Potential Energy Surfaces of Cyclobutadiene: Ab Initio SCF and CI Calculations for the Low-Lying Singlet and Triplet States

J. A. Jafri and M. D. Newton*[1]

Contribution from the Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973. Received December 27, 1977

Abstract: The four low-lying triplet and singlet states of cyclobutadiene have been examined for square, rectangular, rhomboid, and trapezoidal structures in terms of ab initio 2-configuration SCF and larger CI wave functions which include both σ- and π-electron correlation. The 2-configuration SCF level correctly finds the rectangular singlet to be the ground state of the molecule and gives the same value for the barrier separating the two rectangles (12 kcal/mol) as the $(\pi + \sigma)$-electron CI calculation, thus ruling out the possibility of rapid (i.e., $\geq 10^{12}$ s^{-1}) interconversion of rectangular singlets through a square intermediate. For the square, the triplet is found ~10 kcal/mol above the lowest singlet, and the $^1A_{1g}$ state ~30 kcal/mol below the $^1B_{2g}$ state. Because of its importance for proper separation of states, π-electron CI is found necessary for understanding the stability of all states of the square with respect to a b$_{2g}$ (rhomboid) distortion (the first excited singlet state is *unstable* with respect to the b$_{2g}$ mode at the SCF level). The CI results imply that the square is the lowest energy intermediate for interconversion of rectangular singlets.

I. Introduction

Recent infrared,[2] NMR,[3] and crystal structure[4] studies of cyclobutadiene and its alkyl derivatives have given new impetus to ab initio theoretical investigation[5-9] of this species which plays a pivotal role in the theory of π-electron systems. A fundamental theoretical question is to understand the relative energetics of the singlet state, long expected to exist as a rectangle due to simple arguments based on perturbation theory, and the triplet state, for which a square geometry is the most likely candidate.[5-9] The most elaborate of the recent ab initio calculations are in agreement in predicting that the lowest energy structure is a singlet rectangle and furthermore that interconversion of the rectangles via a square intermediate would not be expected to occur on a vibrational time scale, since the intervening barrier is several kilocalories per mole. While calculations at the SCF level indicate that the square triplet lies a few kilocalories per mole *below* the square singlet, configuration interaction studies have shown that when correlation energy is included, the singlet state lies below the triplet state for *all* reasonable rectangular or square framework geometries.[7,8,10] For both singlet and triplet states, the calculations show that the equilibrium square structure corresponds to a stationary point on the potential energy surface, being a local minimum in the case of the triplet[5,8] and a transition state in the case of the singlet.[8]

The data of primary interest for the parent are the four infrared bands (3040, 1236, 653, and 573 cm^{-1}) assigned to the matrix isolated species.[2] The assignment of the 653-cm^{-1} band has recently been clouded since most or all of its intensity appears to arise from CO$_2$ formed as a by product in the photolysis.[2c,f] The small number of bands and the location of a band at 1236 cm^{-1} are most easily interpreted as arising from a square structure,[2b] which would accordingly be expected to correspond to the triplet state since the singlet has a rectangular equilibrium geometry.[5-9] The assignment of the 1236-cm^{-1} band to the in-plane framework deformation of the triplet is plausible since it is intermediate between C–C single and double bond stretching frequencies[11] and is observed to shift by only a small amount (~10 cm^{-1}) upon deuterium substitution.[2b,e] The problem with the square triplet assignment for the parent species is the incompatibility with ab initio calculations noted above and the failure to observe an ESR signal in the matrix isolated species.[12]

The situation for the alkyl derivatives is more clear cut. The data come primarily from NMR and X-ray studies[3,4] and

appear to be consistent with a singlet electronic state and a framework geometry only moderately distorted from the rectangle expected from normal single and double bond lengths.[13] In the case of the tetrakis(trifluoromethyl) derivative, a band at 1700 cm^{-1} was tentatively assigned to the double-bond stretching mode.[2g] Since the alkyl groups in the various derivatives tend to be bulky (e.g., as in the tri-*tert*-butyl derivative), the relevance of the data for the derivatives to the nature of the parent is not entirely clear, especially since the calculated singlet-triplet splittings are of the order of only a few kilocalories per mole.[5-9] No analogue to the 1236-cm^{-1} band of the parent has been found for any of the derivatives.

In order to resolve the remaining questions regarding the parent species, more spectroscopic data (e.g., Raman) will undoubtedly be necessary, and further calculations are required, especially those involving distorted structures associated with vibrational modes or interconversion pathways. Furthermore, even if the singlet is the lowest electronic state of the parent, the vibrational modes and potential energy surface of the low-lying triplet are still of great interest.

