The most obvious explanation for a more contracted d orbital is a higher effective nuclear charge on Ti. A higher effective nuclear charge on $TiCl_2Be_4$ than $Ti(CH_3)_2Be_4$ could arise from the electronegative difference between Cl and CH_3. Thus, the Cl ligand withdraws more electrons in forming more polar Ti–Cl bonds. In other words the closed-shell CH_3^- ligand is a better σ donor than the Cl^- ligand. Recently, Cioslowski and co-workers[19] compared three methods of population analysis on three inorganic molecules, using a variety of basis sets to determine which method gave the best (most stable) results. Their conclusion suggested that the Bader topological analysis of molecular charge densities[20-26] is the most stable and reliable. We used this method to determine the total charge within the Ti atomic basin. The integrated electron count was 21.13 and 21.04 electrons on $Ti(CH_3)_2Be_4$ and $TiCl_2Be_4$, respectively. Although not a large difference the additional 0.1 electron on the CH_3 derivative contributes to the expansion of the d orbital as shown in Figure 2.

Summary

Experimentally, $Ti(CH_3)_2(dmpe)_2$ has a singlet ground state while the similar $TiCl_2(dmpe)_2$ has a triplet ground state. Simple orbital splitting arguments suggest that if these molecules have different ground states $Ti(CH_3)_2(dmpe)_2$ should have a triplet ground state and $TiCl_2(dmpe)_2$ a singlet ground state. In order to predict this behavior in a semiquantitative fashion one must include a significant fraction of the d electron dynamical correlation. The most efficient approach to this appears to be a large CISD from an SCF solution in a reasonably large basis set which includes at least one f function. Physically, the origin of the difference between these compounds arises from a difference in the magnitude of the electron–electron repulsion which is reflected in the d orbital size. In ligand field terms this difference would be ascribed to the nephelauxetic effect. Thus, the Cl ligand in $TiCl_2(dmpe)_2$ withdraws more charge from Ti than the CH_3 ligand in $Ti(CH_3)_2(dmpe)_2$. The resulting higher effective nuclear charge causes the Ti orbitals on $TiCl_2(dmpe)_2$ to be more contracted. Therefore, the singlet state is disfavored in $TiCl_2(dmpe)_2$ but favored in $Ti(CH_3)_2(dmpe)_2$ which has weaker d electron repulsions.

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Stabilization Calculations on the π^* Anion States of 1,4-Cyclohexadiene: Confirmation of the π_-^* below π_+^* Orbital Ordering

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Abstract: The stabilization method is used to calculate the energies of the π^* anion states of 1,4-cyclohexadiene. These calculations show that the ground state anion is ^2A_u while the first excited state anion is $^2B_{2g}$. This order of the anion states is opposite that which would prevail were only through-space interactions present and is due to the domination of through-bond interactions. Stabilization calculations at Koopmans' theorem and single excitation CI levels of theory give splittings of 1.20 and 0.89 eV, respectively, as compared to the 0.92 eV splitting found experimentally.

I. Introduction

1,4-Cyclohexadiene (CHD) is a classic example of a species in which both through-bond (TB) and through-space (TS) interactions[1] are important. It is now well-established that TB interactions dominate over TS interactions in the occupied orbital space of CHD, causing the the b_{1u} (π_+) orbital to lie above the b_{3g} (π_-) orbital.[2,3] (The symmetry labeling of the orbitals is based on a molecular orientation with the carbon atoms lying in the *xz* plane and the methylene groups lying in the *xy* plane.) This inversion of the π orbitals relative to their "natural", i.e., TS, ordering is due to the strong hyperconjugative TB mixing of the

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π_+ orbital with the CH_2 pseudo-π orbitals. The π_- orbital, for reasons of symmetry, does not mix with the CH_2 pseudo-π orbitals. The inversion of the π levels of CHD has been confirmed by MO calculations and photoelectron spectroscopy.[2,3]

The situation regarding the π^* levels of CHD is less clear. Hoffmann proposed that the π^* levels are inverted, i.e., are ordered a_u (π_-^*) below b_{2g} (π_+^*).[1] Jordan, Michejda, and Burrow[4] have reported the electron transmission (ET) spectrum of CHD. The vertical electron attachment energies (the negatives of the electron affinities) of CHD as determined from the ET spectrum are 1.75 and 2.67 eV. Based on the comparison of the vertical attachment energies (AE) of ethylene (1.74 eV), *cis*-2-butene (2.22 eV), cyclohexene (2.07 eV), and CHD, Jordan et al. concluded that the anion states (and hence the π^* orbitals) of CHD have the natural ordering (i.e., π_+^* below π_-^*). The crux of their agrument follows.

ET measurements indicate that the π^* anion state of *cis*-2-butene is destabilized (relative to that of ethylene) by 0.48 eV. A perturbation molecular orbital (PMO) analysis indicates that the TB destabilization of the π_+^* level of CHD should be approximately twice as large as the hyderconjugative destabilization of the π^* orbital of *cis*-2-butene.[5] The PMO model therefore leads one to expect the TB coupling with the CH_2 pseudo-π orbitals to cause about a 1.0-eV destabilization of the π_+^* orbital of CHD (relative to the energy it would have if only TS interactions were present). Because the TS splitting between the ethylenic π^* orbitals of CHD is about 1.3 eV,[6] the TB destabilization of the π_+^* orbital would have to be at least 1.5 eV, about 50% larger than that predicted by the PMO model, to be consistent with the π_+^* anion state being at 2.67 eV. In addition, because an inverted sequence requires the π_-^* level to be at 1.75 eV (approximately degenerate with the π^* level of ethylene), there would have to be an interaction which compensates for the TS destabilization of the π_-^* level. However, such an interaction was not anticipated. These considerations led Jordan et al. to conclude that the π^* levels of CHD have the natural ordering.

