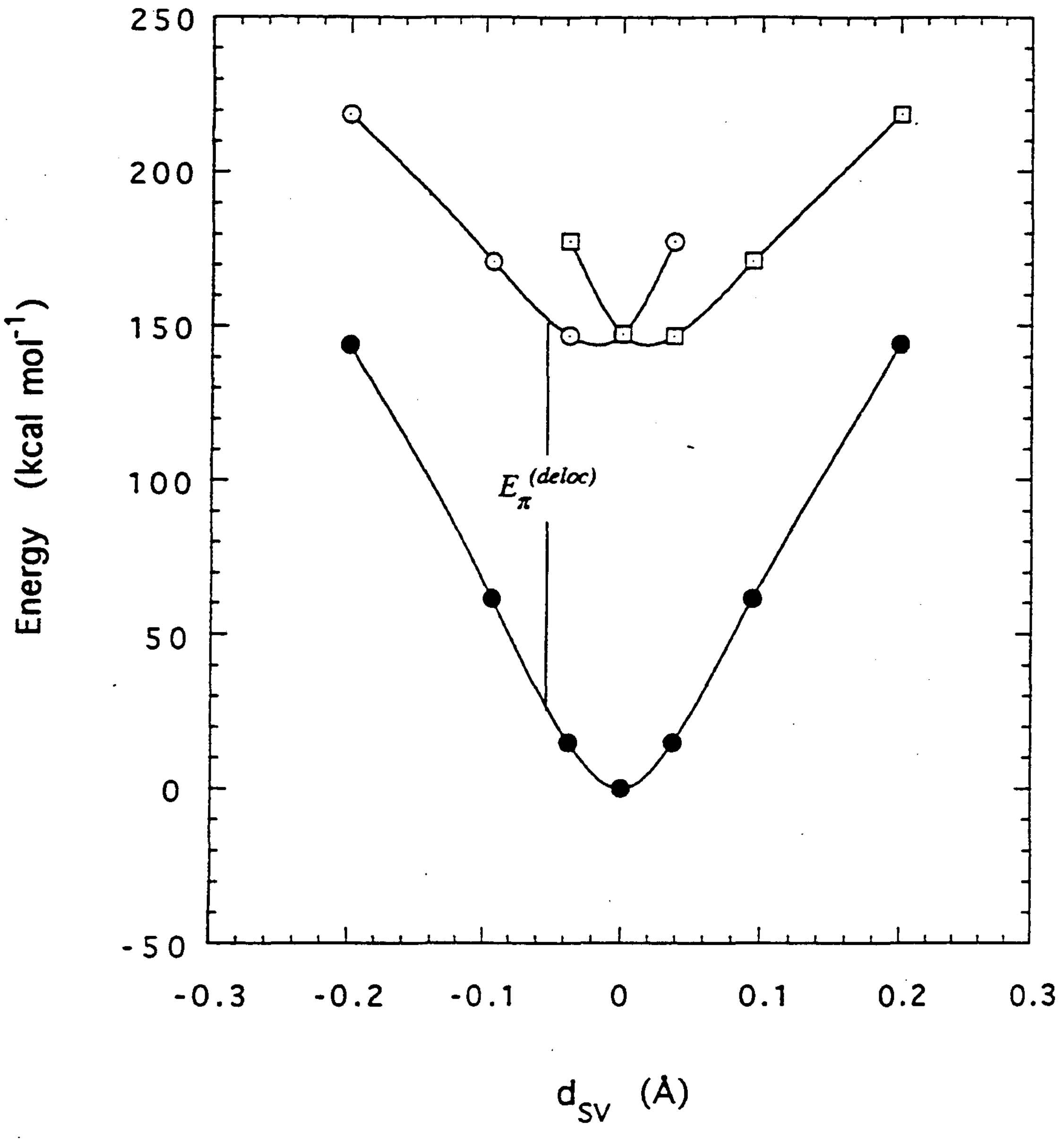
[a]Distances in Å, energies in a.u.