A point of particular interest has recently been raised regarding the interconversion of rectangular singlet structures;[9e] if the square can be ruled out as an intermediate, then alternatives should be considered, and group theory suggests that a rhomboid structure might provide an energetically feasible means of bypassing the square. This hypothesis was not supported by a recent ab initio study.[8]

In the present theoretical study we have addressed some of the problems noted above, utilizing SCF and CI models with flexible atomic orbital basis sets which allow us to consider several features of the singlet and triplet potential energy surfaces at a reliable and reasonably uniform computational level. After describing the theoretical models in the next section, we present the results of the calculations and attempt to assess the relative importance of configuration interaction for different geometrical structures, considering both σ- and π-electron contributions. Comparison is also made between the present results and those of three previous CI studies,[7,8,10] which generally employed less flexible atomic orbital basis sets and differed in other aspects of methodology. The reasons for finding no stabilization associated with the rhomboid distortion of the square are discussed in detail.

II. Theoretical Models and Computational Details

A. SCF Calculations. The molecular orbitals (MO's) employed in the various multiconfiguration wave functions were

Table I. Correlation of Irreducible Representations in Cyclobutadiene[a]

	D_{2h} (rhombus) $\leftarrow D_{4h}$ (square) $\rightarrow$ D_{2h} (rectangle)		
(A) molecular orbitals for carbon framework			
π electron			
ϕ_1 (bonding)	b_{1u}	a_{2u}	b_{1u}
ϕ_2, ϕ_3 (nonbonding)	b_{2g}, b_{3g}	ϵ_g	b_{2g}, b_{3g}
ϕ_4 (antibonding)	b_{1u}	b_{1u}	a_u
σ electron			
(bonding)	a_g	a_{1g}	a_g
	b_{2u}, b_{3u}	ϵ_u	b_{2u}, b_{3u}
	b_{1g}	b_{1g}	a_g
(antibonding)	b_{1g}	a_{2g}	b_{1g}
	b_{2u}, b_{3u}	ϵ_u	b_{2u}, b_{3u}
	a_g	b_{2g}	b_{1g}
(B) low-lying electronic states			
	$^1B_{1g}$	$^1B_{1g}$	^1A_g
	$^3B_{1g}$	$^3A_{2g}$	$^3B_{1g}$
	^1A_g	$^1A_{1g}$	^1A_g
	^1A_g	$^1B_{2g}$	$^1B_{1g}$

[a] In D_{4h} the B_{1g} and B_{2g} representations are antisymmetric and symmetric, respectively, with respect to reflection through the planes containing the carbon atoms.

expanded in a flexible atomic orbital basis set (the so-called 6-31G* basis[14]) and obtained from appropriate 2-configuration SCF calculations as described below. The relative energies of rectangular singlet and square triplet cyclobutadiene (CBD) appear to be rather insensitive to the presence (6-31G*) or absence (4-31G) of 3d polarization functions on carbon atoms.[15] However, such polarization functions are often important in treating the energetics of strained hydrocarbons,[5,15] and since the various distortions of square and rectangular CBD undoubtedly involve changes in strain energy, the use of the 6-31G* basis was felt to be warranted (some comparisons of 4-31G and 6-31G* results are included in section III).

The molecular orbitals of primary importance are the four valence π-electron MO's which are schematically represented below in terms of their nodal structure. The unprimed ϕ's are appropriate for all of the molecular structures which we shall consider except the rhomboid structure, for which ϕ_2' and ϕ_3' are the appropriate set. The irreducible representations associated with the ϕ's in various point groups are given in Table IA, which also includes the representations spanned by the valence bonding and antibonding σ MO's of the carbon framework.
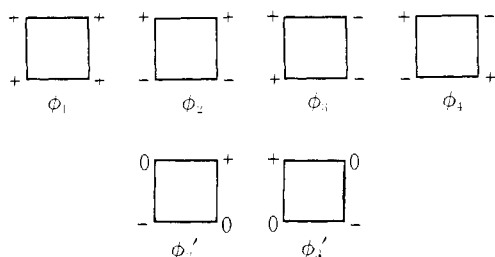
The low-lying electronic states of interest are those which can be constructed by placing four π electrons in ϕ_1, ϕ_2, and ϕ_3 (or ϕ_1, ϕ_2', and ϕ_3'): $^3A_{1g}$, $^1B_{1g}$, $^1A_{1g}$, and $^1B_{2g}$ (see Table IB for D_{2h} symmetry). Hence in the traditional fashion, the full wave functions are summarized in terms of various 2π-electron 2-configuration functions (since ϕ_1 is doubly occupied in all the principal configurations), and the 24-electron core is not explicitly discussed below, except where CI involving the σ framework is considered. Three general functional forms arise:

