Resolving a Puzzling Anomaly in the SCGVB Description of Benzene

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ABSTRACT

In an earlier study of benzene Small and Head-Gordon found that the SCGVB wave function for the π system predicted a distorted (non-D_{6h}) geometry, one with alternating CC bond lengths. However, the variations in the energy were very small and the predictions were made using a very small basis set (STO-3G). We re-examined this prediction using a much larger basis set (aug-cc-pVTZ) to determine the dependence of the energy of benzene on the distortion angle, $\Delta\theta_{CXC}$ ($\Delta\theta_{CXC} = 0^{\circ}$ corresponds to the D_{6h} structure). We also found a distorted geometry with the optimum $\Delta\theta_{CXC}$ being 0.31˚ with an energy 0.040 kcal mol^{-1} lower than that for the D_{6h} structure. In the optimum geometry, adjacent CC bond lengths are 1.3861 Å and 1.4004 Å. Analysis of the SCGVB wave function led us to conclude that the cause of the unusual non-D_{6h} geometry predicted by the SCGVB calculations seems to be a result of the interaction between the Kekulé and Dewar components of the full SCGVB wave function. The addition of doubly ionic configurations to the SCGVB wave function leads to the prediction of a D_{6h} geometry for benzene and a dependence on $\Delta\theta_{CXC}$ essentially the same as that predicted by the CASSCF wave function.

Introduction

The concept of aromaticity is one of the key concepts in organic chemistry and has profound implications for the structures and reactivities of organic molecules. The prototype aromatic molecule, benzene, is planar with all of the CC bonds of equal length—a D_{6h} structure. Traditionally, the D_{6h} structure of benzene is attributed to aromaticity, i.e., resonance between the two Kekulé structures of benzene. More recently, there has been a spirited debate in the literature about the role played by the σ and π bonds in determining the symmetric structure of benzene. Shaik and coworkers have argued that the electrons in the π orbitals of benzene favor a geometry with unequal bond lengths and that the hexagonal structure of benzene is a result of the σ bonds (see the summary of these discussions in Ref. 1). Given the importance of benzene in organic chemistry, it is not surprising that others addressed this question, reporting evidence to the contrary; see, e.g., Glendening et al.[2] However, definitive statements as to the role of the σ and π bonds in determining the structure of benzene requires their contributions to the total energy to be cleanly separated and, even for the simplest level of theory, i.e., Restricted Hartree-Fock (RHF) theory, there are terms in the energy that couple the σ and π orbitals ($J_{\sigma\pi}$, $K_{\sigma\pi}$).

Against this backdrop, Small and Head-Gordon[3] reported that a Spin-Coupled Generalized Valence Bond (SCGVB) wave function that kept the σ orbitals doubly occupied but included all possible spin functions for the six electrons in the six SCGVB π orbitals predicted a structure for benzene that has alternating CC bond lengths. However, the basis set used in that study was very small (STO-3G) as was the

predicted energy lowering (less than 0.05 kcal mol^{-1}). Nonetheless, this is a surprising result given that the SCGVB wave function for the electrons in the π orbitals of benzene includes the two Kekulé spin coupling modes plus the three Dewar (para-bonded) spin coupling modes, which, taken together, treat the CC bonds symmetrically. Thus, it is surprising that the SCGVB wave function predicts a non-D_{6h} structure for benzene. We note that the topic of symmetry breaking in the benzene molecule has also been investigated for a variety of SCGVB-related methodologies by Van Voorhis and Head-Gordon,[4,5] Lawler, Beran and Head-Gordon,[6] and Parkhill and Head-Gordon.[7]

The current paper reports high level calculations on the benzene molecule using the RHF, SCGVB, CASSCF and CCSD(T) methods. For the latter method, calculations are reported for correlating the electrons in the π system as well as the full valence ($\sigma + \pi$) system. A much larger basis set was used in these studies than in Ref. 3: the aug-cc-pVTZ basis sets for the carbon and hydrogen atoms.[8,9] The aug-cc-pVTZ basis sets are expected to yield results close to the complete basis set limit for the RHF, SCGVB and CASSCF methods.