In the years since the paper of Jordan et al., several papers have appeared which argue that the π^* levels of CHD are ordered π_-^* below π_+^*. Doering and McDiarmid have carried out an electron energy loss study of the $\pi \rightarrow \pi^*$ excited states of CHD and, based on the intensities of the various transitions, have argued that the π_-^* level is below π_+^*.[7] On the basis of the trends in the experimental AE's of CHD, γ-pyran, and 1,4-dioxin, Modelli at al. concluded that the ordering is π_-^* below π_+^* in all three compounds.[8]

Although Hartree–Fock (HF) calculations on neutral CHD using the STO-3G basis set place the π_+^* orbital just below the π_-^* orbital,[6,9] HF calculations with the more flexible 3-21 G and Dunning split-valence basis sets place the π_-^* orbital 0.35 and 0.95 eV, respectively, below the π_+^* orbital.[9,10] Calculations using the HAM-3 semiempirical method also give π_-^* below π_+^*.[11]

In spite of the growing body of evidence that the π^* levels of CHD are inverted, in our view none of this evidence can be considered definitive. The order of the various $\pi \rightarrow \pi^*$ excited states depends not only on the differences between the π and π^* orbital energies but also upon exchange and Coulomb terms as well as electron correlation effects. Morevoer, the π^* orbitals appropriate for describing the $\pi \rightarrow \pi^*$ excited states could differ appreciably from those giving rise to the π^* anion states. For these reasons, the order of the π^* orbitals as deduced from the electronic excitation spectrum of the neutral molecule need not be the same as that implied by the ordering of the anion states. Of the studies published to date the analysis of Modelli et al. provides, perhaps, the strongest evidence for an inverted ordering of the π^* levels of CHD. However, in the analysis of the trends in the AE's along the sequence CHD, γ-pyran, and 1,4-dioxin, Modelli et al. used a PMO approach in accounting for the changes in the magnitudes of the inductive and hyperconjugative interactions as well as in the TS interactions between the ethylenic groups brought about by the replacement of the CH_2 groups by oxygen atoms. It was noted in the Introduction that the PMO approach is unable to explain the trends in the π^* levels along the sequence ethylene, *cis*-2-butene, and CHD, and it is therefore not clear that this approach is adequate for analyzing the trends along the CHD, γ-pyran, and 1,4-dioxin series of molecules.

On the theoretical side, studies[12] on other compounds have shown that the HAM-3 method does poorly at treating TB interactions. Thus, this method also does not lead to an unambiguous assignment of the anion states of CHD. The ab initio calculations carried out to date also cannot be considered definitive. The reasons for this are twofold: Firstly, it is usually necessary to use a basis set which is more flexible than a split-valence set to describe adequately long-range intramolecular interactions, which can be especially important in anion states.[13] Secondly, because the unfilled orbitals of CHD are unbound (i.e., lie in the continuum of the neutral molecule plus a free electron), they are prone to collapse onto approximations to contiuum functions as the basis set is enlarged.[14] It remains to be shown that the lowest energy b_{2g} and a_u unfilled orbitals from Hartree–Fock (HF) calculations on the neutral molecule using the split-valence basis sets correspond to anion states in the Koopmans' theorem (KT) sense rather than to approximations to continuum solutions.[14]

In light of the central importance of CHD as a model for TB interactions, more direct experimental measurements and more rigorous theoretical calculations in order. This has motivated new experimental studies by Stephen and Burrow as well as the present theoretical investigation. Stephen and Burrow[15] have measured angular distributions for the scattering of electrons from CHD, along with the cross sections for exciting various vibrational modes via the temporary anions. In the present study the stabilization method[16] is employed to calculate the energies of the π^* levels of CHD. The stabilization method allows one to characterize the temporary anion states, even when using flexible basis sets. The stabilization calculations and the measurements of Stephen and Burrow provide compelling evidence that the anion states of CHD are inverted from the natural ordering, in agreement with the other evidence discussed above.

II. Computational Approach

Temporary anion states (or resonances) may be viewed as a discrete state coupled to the continuum for electron–molecule scattering. Finite basis set calculations of the eigenvalues of an electron–neutral molecule system in general yield both resonance solutions and discretized ap-

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(5) The PMO argument that the TB destabilization of the π_+^* (π_+) orbitals of CHD should be twice that found in going from the π^* (π) orbital of ethylene to the $\pi^*(\pi)$ orbital of *cis*-2-butene proceeds as follows: The π_+^* orbital of CHD may be written, neglecting overlap, as $(1/\sqrt{2})(\pi_a^* + \pi_b^*)$ in terms of the localized ethylenic orbitals, π_a^* and π_b^*. If we let ϕ represent the "+" combination of the two pseudo-π CH_2 orbitals, the second-order shift of the energy of the π_+^* orbital due to mixing with ϕ is $|\langle\pi_+^*|H|\phi\rangle|^2/(\epsilon_{\pi_+^*} - \epsilon_\phi)$, or $2|\langle\pi_a^*|H|\phi\rangle|^2/(\epsilon_{\pi_+^*} - \epsilon_\phi)$. Similarly, the destabilization of the π^* orbital of ethylene in going to *cis*-2-butene may be written as $|\langle\pi_a^*|H|\phi\rangle|^2/(\epsilon_{\pi^*} - \epsilon_\phi)$. Since $(\epsilon_{\pi_+^*} - \epsilon_\phi)$ is approximately equal to $(\epsilon_{\pi^*} - \epsilon_\phi)$ we conclude that the TB destabilization of the π_+^* orbital in CHD should be approximately twice the hyperconjugative destabilization of the π^* orbital of *cis*-2-butene. A similar analysis holds for the filled orbitals.

(6) An estimate of the TS interaction in the π and π^* manifolds of CHD may be obtained from HF calculations on an ethylene dimer with the ethylenic groups separated as in CHD. (See ref 9.) As discussed later in the paper, HF calculations with the 3-21G basis set give a π_+^*/π_-^* splitting of 1.30 eV for the dimer.

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proximations to the continuum, hereafter designated as discretized continuum (DC) solutions. Although the resonance states necessarily involve some admixture of the continuum, in finite basis set calculations, they may mix too strongly with DC solutions, and in some cases, it may not be possible to associate a single eigenvalue with the resonance solution. Furthermore, even if the resonances are not strongly mixed with DC solutions, one needs a procedure for distinguishing the resonances from the DC solutions. A simple approach to doing so is to compare the eigenvalues obtained from the calculations on the electron–molecule system to those of a "free" electron as described by the same basis set. When a minimal basis set is employed, the lowest energy DC solutions of the "free" electron are found to lie much higher in energy than do the lowest eigenvalues obtained from calculations on the anion. In such cases we can be confident that the wave functions for the low-lying anion eigenvalues have not collapsed onto DC solutions, but indeed correspond to resonance solutions. As the basis is enlarged, both the DC and resonance solutions drop in energy, with the former generally decreasing more rapidly.