$$^3\psi_I(\phi_2,\phi_3) = |\phi_2\bar{\phi}_3| - |\phi_3\bar{\phi}_2| \tag{1}$$

$$^1\psi_{II}(\phi_2,\phi_3) = |\phi_2\bar{\phi}_3| + |\phi_3\bar{\phi}_2| \tag{2}$$

$$^1\psi_{III}(\phi_2,\phi_3) = a|\phi_2\bar{\phi}_2| + b|\phi_3\bar{\phi}_3|, \quad a^2 + b^2 = 1 \tag{3}$$

For rhomboid structures, ϕ_2 and ϕ_3 must be replaced by ϕ_2' and ϕ_3' in the singlet functions ($^1\psi_{II}$ and $^1\psi_{III}$). Of course, for D_{4h} geometry either the primed or unprimed sets can be used; e.g.,

$$^1\psi_{II}(\phi_2,\phi_3) = {}^1\psi_{III}(\phi_2',\phi_3') \tag{4}$$

with $a = 2^{-1/2}$, $b = -2^{-1/2}$. Self-consistent field (SCF) calculations[16] were carried out for the following functions (the notation is for D_{4h}; see Table IB for other geometries):

$$\psi_{3A_{2g}} = {}^3\psi_I(\phi_2,\phi_3) \tag{5}$$

$$\psi_{1B_{2g}} = {}^1\psi_{II}(\phi_2,\phi_3) \tag{6}$$

$$\psi_{1B_{1g}} = {}^1\psi_{III}(\phi_2,\phi_3), \quad a = 2^{-1/2}, b = -2^{-1/2} \tag{7}$$

For symmetry lower than D_{4h} the CI coefficients are not fixed by symmetry and are determined by the SCF procedure.[16b,c] Alternatively, one might carry out the lower symmetry SCF calculations in terms of a single configuration.[5,8] However, uniform use of $^1\psi_{III}(\phi_2,\phi_3)$ for *all* molecular structures allows one to obtain more meaningful energetics at the SCF level (e.g., for the barrier separating rectangular singlets). The 2-configuration $^1A_{1g}$ wave function,

$$\psi_{1A_{1g}} = \psi_{III}(\phi_2,\phi_3), \quad a = 2^{-1/2}, b = 2^{-1/2} \tag{8}$$

was evaluated using ϕ_2 and ϕ_3 from the $^1B_{1g}$ calculation. Except as noted, all SCF calculations were constrained to be spin and spatial eigenfunctions (RHF).[16f]

B. CI Calculations. Larger scale, non-SCF CI calculations for the lowest four states of CBD were carried out using MO's obtained either from the $^3A_{2g}$ or $^1B_{1g}$ SCF calculations (the corresponding functions in the D_{2h} rectangular or rhomboid geometries are $^3B_{1g}$ and ^1A_g or $^1B_{1g}$). The CI calculations employed the method of Whitten and Hackmeyer,[17] in which all single and double excitations from all important reference configurations[17b] are included, subject to the criterion that no configuration is included whose contribution to the total energy (ΔE) is $<10^{-6}$ au, as estimated by the second-order perturbation correction.

Within these constraints full π-electron configuration interaction was carried out as well as a limited π-electron CI which included all excitations involving the set $\phi_1 \rightarrow \phi_4$ supplemented by another set of four which spans the same irreducible representations (i.e., full π-electron CI at the double-ζ level, subject to the perturbation threshold[17]). The virtual orbitals for the limited π-electron CI were selected on the basis of the lowest eigenvalues of the Fock matrices.