Theoretical Methods

The SCGVB wavefunction considered here for the six electrons in the π system of the benzene molecule is:

$$\Psi_{\mathrm{SCGVB}} = \hat{\mathcal{A}}\varphi_{\mathrm{C}\pi_1}\varphi_{\mathrm{C}\pi_2}\varphi_{\mathrm{C}\pi_3}\varphi_{\mathrm{C}\pi_4}\varphi_{\mathrm{C}\pi_5}\varphi_{\mathrm{C}\pi_6}\Theta^6_{0,0} \quad (1)$$

The σ orbitals are taken to be doubly occupied in the wave function and are not listed in Eq. (1). The set of orbitals in Eq. (1), $\{\varphi_{\mathrm{C}\pi_i}\}$, are the six singly occupied carbon π orbitals, one for each electron. The spin function for the six electrons in the six carbon π orbitals, $\Theta^6_{0,0}$, is a linear combination of the five linearly independent ways that the spins of these six electrons can be coupled to yield a state with $S = 0$ and $M_S = 0$.[10] Using the Rumer spin functions, these spin couplings correspond to the two Kekulé spin couplings and the three Dewar (para-bonded) spin couplings. In the SCGVB calculation all of the orbitals, including the doubly occupied σ orbitals, as well as the coefficients of the five spin functions are fully optimized.

We also considered three additional wave functions for the electrons in the π orbitals: (1) the restricted Hartree-Fock (RHF) wave function,[11] which restricts the π orbitals to be doubly occupied; (2) the Complete Active Space Self-Consistent Field (CASSCF) wave function,[12] which includes all of the configurations generated by distributing the six electrons in the six π orbitals (i.e., full configuration interaction in that space); and (3) a CCSD(T) wave function[13,14] correlating only the electrons in the π system, leaving the orbitals in the σ system doubly occupied. We also report the results of CCSD(T) calculations for all of the valence electrons to help establish the "ground truth" for the variation of the energy of benzene with the distortion angle.

Following the approach used by Small and Head-Gordon,[3] see also Lawler et al.,[15] we define a deformation angle, $\Delta\theta_{\mathrm{CXC}}$, which is a measure of the deviation from the D_{6h} structure of benzene. A value of $\Delta\theta_{\mathrm{CXC}} = 0^\circ$ corresponds to the D_{6h} structure, while a non-zero value of $\Delta\theta_{\mathrm{CXC}}$ gives adjacent bond angles of $\Delta\theta_{\mathrm{CXC+}} = (60^\circ + \Delta\theta_{\mathrm{CXC}})$ and $\Delta\theta_{\mathrm{CXC-}} = (60^\circ - \Delta\theta_{\mathrm{CXC}})$; see Figure 1. The resulting adjacent CC bond lengths are given by $R_{\mathrm{CC+}} = 2R_{\mathrm{CX}}\sin(\frac{1}{2}\theta_{\mathrm{CXC+}})$ and $R_{\mathrm{CC-}} = 2R_{\mathrm{CX}}\sin(\frac{1}{2}\theta_{\mathrm{CXC-}})$. Note that for D_{6h} geometries, $R_{\mathrm{CC}} = R_{\mathrm{CX}}$.

Most of the calculations presented in this study were performed with the Molpro suite of quantum chemical programs (version 2010.1).[16,17] In particular, the CASVB module in Molpro was used to perform most of the SCGVB calculations[18,19] with additional results obtained using an older program.[20]

Results and Discussion

In Table 1, we list the CC and CH bond lengths, total energies, and energy differences, relative to the SCGVB energy, for the aug-cc-pVTZ basis sets at $\Delta\theta_{CXC} = 0^{\circ}$. The first four calculations in this table refer to calculations on the π system of benzene; the last calculation includes all of the electrons in the valence orbitals. For each of the methods of interest we optimized R_{CX} and R_{CH} for $\Delta\theta_{CXC} = 0^{\circ}$, with $R_{CC} = R_{CX}$.

The variation in R_{CH} is very modest for all of the methods that treated only the π system: RHF (1.0733 Å), SCGVB (1.0732 Å), CASSCF (1.0733 Å), and CCSD(T) (1.0734 Å). As expected, the variation in R_{CX} was somewhat larger, with the RHF method predicting R_{CX} = 1.3829 Å and the SCGVB and CASSCF methods predicting 1.3931 Å and 1.3921 Å, respectively. The CCSD(T) calculations on the π system predicted a value of R_{CX} in between these three values, 1.3888 Å, i.e., a longer bond than predicted by the RHF calculations and a shorter bond than predicted by the SCGVB and CASSCF calculations. The CCSD(T) calculations for the full valence space, ($\sigma + \pi$), predicted larger values for both R_{CH} (1.0839 Å) and R_{CX} (1.3980 Å).