The DC solutions of the electron–molecule system must be orthogonal to the filled MO's, as well as to any lower-lying resonance solutions, and therefore usually lie higher in energy than the corresponding levels of the "free" electron. Hereafter, we refer to the DC solutions associated with molecules as orthogonalized discretized continuum (ODC) solutions and reserve the DC designation for discretized continuum solutions of the "free" electron. Even when there are low-lying ODC solutions, the resonances can often be identified by comparing the eigenvalues and eigenvectors obtained from the anion calculations with those of the DC solutions. In the present study this approach is employed in combination with the Koopman's theorem approximation to identify those virtual orbitals which correspond to temporary anions, and which are referred to as stabilized KT (or SKT) orbitals to distinguish them from the ODC solutions.[17] This approach to identifying the SKT levels can be viewed as a crude application of the stabilization method. It ceases to be useful for very large basis sets due to the large number of ODC solutions that fall close in energy to the SKT levels.

We also utilize a more rigorous stabilization method, in which the molecule of interest is surrounded by a positively charged sphere of radius R and charge q.[18,19] If q/R is sufficiently large, the potential due to the sphere converts the anion states of interest into bound states. The energies of the anion states in the absence of the sphere can be estimated by adding q/R (in atomic units) to the appropriate eigenvalues of the molecule–sphere problem. The electron–sphere system itself has a set of bound eigenvalues, called sphere solutions, which, after the q/R shift, can be viewed as providing a discretized representation of the continuum. In general, the energies of the sphere solutions vary more rapidly with the sphere parameters (q or R) than do the energies of the resonance solutions which, providing they are well-separated from sphere-type solutions, depend only weakly on the sphere parameters. Hence, by examining the variation of the eigenvalues with the sphere parameters, one can usually distinguish the sphere and temporary anion solutions. In the present work, R is fixed and q is varied. If q is varied over a sufficiently wide range, avoided crossings may occur between the resonance and sphere solutions. In such cases one can obtain an estimate of the energy of a particular resonance by inspection, for example by associating it with the mean of energy of the two eigenvalues at their point of closet approach. A more accurate determination of the energy of the resonance can be accomplished by the method of Simons[20] or by analytic continuation of the eigenvalues involved in the avoided crossing.[18] An advantage of this approach to stabilization is that the number of sphere solutions in the same energy range as the resonance is determined by the spectrum of the electron–sphere problem and does not grow indefinitely as the basis set is enlarged.

In this study the stabilization procedure outlined in the preceding paragraph is used in combination with KT and also with the multireference single-excitation configuration interaction (SECI) procedure. In the KT stabilization approach the virtual orbitals are obtained from HF calculations on the neutral molecule sphere system, and those virtual orbitals associated with the SKT levels are identified. The SECI stabilization procedure includes the relaxation corrections and gives energies for the anion states nearly the same as those which would be obtained at the HF level of theory. The reason that the HF method was not used in calculations on the temporary anion states is that with flexible basis sets the HF wave function would collapse onto a wave function describing the neutral molecule plus an electron in a sphere-type orbital. This problem is remedied by use of the SECI stabilization method with which the energies of the anion states can be determined, even if there are lower energy sphere solutions.

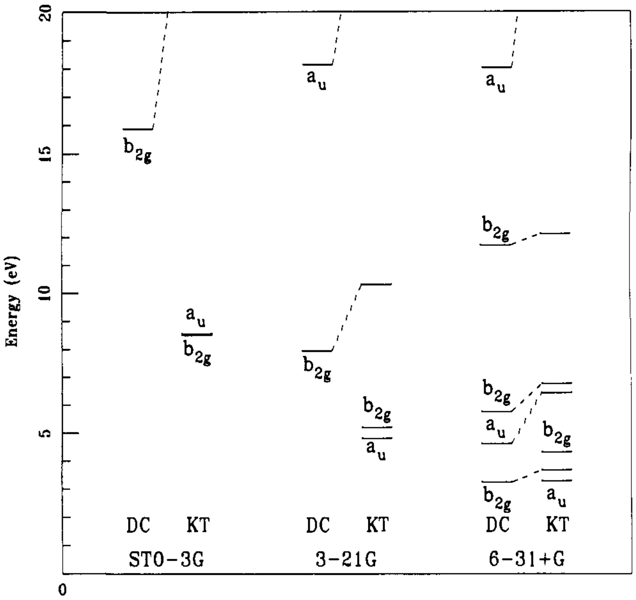

Figure 1. Correlation diagram giving the energies of the discretized continuum solutions and virtual orbitals of 1,4-cyclohexadiene obtained with the STO-3G, 3-21G, and 6-31+G basis sets. The energies of the discretized continuum solutions associated with the "free" electron and of the virtual orbitals of CHD are designated by the labels DC and KT, respectively.

The reference spaces for the CI calculations for the $^2B_{2g}$ and ^2A_u anion states consist of all configurations of the form $\{HF\}nb_{2g}$ and $\{HF\}na_u$, respectively, where $\{HF\}$ designates the HF configuration of the neutral molecule, and n ranges through all virtual orbitals of the designated symmetry in a given basis set. The SECI calculations include all configurations formed by a single excitation from one of the reference configurations, with the restriction that the six lowest energy MO's (those which are predominantly C_{1s} in nature) are kept frozen. With the multireference SECI stabilization procedure, the energies are relatively insensitive to the choice of MO's; here the HF MO's of the neutral molecule are used. The energies of the anion states and of the sphere solutions are reported relative to the HF energy of the neutral molecule.

The SECI procedure includes the relaxation corrections but neglects most of the electron correlation corrections to the KT attachment energies. As a result, the anion states calculated in the SECI approximation should lie energetically below the KT predictions but above the experimental results. On the other hand, electron correlation is not expected to prove very important for the *splitting* between the π^* anion states. Evidence supporting this expectation is presented later in the paper.