The σ-electron framework is clearly of importance in understanding the potential energy surfaces of CBD, and σ-π correlation can be of particular importance when comparing molecular structures where the relative amounts of ionic and diradical or covalent character in the π-electron parts of the wave functions are expected to differ significantly.[18] As noted above, it was hoped that the SCF calculations with the 6-31G* basis would give proper account of differential strain energy effects. However, comparisons of the square and rectangular geometry involve large differences in the nature of the framework bonding, and differential correlation energy associated with σ as well as π electrons must be considered. Accordingly, the variably occupied MO basis for the limited π-electron CI was supplemented by including the set of four high-lying occupied MO's which spans the representations of the CC bonding σ orbitals and the lowest set of virtuals which spans the representations of the corresponding antibonding
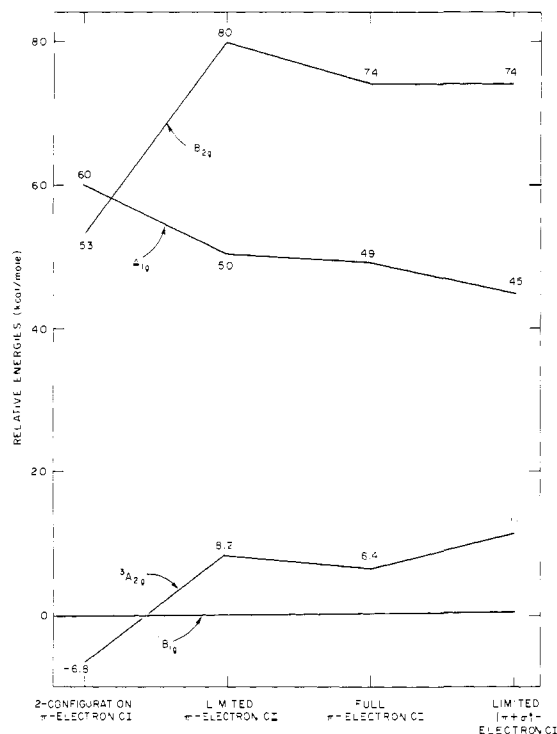
Figure 1. Energies of the four lowest states for D_{4h} geometry (r_{CC} = 1.423 Å) relative to the $^1B_{1g}$ energy. The absolute energies of the $^1B_{1g}$ state at the four levels of CI are −153.633 17, −153.701 08, −153.704 49, and −153.737 17 au. The calculations for the singlet and triplet states are based on the SCF MO's for the $^1B_{1g}$ and $^3A_{2g}$ states, respectively.

orbitals (see Table IA). In the following discussion, the various SCF and CI levels are referred to as "2-configuration π", "limited π", "full π", and "limited ($\pi + \sigma$)". All four levels were used for the states of the square. For the rectangle, limited π and limited ($\pi + \sigma$) CI was carried out, while for the rhombus only π-electron CI was performed. Insight into the need for CI is provided by considering some symmetry-broken SCF solutions for square and rectangular geometries.

C. Structural Details. Calculations were carried out for square, rectangular, rhomboid, and trapezoidal geometries. The CH bonds were kept fixed at a reasonable bond length, 1.075 Å, based on hybridization arguments and experimental data.[13] The CH bonds were constrained to bisect their associated CCC angles. The geometries of the $^3A_{2g}$ and $^1B_{1g}$ states of the square were optimized at the SCF level. The comparisons of the square, rhombus, and trapezoid were based on a D_{4h} structure with r_{CC} = 1.424 Å (close to the SCF equilibrium value): for the rhombus, the CCC angles were changed in increments of 5°; the trapezoid was obtained by ±0.02-Å distortions of two of the parallel bonds in the square. The calculations for the rectangle were based on r_{CC} = 1.564 and 1.334 Å, as obtained previously from 2-configuration SCF calculations using the 4-31G[5] basis. The trapezoidal distortion of the rectangle was obtained analogously to that of the square by distorting the long bonds.

III. Results and Discussion

A. General Comments. The relative energies for the electronic states of the square are presented in Figure 1. The 2-configurational wave functions for the $^3A_{2g}$ and $^1B_{1g}$ states were obtained self-consistently, and the MO's from these calculations were used in constructing the other wave functions.[19] The relative energies of square, rectangle, and rhombus are displayed in Table II. The limited π-electron CI calculations typically involved ~100 spin-adapted configurations,

Table II. $D_{4h} \rightarrow D_{2h}$ Distortion Energies for Square Singlets

	ΔE, kcal/mol[a,b]			
	π-electron CI			limited ($\pi + \sigma$)-electron CI
	two-config	limited	full	
(A) rectangle (R_{CC} = 1.334, 1.564 Å)				
$^1B_{1g} \rightarrow {}^1A_g$	−12	−6.1		−12
(B) rhombus ($\angle CCC$ = 85, 95°)				
$^1B_{1g} \rightarrow {}^1B_{1g}$	4.5	4.6	4.4	
$^1A_{1g} \rightarrow {}^1A_g$	12[c]	1.7[d]	0.9[d]	
$^1B_{2g} \rightarrow {}^1A_g$	−2.6[d]	8.8[c]	8.1[c]	

[a] Energies relative to the square structure, with R_{CC} = 1.423 Å. [b] All calculations are based on the MO's of the SCF $^1B_{1g}$ calculations (D_{4h}), and A'$_g$ or 'B$_{1g}$ (D_{2h}), as described in section II. [c] First excited ^1A_g state (2^1A_g). [d] Lowest ^1A_g state (1^1A_g).

while the larger CI calculations generated ~500–1200 configurations.