The energy of the RHF wave function is 39.4 kcal mol^{-1} higher than that of the SCGVB wave function. This is a measure of the non-dynamical correlation energy in the π system of benzene. The CASSCF energy, on the other hand, is only 4.8 kcal mol^{-1} lower than the SCGVB energy. Thus, the SCGVB wave function accounts for 89.1% of the difference between the CASSCF and RHF energies, very similar to the 89.6% reported by Karadakov and Cooper for the 6-311G(d,p) basis set.[21] The CCSD(T) calculations for the π system of benzene yielded an energy 33.9 kcal mol^{-1} lower than the SCGVB energy. This is a measure of the dynamical correlation energy of the benzene π system. Thus, in this case the non-dynamical correlation energy is slightly larger than the dynamical correlation energy. For comparison, the CCSD(T) calculations on the full valence ($\sigma + \pi$) system gives an energy that is 578.1 kcal mol^{-1} lower than the CCSD(T) calculation on the π system alone.

One of the SCGVB π orbitals in benzene is plotted in Figure 2. The other five orbitals can be obtained by rotating this orbital around the ring in 60° increments. This orbital is very similar to the SCGVB orbitals reported earlier for benzene by the Gerratt group.[22-25] As can be seen, the SCGVB π orbital it is largely localized on one of the carbon atoms, but is polarized toward the carbon atoms on each side of that atom. In this way the SCGVB π orbitals of benzene reflect the bonding motif found in the Kekulé spin couplings, where each carbon atom is bonded to both neighboring carbon atoms in the combined Kekulé spin couplings.

Figure 3 is a plot of the relative energies of the distorted benzene molecule, referenced to the energy at $\Delta\theta_{CXC} = 0^{\circ}$ (D_{6h} symmetry) for the RHF, SCGVB, CASSCF and CCSD(T) calculations on the π system with the values of R_{CX} and R_{CH} fixed at the optimum values for $\Delta\theta_{CXC} = 0^{\circ}$. Note that the curves from the RHF and CASSCF calculations are virtually on top of one another. We also carried out full valence CCSD(T) calculations as a function of $\Delta\theta_{CXC}$; the resulting curve is essentially indistinguishable from that for the CCSD(T) calculations on the π system only and, therefore, is not shown. The first feature to note is that the energies of the RHF, CASSCF and CCSD(T) wave functions increase monotonically with increasing $\Delta\theta_{CXC}$, i.e., the optimum geometries are for $\Delta\theta_{CXC} = 0^{\circ}$, yielding a D_{6h} geometry for benzene. The curves for the RHF and CASSCF calculations lie essentially on top of one another, while that for the CCSD(T) calculations is only slightly higher. The energy of the SCGVB wave function, on the other hand, initially decreases with increasing $\Delta\theta_{CXC}$, having a minimum of -0.040 kcal mol^{-1} at $\Delta\theta_{CXC} = 0.31^{\circ}$. The resulting optimum bond lengths are: R_{CC+} = 1.4004 Å and R_{CC-} = 1.3861 Å, i.e., a difference of ΔR_e = 0.0143 Å. This is in basic agreement with the findings of Small and Head-Gordon,[3] who reported a minimum of approximately -0.047 kcal mol^{-1} at $\Delta\theta_{CXC} \approx 0.39^{\circ}$.

We also carried out SCGVB calculations that optimized R_{CX} and R_{CH} for each distortion angle, $\Delta\theta_{CXC}$. The changes in R_{CX} and R_{CH} were sufficiently small, e.g., ~10^{-4} Å for R_{CX} and ~10^{-6} Å for R_{CH} at $\Delta\theta_{CXC}$ = 0.31˚, that any changes from the results described above were negligible.

To gain insights into the underlying reason or reasons that the SCGVB calculations predict a non-D_{6h} structure for benzene, we first calculated the difference between the energies of the CASSCF and SCGVB wave functions as a function of $\Delta\theta_{CXC}$. This difference is plotted in Figure 4 and provides no obvious reason for the unusual dependence of the SCGVB energy on distortion angle: the energy difference increases steadily from $\Delta\theta_{CXC}$ = 0˚ to $\Delta\theta_{CXC}$ = 1˚, increasing nearly linearly in the vicinity of $\Delta\theta_{CXC}$ = 0.31˚.