Table II. Benzene Geometries and Energies along the d_{SV} Distortion Coordinate[a]

d_{SV}	R_{CC} (long)	R_{CC} (short)	∠HCC	E_0	$E^{(loc)}$	$E_\pi^{(SH)}$	$E_\pi^{(JK)}$	$E_\pi^{(SV)}$
0.0000	1.3862	1.3862	120	-230.70314	-230.46867	-6.40980	-9.29506	-1.1592
0.0376	1.4078	1.3702	110	-230.67951	-230.46939	-6.40604	-9.30223	-1.1602
0.0939	1.4468	1.3529	100	-230.60539	-230.43100	-6.38964	-9.33244	-1.1628
0.2002	1.5290	1.3288	90	-230.47374	-230.35497	-6.34413	-9.42709	-1.1683

[a] Distances in Å, angles in degrees, energies in a.u.


200
150
100
50
0
-50
Energy (kcal mol^{-1})
-0.4
-0.2
0
0.2
0.4
d_{SH} (Å)
$E_\pi^{(deloc)}$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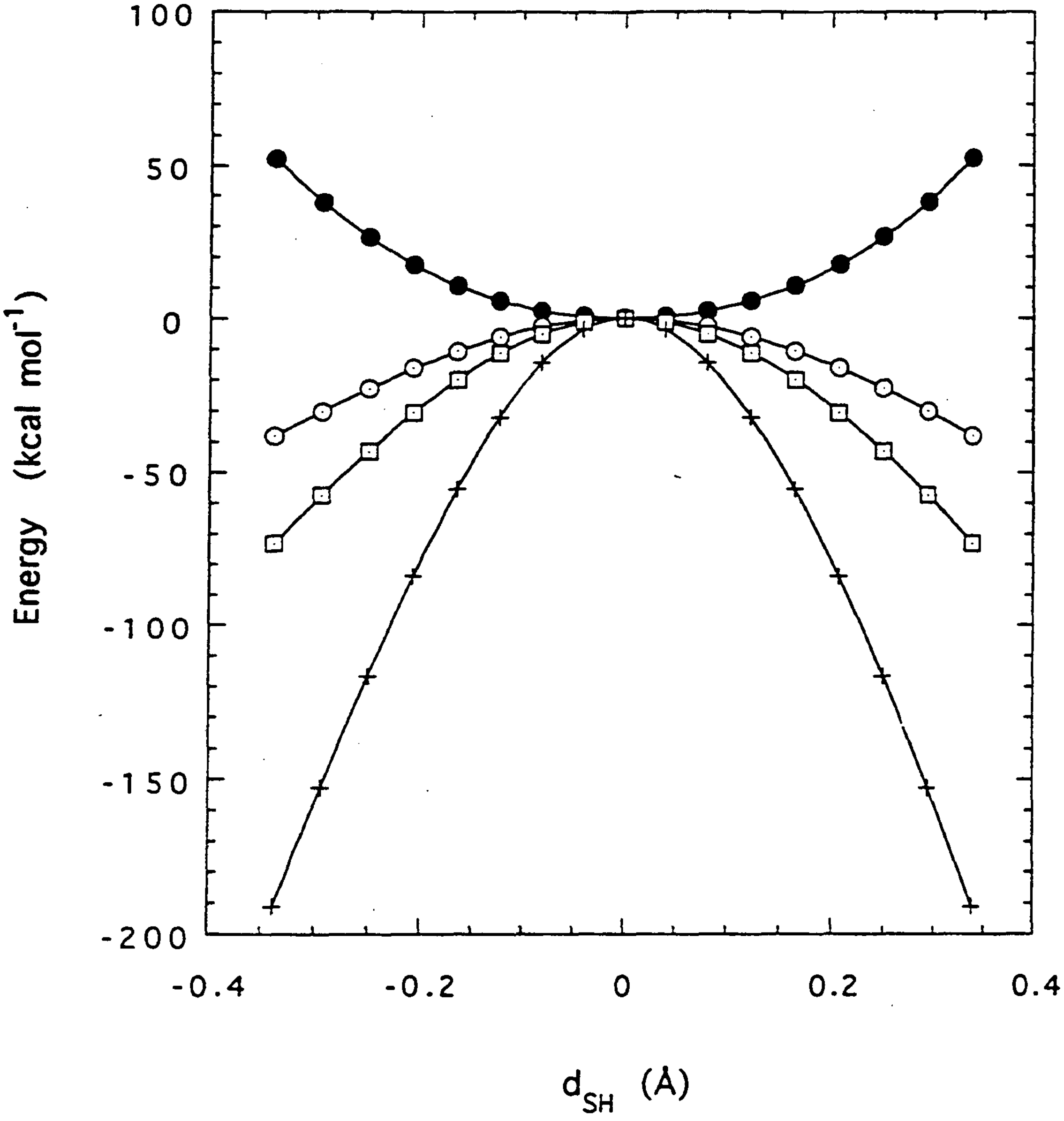
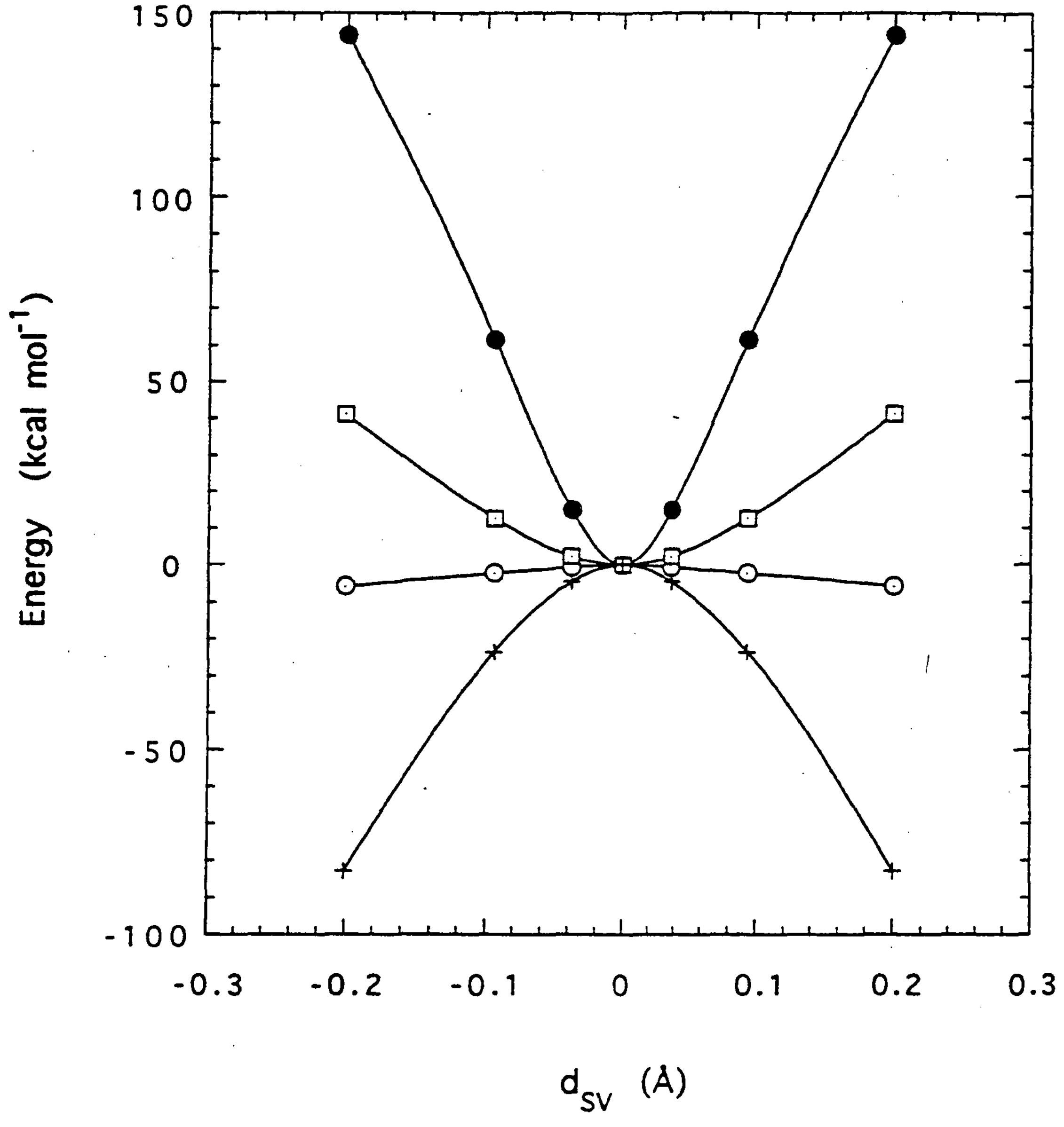
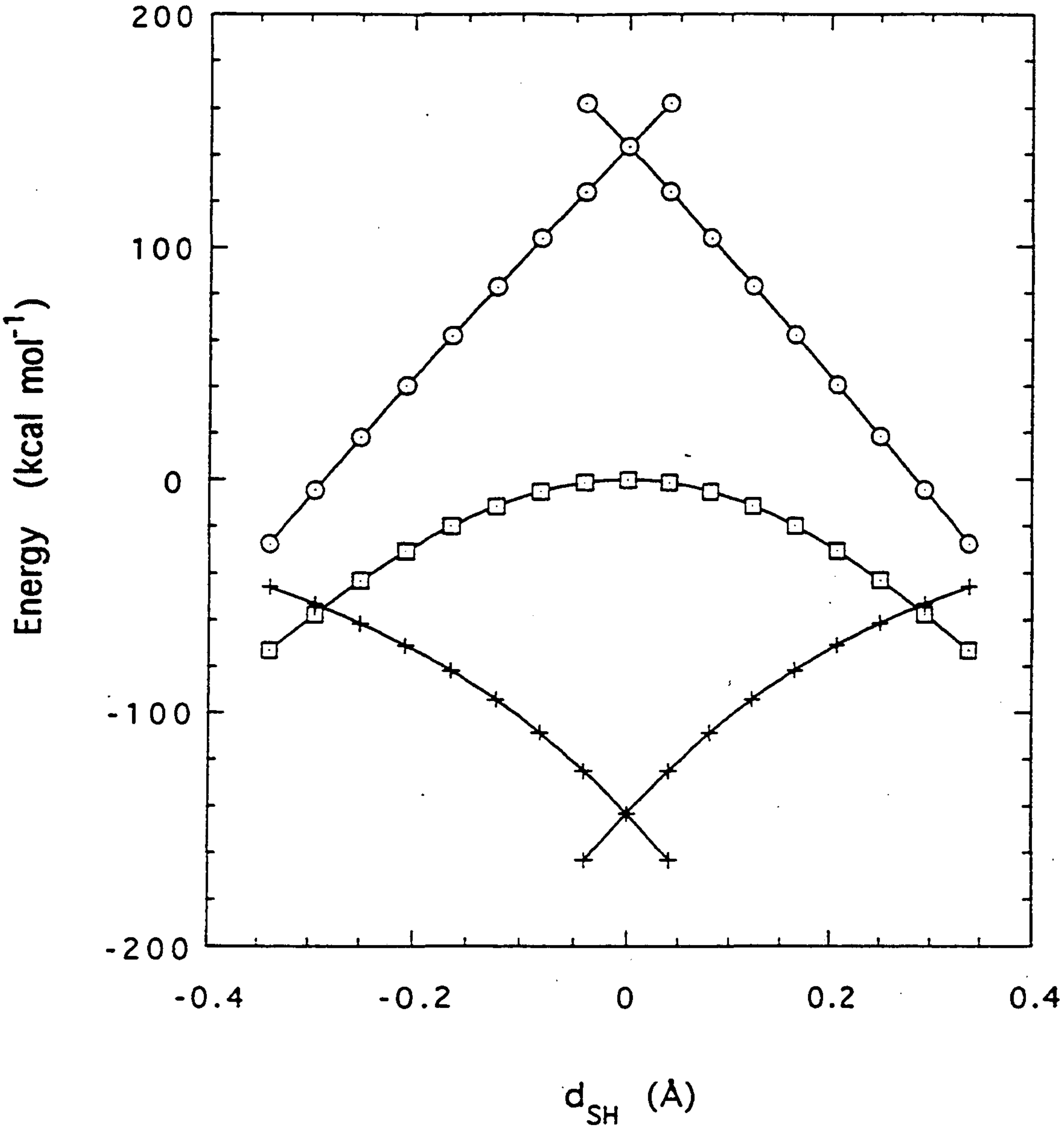
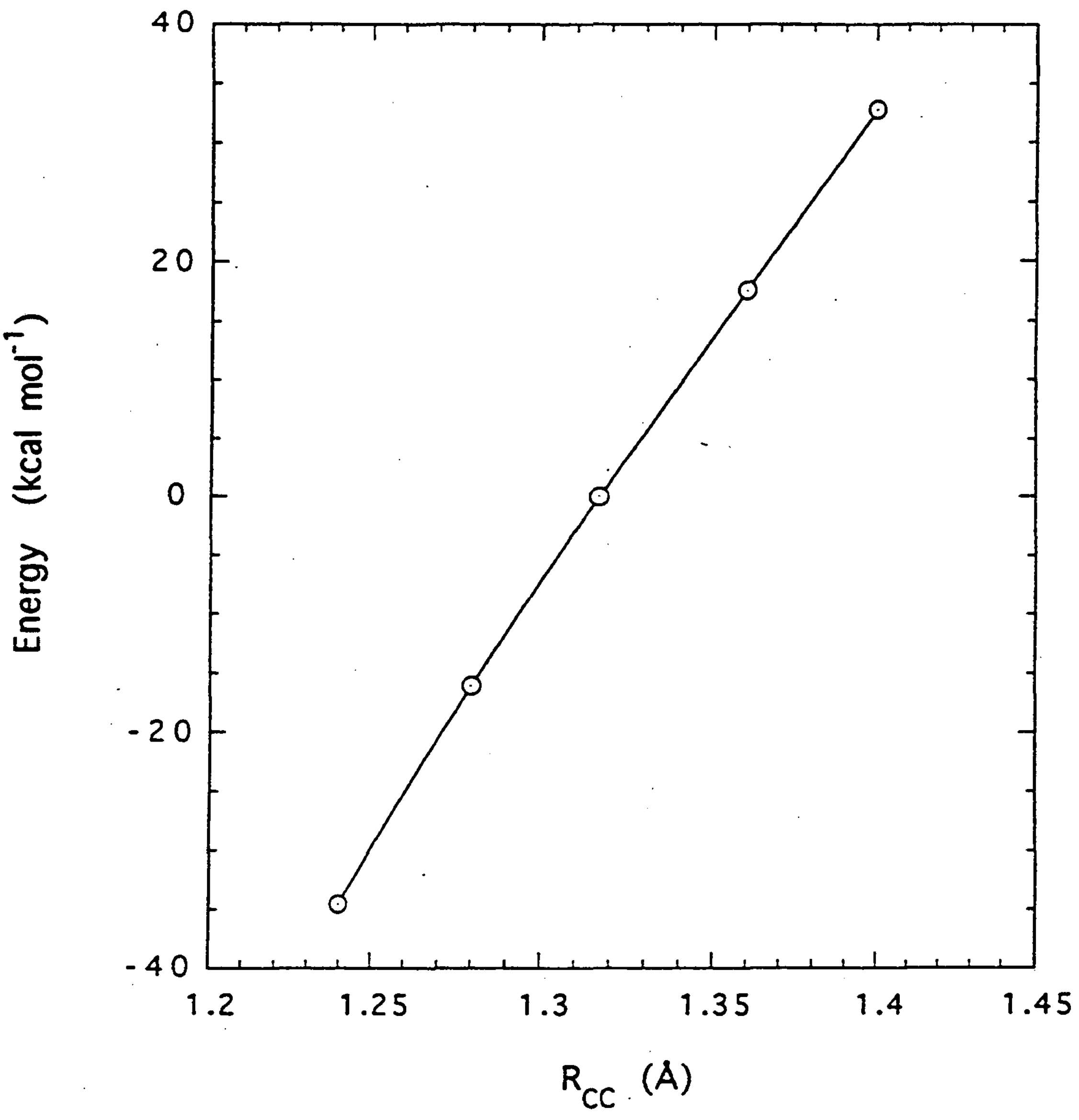
200
150
100
50
0
-50
Energy (kcal mol^{-1})
-0.3
-0.2
-0.1
0
0.1
0.2
0.3
d_{SV} (Å)
$E_\pi^{(deloc)}$



100
50
0
-50
-100
-150
-200
Energy (kcal mol^{-1})
-0.4
-0.2
0
0.2
0.4
d_{SH} (Å)


150
100
50
0
-50
-100
Energy (kcal mol^{-1})
-0.3
-0.2
-0.1
0
0.1
0.2
0.3
d_{SV} (Å)


200
100
0
-100
-200
Energy (kcal mol^{-1})
-0.4
-0.2
0
0.2
0.4
d_{SH} (Å)


40
20
0
-20
-40
Energy (kcal mol^{-1})
1.2
1.25
1.3
1.35
1.4
1.45
R_{CC} (Å)

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