The object of the present study is to understand the states of the square and their sensitivity to distortions which lower the symmetry. We wish to know which, if any, of the important characteristics can be accounted for at the SCF level and which phenomena require the more elaborate CI treatment. Second-order perturbation theory is extremely useful in helping one to anticipate the most energetically feasible distortions of the square.[20] The most familiar example is the rectangular distortion of the $^1B_{1g}$ state, which is driven by the b_{1g} (rectangular) vibrational mode; this mode couples the $^1B_{1g}$ state to the low-lying $^1A_{1g}$ state.[5,7,8] Such coupling generally causes distortion to a lower symmetry equilibrium structure if the energy gap between the pertinent states is small ($\lesssim$100 kcal/mol).[21] Clearly CI is important for such a phenomenon if it has a significant effect on the relative energies of the zeroth order electronic states of the reference geometry (D_{4h} in the present case). In the absence of an actual change of equilibrium geometry, the same type of coupling can still lead to marked reduction in force constants. Such a result is expected[5,8] for the triplet state of the square as discussed below. A final pertinent example involves the higher singlet states ($^1A_{1g}$ and $^1B_{2g}$) of the square, which are coupled by the b_{2g} (rhomboid) vibration. A glance at Figure 1 shows that this is indeed a case where CI has a profound effect on the splitting (as well as relative order) of the zeroth order states. This situation, as well as uncertainty regarding strain energy, makes it clear that detailed calculations are required to ascertain whether the rhombus might in fact provide a lower energy alternative to the square.[9e] Recent CI calculations with and STO-3G basis have concluded that all the states of the rhombus are higher than those of the square.[8]

B. SCF Calculations. Before giving a general discussion and comparison of the SCF and CI results we note here a few specific results of interest based on the SCF calculations.

Equilibrium Geometries and Force Constants. The 6-31G* equilibrium geometries obtained for the square singlet ($^1B_{1g}$) and triplet ($^3A_{2g}$) are very similar (r_{CC} = 1.428 and 1.425 Å, respectively) and are also similar to the results of previous studies.[5–9] As expected, the force constants for totally symmetric (a_{1g}) or rectangular (b_{1g}) distortions of the carbon framework (~7.6 mdyn/Å for both) are intermediate between those of ethane (4.9 mdyn/Å) and ethylene (11.5 mdyn/Å); the 4-31G and 6-31G* bases give very similar values.[5] The force constant for the ϵ_u (trapezoidal) distortion of the $^3A_{2g}$ square is considerably smaller (~4.1 mdyn/Å) than for the a_{1g} and b_{1g} modes, a result attributable in part to the proximity of the ^3E_u state (see above).[5,8,22] We have previously noted[5]

that unrestricted Hartree-Fock (UHF) SCF calculations[16e] yielded a much smaller (~1 mdyn/Å with a 4-31G basis) or even negative (with the STO-3G basis) value. The UHF 6-31G* level also gives a small value (~1.6 mdyn/Å). Here is an example of surprising sensitivity both with respect to basis set and the nature of the SCF calculation (RHF vs. UHF). Our RHF SCF result is similar to the value (4.6 mdyn/Å) obtained from STO-3G CI calculations.[8] The $^3A_{2g}$ and $^1B_{1g}$ states of the square give identical force constants (2.07 mdynÅ/rad^2) for the rhomboid (b_{2g}) distortion, and the magnitude is reasonable for angular distortion of a rigid, strained framework.[5]

Symmetry-Broken Solutions. Symmetry-broken solutions were obtained for the lowest ^1A_g state of the rectangle and the $^1B_{2g}$ state of the square, thus underscoring the fact that the SCF model must be used with caution in studying potential energy surfaces and state separations in molecules. The ^1A_g state is triplet unstable,[23] as revealed by the fact that a UHF calculation based on a single configuration (with $M_s = 0$) at the equilibrium rectangular geometry ($r_{CC} = 1.334, 1.564$ Å) is 1 eV lower in energy than the RHF wave function and has an effective spin quantum number (S') of 0.62, obtained by setting $\langle S^2 \rangle = S'(S' + 1)$. Thus while dynamic-spin polarization and the importance of CI have been emphasized for the square singlet,[7,8] it is clear that analogous considerations apply also to the rectangular singlet, which is still associated with a rather low-lying triplet state (i.e., within ~1 eV at the SCF level).