The basis sets used in the stabilization calculations include 6-31+G, 6-31+G+p, 6-31+G+3p, and 6-31+G*. The 6-31+G basis set, originally designed for treating bound anion states, consists of the 6-31G basis set plus a set of diffuse sp Gaussian-type functions (with exponent α = 0.0438) on the carbon atoms.[21] The 6-31+G+p basis set is formed by adding a diffuse p function with an exponent 0.0146 to the 6-31+G carbon basis set. The 6-31+G+3p basis set is formed by adding to the 6-31+G carbon basis sets three diffuse p functions with exponents of 0.0146, 0.004867, and 0.00162. The 6-31+G* basis set includes d polarization functions on the carbon atoms. All four basis sets were used in the KT stabilization calculations, while only the 6-31+G basis set was used in the SECI stabilization calculations. Finally, MO calculations, without stabilization, were also performed with the STO-3G, 3-21G, 6-31G, and 6-31+G basis sets[22] of Pople and co-workers as well as Dunning's split-valence basis set (9s5p/3s2p on the carbon atoms and 4s/2s on the hydrogen atoms).[23] The HF calculations were carried out with the Gaussian 88 program;[24] the SECI calculations were carried out

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(17) In some molecules all the virtual orbitals obtained from HF calculations with use of the STO-3G minimal basis set correspond to SKT levels: Choi, Y.; Falcetta, M. F.; Jordan, K. D. Unpublished results.

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with the unitary group CI program of Shepard and co-workers.[25] All calculations on CHD were carried out at the MP2/6-31G* optimized geometry which is close to the experimental geometry.

III. Results and Discussion

A. MO Calculations. As mentioned previously, the HF/STO-3G calculations predict the π_+^* and π_-^* orbitals to be nearly degenerate, while calculations using split-valence basis sets place the π_-^* orbital below the π_+^* orbital. The amount by which the π_-^* orbital is below the π_+ orbital depends on the diffuseness of the outer p function, being 0.35, 0.46, and 0.95 eV in the 3-21G, 6-31G, and Dunning split-valence basis sets, respectively. Figure 1 presents a correlation diagram of the a_u and b_{2g} virtual orbitals of CHD obtained from HF calculations on the neutral molecule, using the STO-3G, 3-21G, and 6-31+G basis sets. This figure also includes the energies of the DC solutions for the "free" electron problem obtained with these three basis sets. For the STO-3G and 3-21G basis sets (as well as for the 6-31G and Dunning 3s2p basis sets), the lowest unfilled a_u and b_{2g} levels of CHD lie energetically below the DC solutions of the same symmetry and can therefore be assigned to SKT solutions. For the split-valence basis sets the lowest energy DC level of a_u symmetry lies far above (by at least 7 eV) the lowest SKT level of a_u symmetry, while the lowest DC solution of b_{2g} symmetry lies only 2–3 eV above the lowest b_{2g} SKT solution. Thus, while it appears unlikely that the energy of the a_u SKT level is artificially depressed due to mixing with DC levels, such mixing could be important in the b_{2g} symmetry block. The splitting between the SKT and the lowest energy ODC levels of b_{2g} symmetry is 5–7 eV for the split-valence basis sets. Consequently, we conclude that in the calculations using the split-valence basis sets the b_{2g} SKT level of CHD also does not mix strongly with the higher lying ODC levels. Since the Dunning basis set is more flexible than the 3-21G and 6-31G basis sets (particularly with regard to the diffuseness of the outer p function), we expect the π_+^*/π_-^* splitting obtained with the Dunning basis set to most closely reflect that found in the stabilization calculations using flexible basis sets.

We now consider the results obtained with the 6-31+G basis set, for which the exponent of the outer p function is about half that of the outermost p function in the Dunning basis set. With the 6-31+G basis set the a_u and b_{2g} DC solutions for the "free" electron are much lower in energy than with the 6-31G basis set. The lowest a_u DC level still lies above (but by only 1.2 eV) the lowest unfilled a_u orbital on CHD. Thus we can still associate the lowest unfilled a_u orbital with a SKT level, but there may be considerable mixing between the ODC and SKT levels. The identification of the b_{2g} SKT level is less clear-cut, since there is only a 0.7-eV separation between the two lowest unfilled b_{2g} orbitals of CHD and since with the 6-31+G basis set the lowest b_{2g} DC solution lies 0.5 eV below the lowest unfilled b_{2g} orbital of CHD. Examination of the coefficients of the two MO's leads us to conclude that the lowest b_{2g} orbital is an ODC solution and that it is the second b_{2g} orbital that now corresponds to the SKT level, although it is possible that the b_{2g} SKT level is shifted by mixing with the nearby ODC level. Both the π_+^* and π_-^* SKT orbitals are lowered in going from the 6-31G to the 6-31+G basis set, with the energy decrease of the π_-^* level being greater, leading to an increased splitting (1.08 eV) between the π_+^* and π_-^* levels. However, there is uncertainty in this splitting due to the possibility of mixing between the ODC and SKT levels of b_{2g} symmetry. Also, it remains to be demonstrated that the π_+^*/π_-^* splitting is not significantly changed upon the adoption of basis sets more flexible than the 6-31+G. To resolve these issues, stabilization calculations have been carried out.