Next, we calculated separately the energies of the Kekulé and Dewar components of the SCGVB wave function using the optimum SCGVB orbitals for each distortion angle. The energies of the resulting SCGVB(Kekulé) and SCGVB(Dewar) wave functions increase with increasing $\Delta\theta_{CXC}$, predicting a D_{6h} geometry for benzene, although their behavior near $\Delta\theta_{CXC}$ = 0˚ is certainly unusual (see Figure 5). Given that, individually, the two components of the full SCGVB wave function predict that benzene has a D_{6h} geometry, we are led to conclude that the cause of the unusual non-D_{6h} geometry predicted by the SCGVB calculations seems to be a result of the interaction between the Kekulé and Dewar components of the full SCGVB wave function.

We then calculated the interaction between the Kekulé and Dewar components of the SCGVB wave function (H_{12}) as well as the overlap of these components (S_{12}). These results, as a function of the distortion angle, are plotted in Figure 6. Again, there is little hint in these plots about the cause of the non-D_{6h} geometry of benzene predicted by the SCGVB wave function, although the magnitude of the overlap of the Kekulé and Dewar components (0.992–0.980) is surprisingly large and may be implicated in the unusual prediction of the non-symmetric structure for benzene. With this in mind, we also examined the energy of the orthogonal complement to the Kekulé space and the value of the corresponding off-diagonal Hamiltonian matrix element. We found for both quantities that the variation with distortion angle, $\Delta\theta_{CXC}$, is smooth and monotonic with no unusual features near either $\Delta\theta_{CXC}$ = 0˚ or $\Delta\theta_{CXC}$ = 0.31˚.

Finally, we investigated the addition of ionic terms to the SCGVB wave function, a topic explored earlier by Van Voorhis and Head-Gordon.[5] As first noted by Coulson and Fischer,[26] the SCGVB wave function largely accounts for singly ionic structures, so that the first ionic configurations of importance are the doubly ionic ones. If we simply add the doubly ionic configurations to the SCGVB wave function, we obtain the dashed curve in Figure 7, which has a remarkable resemblance to the corresponding curve for the Kekulé wave function in Figure 5. The energy of this wave function at the D_{6h} geometry is 0.47 kcal/mol higher than the CASSCF energy. If we optimize the orbitals for the SCGVB+(*ion*=2) wave function, the energy decreases to -230.852311 hartrees, which is 0.30 kcal/mol higher than the CASSCF energy. Furthermore, the SCGVB+(*ion*=2) wave function predicts that benzene has a D_{6h} geometry. In fact, the dependence of the energy on distortion angle for the SCGVB+(*ion*=2) wave function, see Figure 7, is essentially identical to that for the CASSCF wave function, differing by just 0.009 kcal/mol at $\Delta\theta_{CXC}$ = 1˚. Clearly, higher ionic configurations make only minor improvements to the SCGVB+(*ion*=2) wave function. Further numerical experiments indicated that the *ion*=2 structures in which the negative charges are *para* to one another are of particular importance in reproducing the correct dependence of the energy on $\Delta\theta_{CXC}$.

Conclusions

Small and Head-Gordon[3] found that the SCGVB wave function for benzene predicted a non-D_{6h}

geometry, a surprising result given that the combinations of the Kekulé and Dewar spin couplings in the SCGVB wave function can describe all CC bonds equally. The distortion from a D_{6h} geometry was very small ($\Delta\theta_{CXC}$ = 0.39˚) as was the energy lowering, ΔE = -0.047 kcal mol^{-1}. Since those calculations used a very small basis set for the carbon and hydrogen atoms (STO-3G), we decided to repeat this study, obtaining similar results with an aug-cc-pVTZ basis set, namely, $\Delta\theta_{CXC}$ = 0.31˚ and ΔE = -0.040 kcal mol^{-1}. The aug-cc-pVTZ basis set should provide results very close to the complete basis set limit for the SCGVB method, so this puzzling anomaly is an inherent feature of the SCGVB description of benzene.