Calculations for the square $^1B_{2g}$ state indicated singlet instability[23] associated with mixing in of the higher (at the 2-configuration level) $^1A_{1g}$ state; i.e., the wave function displayed the D_{2h} symmetry of the rhombus. In particular, an SCF calculation based on the single closed shell configuration

$$^1\psi_{IV}(\phi_2',\phi_2') = |\phi_2' \, \bar{\phi}_2'| = 2^{-1/2}(\psi_{1B_{2g}} + \psi_{1A_{1g}}) \quad (9)$$

gives an energy 0.54 eV lower than that for the RHF $^1B_{2g}$ function. The energy of $^1\psi_{IV}(\phi_2',\phi_2')$ for the square is very similar to that obtained in the limit of $\angle CCC = 90°$ from the 2-configuration SCF ^1A_g state of the rhombus, where ϕ_2' is the function whose nonzero components are on the centers separated by the *larger* diagonal (non-nearest-neighbor) distance (the mixing in of $|\phi_3'\bar{\phi}_3'|$ is found to be very small). This behavior is displayed in Figure 2, which also shows the physically more reasonable energetics exhibited by the limited π-electron CI calculations.

Function $^1\psi_{IV}(\phi_2',\phi_2')$ is characterized by appreciable polarization of σ- and π-electron density since the "nonbonding" π-electron density is primarily restricted to two centers,[24] as opposed to the other states, in which the electron density is rather uniformly spread over all centers; i.e., the populations for the nonequivalent carbon atoms of the symmetry-broken square or the rhombus ($\angle CCC = 85, 95°$) are nearly identical for the $^1B_{1g}$ state, while for the ^1A_g state there is a difference of ~0.5 e. The occurrence of symmetry breaking for the $^1B_{2g}$ SCF state and the associated distortion of σ- and π-electron density from D_{4h} symmetry suggests that both σ- and π-electron CI might be important for this state, and this point will be considered below.

C. CI Calculations. Inspection of Figure 1 and Table II allows several important conclusions to be reached. Most significant for the square geometry is the role of CI in (1) pushing the $^1B_{1g}$ state ~10 kcal/mol below the $^3A_{2g}$ state and (2) reversing the order and greatly increasing (by ~20 kcal/mol) the separation of the $^1A_{1g}$ and $^1B_{2g}$ states. From the discussion above, the latter effect would be expected to reduce any tendency for the first excited singlet state of the square to distort to a more stable rhomboid structure, and in fact we find that a small decrease in the energy of the $^1B_{2g}$ state (or its sym-
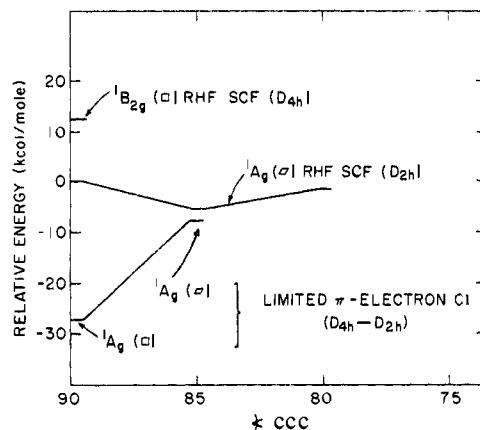

Figure 2. SCF energy for the lowest ^1A_g state of the rhombus (approximated as the closed shell 1-configuration function in eq 9) showing how symmetry breaking leads to a difference between the limiting (90°) energy for the D_{2h} structure and the SCF energy for the 2-configuration RHF $^1B_{2g}$ (D_{4h}) state. The limited π CI results (based on MO's from the $^1B_{1g}$ SCF calculations) are also included for comparison, showing that the square is the equilibrium structure when electron correlation is included. (Note that at the CI level, the ^1A_g state correlates with the $^1A_{1g}$ state of the square.)

metry-broken counterpart) when $\angle CCC$ changes from 90 to 85° at the 1- or 2-configuration levels (see Figure 2 and Table II, respectively) disappears at the larger CI levels, where all states of the square are increased in energy by the b_{2g} distortion. It is interesting to note, however, that the repulsive interaction between $\psi_{1A_{1g}}$ and $\psi_{1B_{2g}}$ (upon b_{2g} distortion) is reflected in the corresponding force constants of ~0.4 mdynÅ/rad^2 and ~4.2 mdynÅ/rad^2 (full π-electron CI, Table II), which straddle the more typical values exhibited by the lowest singlet and triplet states (see section IIB and Table II).