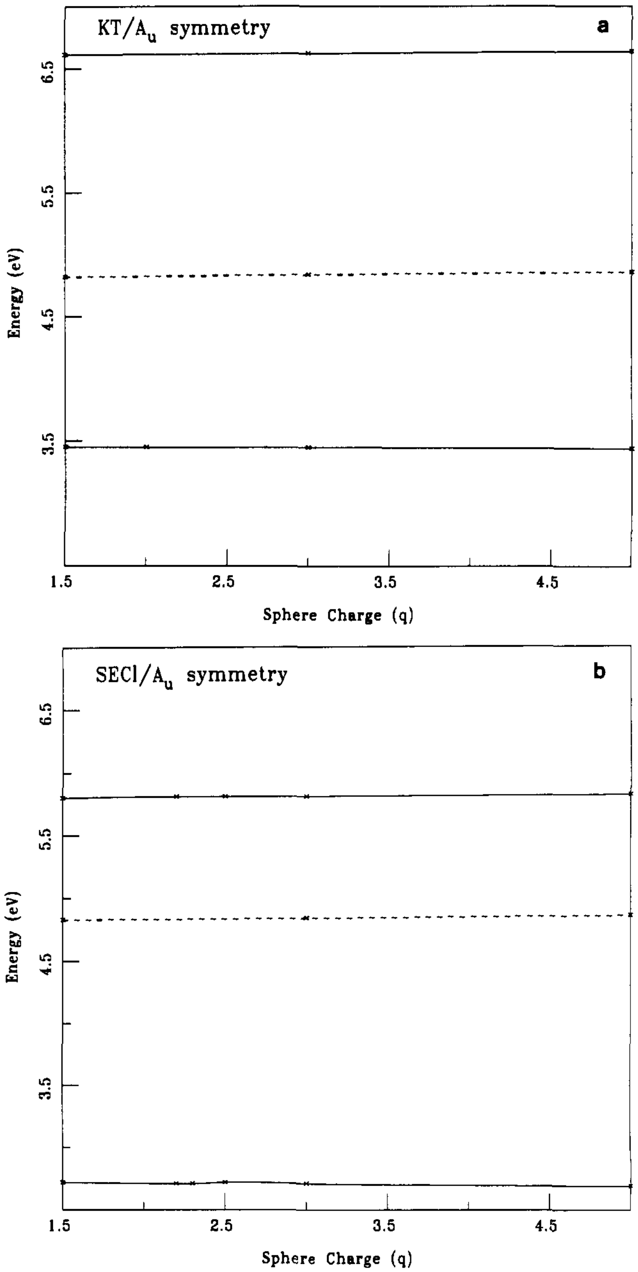

Figure 2. Stabilization graphs for the A_u eigenvalues of CHD obtained with the 6-31+G basis set, a sphere of radius 5 Å, and q ranging from 1.5 to 5: (a) KT, (b) SECI. The eigenvalues for the molecule–sphere and for the electron–sphere problems are represented by the solid and dashed curves, respectively.

B. KT Stabilization Calculations. The energies of the a_u and b_{2g} π^* orbitals obtained from stabilization calculations of CHD using the 6-31+G basis set are shown in Figures 2a and 3a, respectively. These results were obtained with a sphere radius of 5 Å and q varying from 1.5 to 5.0 and include the q/R shift back into the continuum. For comparison, the lowest a_u and b_{2g} sphere solutions, also shifted by q/R, have been included. Over the range of q considered, the lowest a_u sphere solution lies roughly 1 eV above the lowest unfilled a_u orbital obtained from the calculations on the molecule–sphere system. This sphere solution is destabilized by nearly 2 eV in going to the molecule–sphere system, and it is the lower lying a_u orbital at 3.49 eV that corresponds to the SKT solution. In the case of b_{2g} symmetry, the lowest sphere solution is about 0.5 eV lower in energy than the lowest orbital of the molecule–sphere system, and the two lowest unfilled b_{2g} orbitals of the molecule–sphere system are quite close

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[24] Gaussian 88: Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Raghavachari, K.; Binkley, J. S.; Gonzolez, 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.; Fluder, E. M.; Topiol, S.; Pople, J. A. Gaussian Inc.: Pittsburgh, PA, 1988.

[25] The orbitals used in the CI calculations were obtained with the MCSCF program of Shepard et al.: Shepard, R.; Simons, J.; Shavitt, I. *J. Chem. Phys.* **1982**, *76*, 543. The program used to perform the CI calculations is described in: Lishka, H.; Shepard, R.; Shavitt, I. *Int. J. Quantum Chem. Symp.* **1981**, *15*, 91. The CI and MCSCF calculations used integrals over symmetry-adapted contracted Gaussian-type orbitals evaluated with the ARGOS program of R. Pitzer. These programs were adapted to the Model FPS 500EA computer by N. Nystrom.

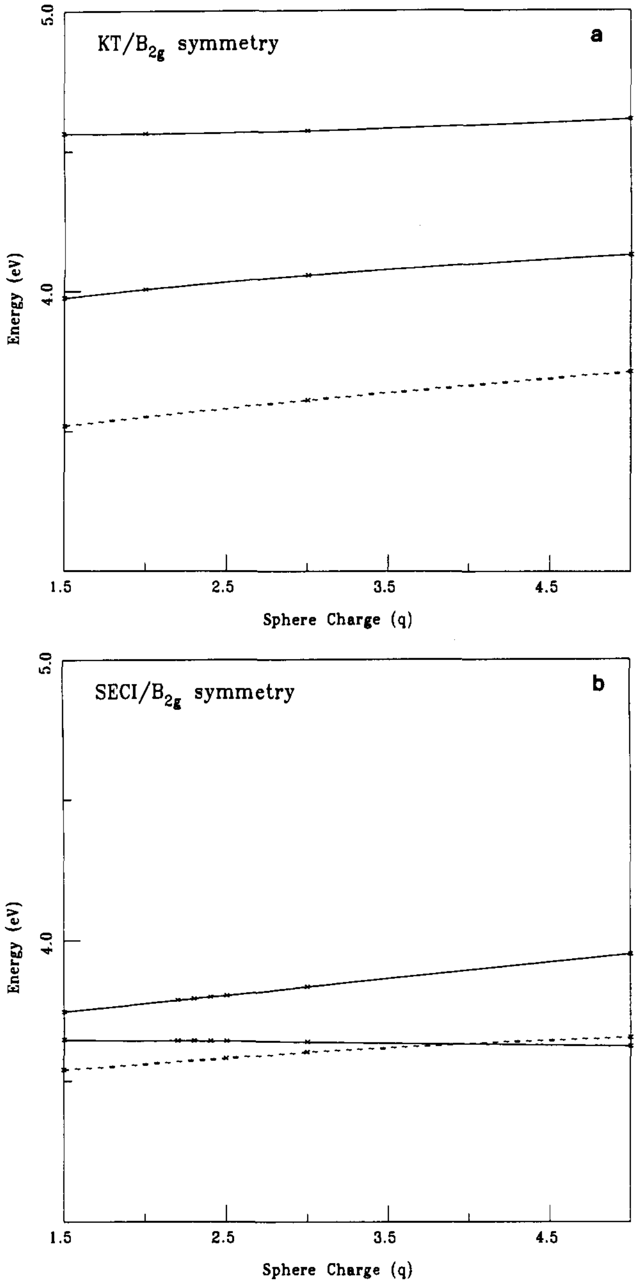

Figure 3. Stabilization graphs for the B_{2g} eigenvalues of CHD obtained with the 6-31+G basis set, a sphere of radius 5 Å, and q ranging from 1.5 to 5.0: (a) KT, (b) SECI. The eigenvalues for the molecule–sphere and for the electron–sphere problem are represented by the solid and dashed curves, respectively.