In an attempt to understand the reason for this unusual prediction by the SCGVB method, we separated the full SCGVB wave function into its two components, the two Kekulé and three Dewar modes of spin coupling, and determined the dependence of the energies of these two components on the distortion angle, $\Delta\theta_{CXC}$, using the optimum SCGVB orbitals for that angle. We found that the Kekulé and Dewar energies increased with increasing $\Delta\theta_{CXC}$, predicting that benzene has a D_{6h} geometry, although the behavior of the resulting curves near $\Delta\theta_{CXC}$ = 0˚ was unusual and unexpected. These results indicate that the non-D_{6h} geometry predicted by the SCGVB calculations could be a result of the interaction between the Kekulé and Dewar components of the full SCGVB wave function. However, examination of the dependence of this interaction, as well as the overlap of the two components, did not provide any insights into the underlying cause of this curious anomaly in the SCGVB description of benzene.

In agreement with Van Voorhis and Head-Gordon,[5] we found that adding the doubly ionic configurations to the SCGVB wave function (the singly ionic configurations are already largely subsumed in the SCGVB wave function) led to the prediction of a D_{6h} geometry for benzene. In fact, if the orbitals in the SCGVB + (*ion*=2) wave function are optimized, the total energy as well as the energies as a function of distortion angle, $\Delta\theta_{CXC}$, are essentially identical to those of the CASSCF wave function. The addition of the doubly excited configurations to the SCGVB wave function clearly corrects the deficiencies in the SCGVB description of benzene, although the orbitals must be reoptimized. Analyzing the doubly ionic configurations contributing to the SCGVB + (*ion*=2) wave function, we found that those configurations with the negative charges *para* to one another were of particular importance in reproducing the correct dependence of the energy on $\Delta\theta_{CXC}$.

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Keywords: SCGVB, Benzene, Non-D_{6h} structure, Kekulé Structures, Dewar Structures

References and Notes

1. S. Shaik, A. Shurki, D. Danovich, P. C Hiberty, *J. Molec. Struct. (Theochem)* **1997**, *398-399*, 155-167.
2. E. D. Glendening, R. Faust, A. Streitwieser, K. P. C Vollhardt, F. Weinhold, *J. Am. Chem. Soc.* **1993**, *115*, 10952-10957.
3. D. W. Small, M. Head-Gordon, *Phys. Chem. Chem. Phys.* **2011**, *13*, 19285-19297.
4. T. Van Voorhis, M. Head-Gordon, *J. Chem. Phys.* **2000**, *112*, 5633-5638.

5. T. Van Voorhis, M. Head-Gordon, *Chem. Phys. Lett.* **2000**, *317*, 575-580.
6. K. V. Lawler, G. J. O. Beran, M. Head-Gordon, *J. Chem. Phys.* **2008**, *128*, 024107.
7. J. A. Parkhill and M. Head-Gordon, *J. Chem. Phys.* **2010**, *133*, 024103.
8. T. H. Dunning, Jr. *J. Chem. Phys.* **1989**, *90*, 1007-1023.
9. R. A. Kendall, T. H. Dunning, Jr., R. J. Harrison, *J. Chem. Phys.* **1992**, *96*, 6796-6806.
10. Pauncz, R. *Spin Eigenfunctions, Construction and Use*; Springer US: Boston, 1979.
11. C. C. J. Roothaan, *Rev. Mod. Phys.* **1951**, *23*, 69-89.
12. B. O. Roos, *Adv. Chem. Phys.* **1987**, *69*, 399-445.
13. R. J. Bartlett, M. Musial, *Rev. Mod. Phys.* **2007**, *79*, 291-352.
14. K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **1989**, *157*, 479-483.
15. K. V. Lawler, G. J. O Beran, M. Head-Gordon, *J. Chem. Phys.* **2008**, *128*, 024107.
16. *Molpro, version 2010.1,* a package of ab initio programs, H-J. Werner, P. J. Knowles, R. D. Amos, A. Bernhardsson, A. Berning, P. Celani, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, T. Korona, R. Lindh, A. W. Lloyd, S. J. McNicholas, F. Manby, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, G. Rauhut, M. Schütz, U. Schumann, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang, see http://www.molpro.net.
17. H-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, *WIREs Comput Mol Sci* **2011**, *2*, 242-253.
18. T. Thorsteinsson, D. L. Cooper, J. Gerratt, P. B. Karadakov, M. Raimondi, *Theoret. Chim. Acta* **1996**, *93*, 343-366.
19. D. L. Cooper, T. Thorsteinsson, J. Gerratt, *Int. J. Quant. Chem.* **1997**, *65*, 439-451.
20. D. L. Cooper, J. Gerratt, M. Raimondi, M. Sironi, T. Thorsteinsson, *Theor. Chim. Acta* **1993**, *85*, 261-270.
21. P. B. Karadakov, D. L. Cooper, *Theor. Chem. Acc.* **2014**, *133*, 1421.
22. D. L. Cooper, J. Gerratt, M. Raimondi, *Nature* **1986**, *323*, 699-701.
23. G. Raos, J. Gerratt, D. L. Cooper, M. Raimondi, *Chem. Phys.* **1994**, *186*, 233-250.
24. G. Raos, J. Gerratt, P. B. Karadakov, D. L. Cooper, *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 4011-4030.
25. G. Raos, J. Gerratt, P. B. Karadakov, D. L. Cooper, *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 4011-4030.
26. C. A. Coulson, I. Fischer, *Philos. Mag.* **1949**, *40*, 386-393.