The major effects of CI on relative energies are seen to be provided by the π-electron manifold; e.g., the $^1A_{1g}$-$^1B_{1g}$ and $^1A_{1g}$-$^1B_{2g}$ separations for the square are little affected by the limited σ-electron CI. These calculated separations are appreciably smaller than those obtained from CI based on a minimal π-electron basis.[8,10] The greatest influence of σ-electron correlation appears to be in increasing (by ~6 kcal/mol) the magnitude of the barrier separating the rectangular structures of the ground singlet state, a result similar to that found from STO-3G CI studies.[8] The barrier of ~12 kcal/mol is close to previous estimates, which were based on smaller scale variational calculations or perturbation-theoretic models[7,8,10] and also turns out to be virtually the same as that obtained at the 2-configuration SCF level. This is in sharp contrast to the situation for the single-configuration RHF treatment of the rectangle, which places it at a *higher* energy than that of the RHF square.

The finding of a symmetry-broken solution for the first excited singlet state of the square with a strongly polarized σ- as well as π-electron density indicated (see section IIB) that σ-π correlation might be especially important for this electronic state. While σ-electron correlation is indeed appreciable (the energy of $^1B_{2g}$ drops ~0.04 au, upon passing from the limited π- to the limited ($\pi + \sigma$)-electron CI levels), the effect is not much different than for any of the other states.

D. Detailed Comparison of the Square and the Rhombus. Let us now consider the effect of electron correlation on the behavior of the higher singlet states in somewhat more detail. In order to have approximate wave functions appropriate for both the square and the rhombus, we express the principal configurations in terms of ϕ_2' and ϕ_3' (refer back to eq 3, 4, 6, and 8):

$$\psi_A \equiv \psi_{1A_{1g}} = \psi_{III}(\phi_2',\phi_3'), \quad a, b = 2^{-1/2} \quad (10)$$

$$\psi_B \equiv \psi_{1B_{2g}} = \psi_{III}(\phi_2', \phi_3'), \quad a = 2^{-1/2}, b = -2^{-1/2} \quad (11)$$

It turns out that two other configurations are very important for the CI associated with the $^1A_{1g}$ state (and its ^1A_g counterpart in rhomboid geometry):

$$\psi_C \equiv \psi_{1A_{1g}}' = |\phi_2'\bar{\phi}_2'\phi_3'\bar{\phi}_3'| \quad (12)$$

$$\psi_D \equiv \psi_{1A_{1g}}'' = |\phi_1\bar{\phi}_1\phi_4\bar{\phi}_4| \quad (13)$$

Considering the problem first at the 2-configuration level, we find that the two states ψ_A and ψ_B are nearly degenerate ($H_{AA} - H_{BB} = 6.5$ kcal/mol) and of course $H_{AB} = 0$, where the matrix elements refer to the full Schroedinger hamiltonian. The corresponding matrix elements for the structure obtained by a five degree rhomboid distortion of the square display the expected interaction ($H_{AB} = 10.0$ kcal/mol) and also the effect of increased strain energy (both H_{AA} and H_{BB} increase by 5.6 kcal/mol, relative to the square).[25] The slight stabilization of the $^1B_{2g}$ state caused by the b_{2g} distortion (-2.6 kcal/mol, Table II) is thus a compromise between the stabilizing H_{AB} interaction and the extra strain energy. As soon as even limited π-electron CI is carried out, however, the H_{AB} interaction is dominated by the much stronger H_{AC} and H_{AD} matrix elements (65 and 78 kcal/mol, respectively) even though H_{CC} and H_{DD} are both ~ 0.5 au above H_{AA}. It is these matrix elements (H_{AC} and H_{AD}) which are primarily responsible for the $^1A_{1g}$ state of the square being pushed ~ 30 kcal/mol *below* the $^1B_{2g}$ state. Thus as far as the perturbation–theoretic analysis of the rhomboid distortion is concerned,[21] the result of CI is a somewhat smaller effective interaction constant and a much larger energy denominator, with the consequence that both the $^1A_{1g}$ and $^1B_{2g}$ states are now stable with respect to the b_{2g} distortion.[26] The original H_{AB} interaction manifests itself only to the extent that the force constants for the b_{2g} distortion of the $^1A_{1g}$ and $^1B_{2g}$ states depart significantly from those for the $^1B_{1g}$ state, as noted above.