in energy, being no more than 0.7 eV apart for the range of q chosen. From Figure 3a it is seen that the q dependence of the lowest unfilled b_{2g} solution of the molecule–sphere problem is nearly the same as that for the lowest b_{2g} level of the sphere potential and that the lowest unfilled b_{2g} orbital of the molecule–sphere problem varies more rapidly with q than does the second. We conclude, therefore, that it is the second b_{2g} eigenvalue of the molecule–sphere, at 4.57 eV, which corresponds to the SKT level.[26]

The results of various stabilization calculations are summarized in Table I. The inclusion of d polarization functions proves unimportant, causing changes in energies of the SKT levels of less than 0.02 eV. The inclusion of still more diffuse p-type basis functions causes small shifts in the energies of the SKT levels, with the energies of the a_u and b_{2g} π^* SKT levels being lowered by 0.22 and 0.10 eV, respectively, in going from the 6-31+G to the 6-31+G+3p basis set. Stabilization calculations using the 6-31+G and 6-31+G+3p basis sets give π_+^*/π_-^* splittings of 1.08 and 1.24 eV, respectively. These splittings are two to three times larger than those obtained with the 3-21G or 6-31G basis sets but only 0.13 and 0.25 eV larger than that obtained with the Dunning split-valence basis set.

Table I. Vertical Electron Attachment Energies and π_+^*/π_-^* Splitting Energies of 1,4-Cyclohexadiene

method/basis set	attachment energies, eV		splitting energies,[c] eV
	^2A_u	$^2B_{2g}$	
KT/6-31+G	3.49	4.57	1.08
KT/6-31+G+p	3.38	4.62	1.24
KT/6-31+G+3p	3.27	4.47	1.20
KT/6-31+G*	3.49	4.58	1.09
SECI/6-31+G	2.77	3.66	0.89
SECI/6-31+G+MP2 correlation[a]	2.08	2.98	0.83
experiment[b]	1.75	2.67	0.92

[a] The correlation corrections are estimated from MP2 calculations using the 6-31G* basis set. [b] From ref 4. [c] A positive splitting energy is consistent with the π_-^* below π_+^* ordering.

C. SECI Stabilization Calculations. The KT stabilization calculations indicated that the π_+^*/π_-^* splitting is not appreciably altered upon adoption of basis sets more flexible than 6-31+G. Therefore, only the 6-31+G basis set was used in the SECI stabilization calculations. (Recall that the SECI procedure recovers very little electron correlation energy. In CI calculations recovering correlation energy, the inclusion of d functions in the basis set would probably prove important.) The results of the stabilization calculations using the SECI method are shown in Figures 2b and 3b, where we have plotted the energies of the two lowest ^2A_u and two lowest $^2B_{2g}$ eigenvalues of both the anion–sphere and electron–sphere problems as a function of q, with q ranging from 1.5 to 5.0. The sphere radius was chosen to be 5 Å, and all eigenvalues have been shifted by q/R. The SECI stabilization graphs are similar to those described above for the KT approximation. The main difference is that, due to the inclusion of relaxation effects, the resonance solutions lie 0.7–0.9 eV lower in energy in the SECI approximation. As a result, at the SECI level of theory, it is the lowest $^2B_{2g}$ eigenvalue of the anion–sphere problem which corresponds to the resonance. The resonance eigenvalues are essentially constant over the range of q considered, and the SECI vertical attachment energies are determined to be 2.77 and 3.66 eV for the ^2A_u and $^2B_{2g}$ states, respectively.[26] At the SECI level of theory the splitting between the two anion states is 0.89 eV, as compared to the 1.08-eV splitting found at the SKT level (using the 6-31+G basis set). The SECI splitting is in excellent agreement with that determined from the ET measurements (0.92 eV), suggesting that the contributions of electron correlation to the energies of the two anion states must be nearly the same.

The vertical attachment energies obtained from the SECI stabilization calculations are about 1 eV larger than those determined experimentally. The overestimation of the attachment energies at this level of theory is due primarily to the neglect of nearly all electron correlation effects. Second-order perturbation (MP2) calculations using the 6-31G* basis set were carried out on CHD and its ^2A_u and $^2B_{2g}$ anion states. The MP2 calculations were carried out with the relatively small 6-31G* basis set to prevent collapse onto DC solutions. The MP2 calculations give energy lowerings (relative to the unrestricted HF energies) of 0.69 and 0.75 eV for the ^2A_u and $^2B_{2g}$ anion states, respectively. Subtracting the MP2 correlation corrections to the AE's from the SECI/6-31+G AE's gives attachment energies of 2.08 and 2.91 eV for the ^2A_u and $^2B_{2g}$ states, respectively. The AE's estimated in this manner are 0.31–0.33 eV larger than the experimental values, and the resulting splitting of 0.83 eV is only 0.09 eV less than that determined experimentally. If these results are further corrected by the shifts in the SKT energies in going from the

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(26) The energies reported for the SKT levels are those for q = 2.0 and are considered reliable to ±0.1 eV. Resonance energies for the SECI approach were taken from the data at q = 2.4 and are considered reliable to ±0.05 eV.