GRAPHICAL ABSTRACT

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Resolving A Puzzling Anomaly in the SCGVB Description of Benzene

One of the six SCGVB π orbitals of benzene

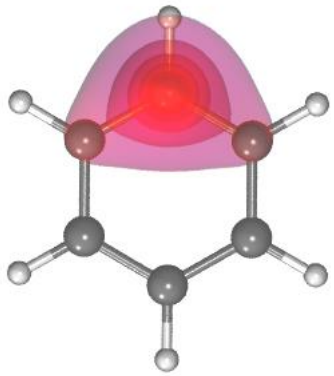

Table 1. Structure and energies for the RHF, SCGVB, CASSCF and CCSD(T) wave functions of benzene (in hartrees) at $\Delta\theta_{CXC} = 0^{\circ}$. Distances ($R_{CC}$, R_{CH}) are in Ångstroms, and total energies (E_h) are in hartrees. Except for the last row, the relative energies are with respect to the SCGVB energy and are in kcal mol^{-1}. Basis set: aug-cc-pVTZ.

	Method	$R_{CC} = R_{CX}$	R_{CH}	E_h	ΔE
π-System Only[a]	RHF	1.3829	1.0733	-230.782351	39.40
	SCGVB	1.3931	1.0732	-230.845140	0.0
	CASSCF	1.3921	1.0733	-230.852789	-4.80
	CCSD(T)	1.3888	1.0734	-230.899220	-33.94
Full Valence	CCSD(T)	1.3980	1.0839	-231.820465	-578.09[b]

[a] All of the electrons were included in the π-System Only calculations, although the σ orbitals were kept doubly occupied.

[b] Relative to the CCSD(T) calculations for the π-System Only.

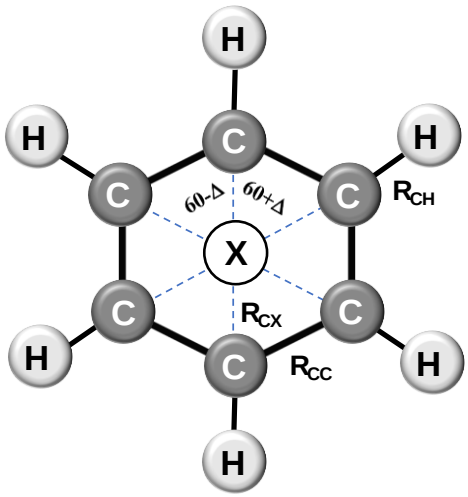

Figure 1. Definition of geometrical parameters for benzene.

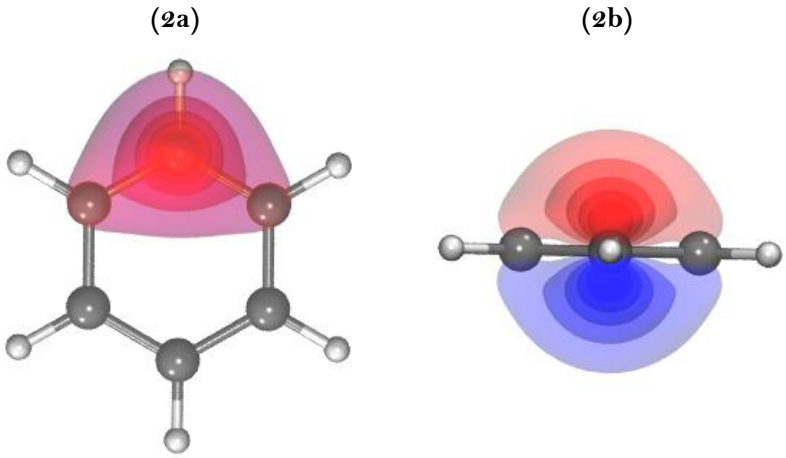

Figure 2. Contour plots of one of the six SCGVB π orbitals for benzene: (2a) top view of the orbital and (2b) side view of the orbital. Contours are shown from 0.05 to 0.25 in increments of 0.05.

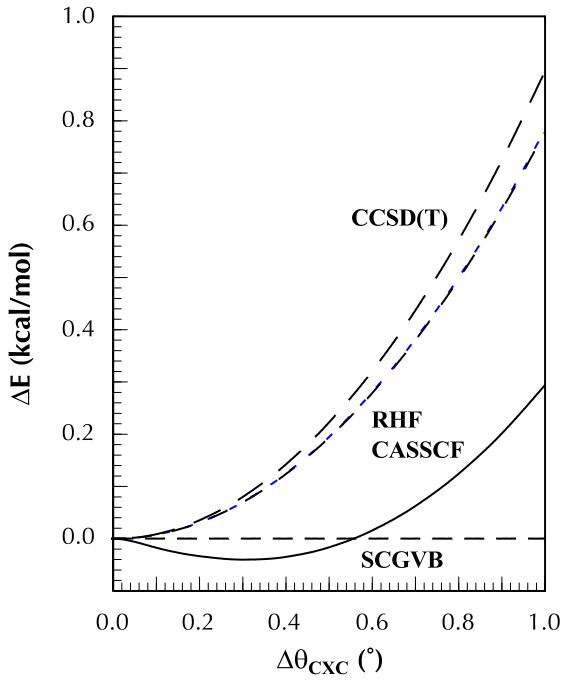

Figure 3. Variation of ΔE with the distortion angle, $\Delta\theta_{CXC}$, for the RHF, SCGVB, CASSCF and CCSD(T) wave functions for the π system. (R_{CX}, R_{CH}) have been fixed at the optimum values for each method at $\Delta\theta_{CXC} = 0^{\circ}$.

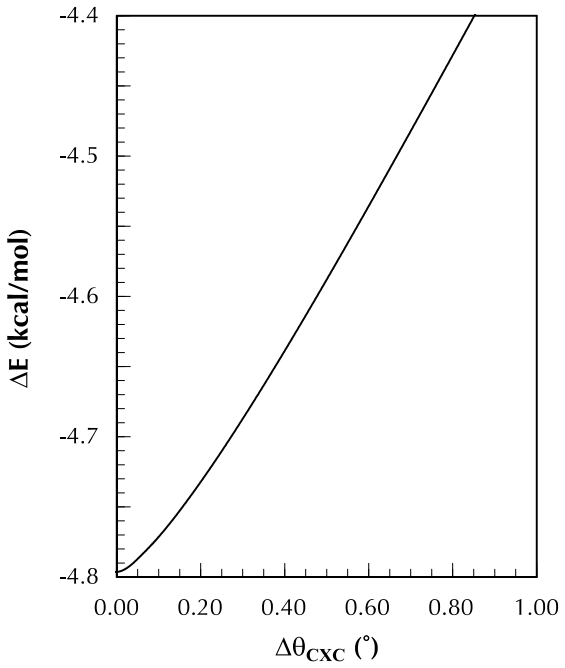

Figure 4. The difference in the CASSCF and SCGVB energies as a function of the distortion angle, $\Delta\theta_{CXC}$. (R_{CX}, R_{CH}) have been fixed at the optimum values for each method at $\Delta\theta_{CXC} = 0^{\circ}$.

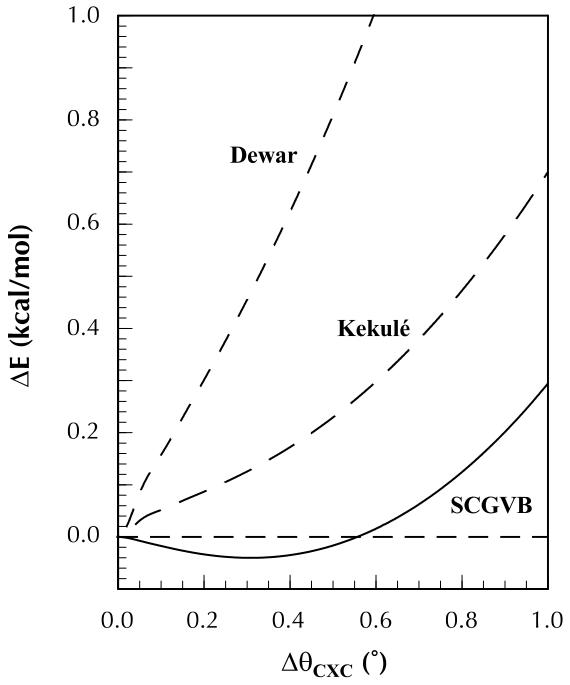

Figure 5. Variation of ΔE with the distortion angle, $\Delta\theta_{CXC}$, for the SCGVB wave function and its Kekulé and Dewar components. The optimum orbitals from the full SCGVB calculations are used in all calculations.