Table II. Ratios (C_{outer}/C_{inner}) of the Ethylenic p_y AO's in the π^* Orbitals Obtained from HF/3-21G Calculations

molecule (orbital)	C_{outer}/C_{inner}	molecule (orbital)	C_{outer}/C_{inner}
ethylene (π^*)	2.46	dimer (π_+^*)	2.56
cis-2-butene (π^*)	2.30	CHD (π_-^*)	2.43
dimer (π_-^*)	2.37	CHD (π_+^*)	2.06

6-31+G to the 6-31+G+3p basis set, the resulting AE's are within 0.14 eV of experiment and the splitting is within 0.03 eV of the experimental value.

D. Analysis of TB and TS Interactions. The stabilization calculations show that the ground-state anion of 1,4-cyclohexadiene is of ^2A_u symmetry, consistent with a π_-^* below π_+^* ordering of the π^* orbitals. However, they do not allow one to readily identify the factors responsible for this ordering. To accomplish this we have performed a series of HF calculations on ethylene, 1,4-cyclohexadiene, *cis*-2-butene, and a model ethylene "dimer", with the ethylenic groups separated as in CHD.[27] The calculations on the dimer provide an estimate of the TS splitting in CHD, and the difference in the energies of the π_+ and π_+^* orbitals of the dimer and those of CHD provide estimates of the TB interactions.[6,28] These calculations are carried out with the STO-3G, 3-21G, and 6-31+G basis sets. For each of the molecules considered the SKT levels lie energetically well below the ODC solutions when using the STO-3G and 3-21G basis sets, and the stabilization procedure is not required. However, to avoid the problem of collapse onto ODC solutions, the calculations with the 6-31+G basis set were carried out with the stabilization procedure.

Figure 4a summarizes the STO-3G orbital energies of ethylene, the ethylene dimer, and CHD. At the HF/STO-3G level of theory, the splitting between the π orbitals of the dimer is 0.88 eV and that between the π^* orbitals is 0.76 eV. The π_+ and π_+^* orbitals of CHD are destabilized by 1.72 and 0.34 eV, respectively, relative to those of the dimer. These TB destabilizations are roughly twice as large as the shifts calculated in the π and π^* levels (1.06 and 0.15 eV, respectively) upon going from ethylene to *cis*-butene. Thus, the HF/STO-3G predictions are consistent with the PMO model.

Figure 4b summarizes the orbital energies obtained with the 3-21G basis set. HF/3-21G calculations on the dimer give a splitting of 1.30 eV between the π_+^* and π_-^* orbitals and a splitting of 1.19 eV between the π_+ and π_- orbitals. The TS splittings predicted with the 3-21G basis set for both the π and π^* spaces are about 0.4 eV larger than those obtained with the STO-3G basis set. With the 3-21G basis set, the π_+ orbital is destabilized by 1.82 eV and the π_+^* orbital by 1.28 eV in going from the dimer to CHD. The TB destabilization of the π_+ orbital is nearly the same in the STO-3G and 3-21G basis sets, while the TB destabilization of the π_+^* level is about four times (or 1 eV) larger with the 3-21G basis set.

The shifts in the energies of the π and π^* orbitals in going from ethylene to *cis*-2-butene are predicted at the HF/3-21G level to be 0.97 and 0.39 eV, respectively. On the basis of these results, the PMO model would lead us to expect TB interactions to destabilize the π_+ and π^* levels of CHD by 1.94 and 0.78 eV, respectively. The PMO prediction for the TB destabilization of the π_+ orbital is within 0.12 eV of that found from the calculations on the dimer and CHD. On the other hand, in the HF/3-21G approximation the PMO model underestimates by 0.50 eV the TB destabilization of the π_+^* level of CHD.

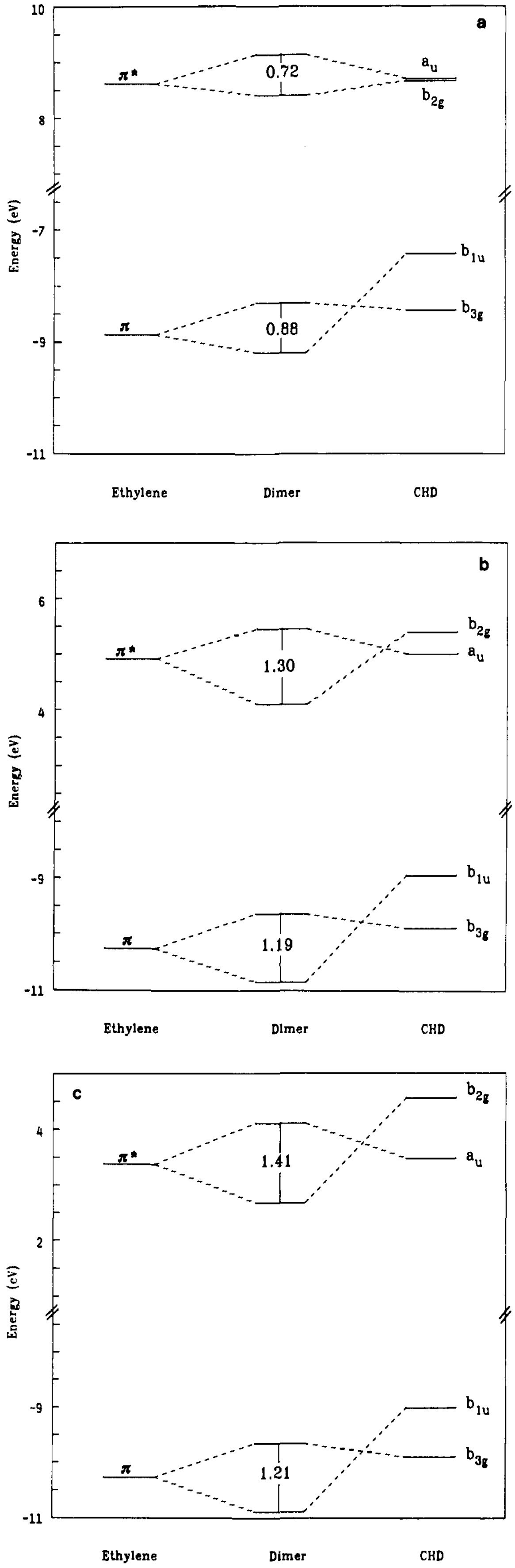

Figure 4. Correlation diagram giving the π and π^* orbital energies for ethylene, the ethylene "dimer", and CHD obtained from HF calculations using (a) the STO-3G basis set, (b) the 3-21G basis set, and (c) the 6-31+G basis set. The energies of the π^* orbitals for the 6-31+G basis set are from stabilization calculations.