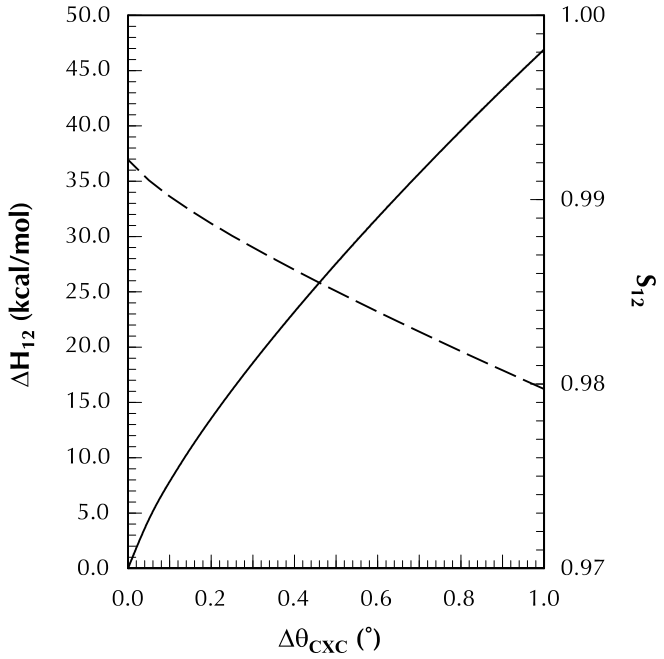

Figure 6. Dependence on distortion angle, $\Delta\theta_{CXC}$, of the variation in the interaction energy, ΔH_{12} (solid line), and overlap, S_{12} (dashed line), for the Kekulé and Dewar components of the benzene SCGVB wave function.

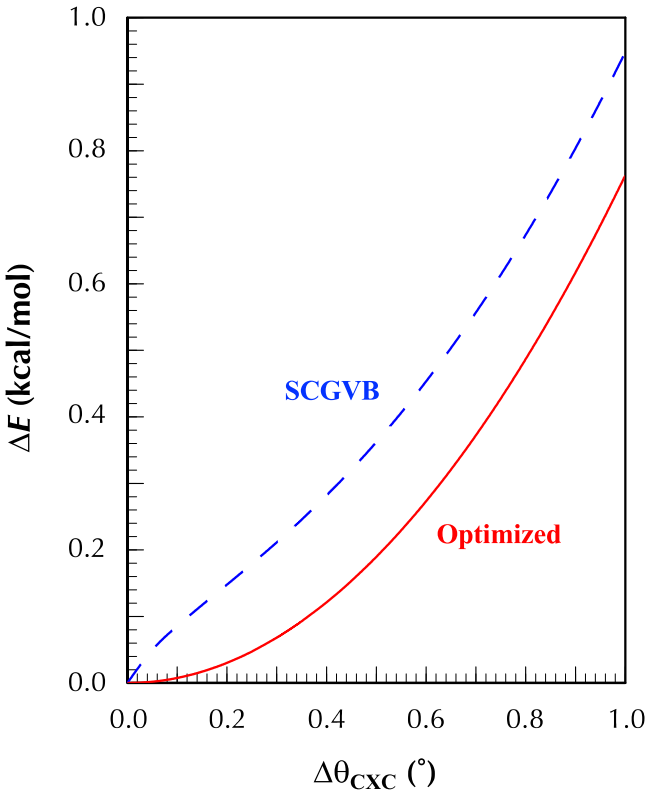

Figure 7. Variation of ΔE with the distortion angle, $\Delta\theta_{CXC}$, for the SCGVB+(*ion*=2) wave function with SCGVB orbitals (blue, dashed) and SCGVB+(*ion*=2) wave function with optimized orbitals (red, solid).