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[27] The CC distances, the CH bond lengths, and the external CCH angles of the ethylene "dimer" are taken to be the same as in CHD. The CH distances are taken to be 1.09 Å and the corresponding CCH angles are set to 140° to keep the internal hydrogen atoms of the two ethylene molecules from being too close. The energies of the π and π^* levels of an isolated ethylene molecule are shifted by less than 0.2 eV when the CCH angles of a pair of cis hydrogens is changed to 140°. The geometry of *cis*-2-butene is generated from that of cyclohexadiene by "stripping" out one of the ethylenic groups and adding hydrogen atoms to the two CH_2 groups.

[28] The decomposition of the net splittings into TS and TB contributions effects is not a precise process. In this study we have followed ref 9 and have used the dimer model to obtain estimates of the TS interaction.

In order to gain additional insight into how the increased flexibility of the 3-21G basis set leads to an increased TB destabilization of the π_+^* orbital of CHD, it is useful to examine the AO coefficients of the π^* orbitals of ethylene, *cis*-2-butene, the ethylene dimer, and CHD. In particular, we focus on the ratios of the coefficients of the outer and inner p_y functions ($C_{\text{outer}}/C_{\text{inner}}$) of the ethylenic carbon atoms which are summarized in Table II. The $C_{\text{outer}}/C_{\text{inner}}$ ratios of both the π_+^* and π_-^* orbitals of the dimer and of the π_-^* orbital of CHD are close to that of the π^* orbital of ethylene (2.46). On the other hand, this ratio is somewhat smaller for the π^* orbital of *cis*-2-butene (2.30) and smaller still for the π_+^* orbital of CHD (2.06). For these two orbitals, the admixture of the pseudo-π orbitals of the CH_2 groups appears to come mainly at the expense of the outer component of the p_y orbitals of the ethylenic groups. The changes in the relative contributions of C_{outer} and C_{inner} in going from ethylene to *cis*-2-butene and from the dimer to CHD are not accounted for by the simple PMO model.

Calculations were also performed on CHD in which the 3-21G basis set was used for the ethylenic carbon atoms and the STO-3G basis set was used for the methylenic carbon atoms and for all hydrogen atoms. These calculations correctly order the π^* orbitals and actually predict a larger splitting than that obtained from calculations employing the 3-21G basis set on all atoms. Although such an unbalanced basis set cannot be trusted to make quantitative predictions, the results do indicate that the enhanced TB destabilization of the π_+^* orbital in going from the STO-3G to the 3-21G basis set is due to the increased flexibility of the basis set on the ethylenic carbon atoms.

A correlation diagram of the orbital energies obtained with the 6-31+G basis set for ethylene, the ethylene dimer, and CHD is given in Figure 4c. These calculations give a splitting between the π_-^* and π_+^* levels of the dimer within 0.1 eV of the 3-21G result. On the other hand, the 6-31+G stabilization calculations indicate that the TB destabilization of the b_{2g} π^* level (upon going from the dimer to CHD) is 1.86 eV, 0.58 eV larger than that found with the 3-21G basis set. Thus, the major role of the diffuse basis functions is not to describe the TS coupling between the ethylenic groups but rather to describe the TB destabilization of the π_+^* orbital. In contrast the calculations using the 3-21G and 6-31+G basis sets give similar values for the TB destabilization of the π_+ orbital of CHD.

Up to this point our attention has been focused on the large TB destabilization of the b_{2g} π^* orbital. Because the TS splitting in CHD is about 1.3 eV, and because the ET studies show that the ^2A_u anion of CHD is stabilized with respect to the ethylene anion, there must be a factor, not yet considered, which more than compensates for the TS destabilization of the π_-^* orbital. At the HF/3-21G level of theory the π_- and π_-^* orbitals of CHD are stabilized relative to the corresponding orbitals of the dimer by 0.25 and 0.45 eV, respectively. Comparison of the atomic changes obtained from Mulliken population analyses reveals that the carbon atoms in ethylene are more negatively charged than are the ethylenic carbon atoms in *cis*-2-butene and CHD (−0.43 vs −0.23 and −0.20). The carbon atoms in the dimer are predicted to have nearly the same charge as those in ethylene. Thus it appears that the alkyl groups in *cis*-2-butene and CHD exert a stabilizing inductive effect[29] on the ethylenic groups, which would lead to a stabilization of the π^* orbitals (and also the π orbitals) of these compounds. If this is indeed the case, then the TB destabilizations of the π_+ and π_+^* orbitals of CHD would be a few tenths of an eV electron larger than those deduced neglecting the inductive stabilization.

IV. Conclusions

The stabilization calculations carried out in this study indicate that the stabilized π_-^* (a_u) orbital of CHD lies below the stabilized π_+^* (b_{2g}) orbital and that the splitting between the ^2A_u and $^2B_{2g}$ anion states is relatively unaffected by relaxation and correlation corrections to the KT prediction. The main factor responsible for the inverted ordering of the π^* levels of CHD is the large TB destabilization of the π_+^* orbital. Since the energy separation between the unmixed π_+^* and CH_2 pseudo-π orbitals is much greater than that between the π_+ and pseudo-π orbitals, one would have expected the TB coupling to be much smaller in the π^* manifold. While this expectation is borne out at the HF/STO-3G level of theory, calculations with the 6-31+G basis set indicate that the TB destabilizations of the π_+^* and π_+ orbitals are comparable. The stronger than expected coupling of the π_+^* and CH_2 pseudo-π orbitals is associated with a radial contraction of the ethylenic π^* components of the π_+^* orbital.

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[29] There is evidence on other systems that alkyl groups can stabilize π^* anion states. See, for example: Jordan, K. D.; Michejda, J. A.; Burrow, P. D. *J. Am. Chem. Soc.* **1976**, *98*, 1295. Brauman, J. I.; Blair, L. K. *J. Am. Chem. Soc.* **1970**, *92*, 5986.