The reduced interaction between ψ_A and ψ_B caused by coupling with ψ_C and ψ_D is also reflected by the relative contributions of ψ_A and ψ_B to the ^1A_g eigenfunction of the rhombus (five degree distortion): ψ_A contributes 80%, compared to only 12, 4, and 3% from ψ_B, ψ_C, and ψ_D, respectively, at the limited π-electron CI level; at the 2-configuration level the mixing is much greater (66% of ψ_A and 34% of ψ_B).[27]

In the absence of an interaction strong enough to push the ^1A_g state of the rhombus below the $^1B_{1g}$ state (cf. ref 9e), we are left with the $^1B_{1g}$ state of the square as the most likely candidate for the transition state between rectangular singlets. Furthermore the calculated energetics of the triplet indicate that it is not low-lying enough to play a role in any of the observed experimental data (e.g., as a long-lived metastable species[9d]). Hence further spectroscopic investigations will be required to allow a definitive accounting of the spectral data which have been observed so far under conditions of matrix isolation,[2] including reconciling these data with what is apparently a rectangular equilibrium singlet structure. In future theoretical attempts to rationalize the spectroscopic data, calculations of expected intensities of vibrational transitions will probably be crucial.

IV. Summary and Comparison with Previous Calculations

The discussion of results in section III makes it clear that the large-scale CI calculations reported in the present work are in general qualitative agreement with earlier ab initio studies[7,8,10] which included electron correlation. To help put all these studies in perspective we emphasize the following points of comparison.

Regarding the separation of the square singlet and triplet, the previous CI calculations showed that basis set improvement tended to reduce the relative stability of the singlet (from 18

kcal/mol for a minimal STO/3G basis[8] to 7.3 kcal/mol for a double-ζ plus 3d-polarization basis[7]). Our results with the 6-31G* basis essentially reproduce the latter number (8.2 kcal/mol) but also reveal that inclusion of σ-electron correlation causes the splitting to increase somewhat (to 11 kcal/mol).

Previously, values of 14 kcal/mol (estimated from double-ζ basis, π-electron correlation calculations[7]) and 8.3 kcal/mol (minimal STO basis, σ-π CI[8]) have been found for the all-important barrier associated with the square which separates the rectangular structures on the ground state potential energy surface. Using the larger 6-31G* basis, we obtain a barrier of 6 kcal/mol at the π-electron CI level, but as in ref 8, we find this value to be roughly doubled upon inclusion of σ- as well as π-electron correlation, leading to the value of 12 kcal/mol as our best estimate. This latter value (which, incidentally, turns out to be the same as that yielded by the 2-configuration SCF model) is of such a magnitude as to be inconsistent with interconversion of the rectangles through a square transition state on anything close to a vibrational time scale.

With respect to the low-lying singlet manifold of the square ($^1B_{1g}$, $^1A_{1g}$, $^1B_{2g}$), the present work yields a much smaller energy spread (0, 45, and 74 kcal/mol relative energies) compared to the minimal STO π-electron CI results (0, 70, and 140 kcal/mol); the difference appears to arise from the more flexible basis in the present work and is little affected by σ-electron CI. In general our limited inclusion of σ MO's in the configuration interaction does not lead to any qualitative changes relative to the limited π-electron CI results. The most notable quantitative effects have been noted above.

The stabilizing effect of a b_{2g} (rhomboid) distortion on the π-electron component of the B_{2g} square singlet (first predicted from simple symmetry considerations in conjunction with a simple semiempirical model[9e] and indirectly inferred from differential distortion energies in a previous STO-3G CI study)[8] has been identified in the present study in terms of an unusually small framework bending force constant. However, as in ref 8, this effect is not large enough to cause a net stabilization of the rhombus with respect to the square. In fact, at the CI level all four low-lying states of the square are stable with respect to the b_{2g} mode, a result attributable in part to resistance to increased strain energy and, in the case of the $^1A_{1g}$ state, to the role of CI in increasing the $^1A_{1g}$-$^1B_{2g}$ separation. These results imply that the square is the lowest energy intermediate for interconversion of rectangular singlets, since nonplanar structures (which were not considered here) do not appear to be likely alternatives.

References and Notes

(1) Address correspondence to this author.
(2) (a) C. Y. Lin and A. Krantz, *Chem. Commun.*, 1111 (1972); (b) A. Krantz, C. Y. Lin, and M. D. Newton, *J. Am. Chem. Soc.*, **95**, 2744 (1973); (c) R. G. S. Pong, B.-S. Huang, J. Laurenl, and A. Krantz, *ibid.*, **99**, 4153 (1977); (d) O. L. Chapman, C. L. McIntosh, and J. Pacansky, *ibid.*, **95**, 614 (1973); (e) O. L. Chapman, D. De La Cruz, R. Roth, and J. Pacansky, *ibid.*, **95**, 1337 (1973); (f) S. Masamune, Y. Suglhara, K. Morio, and J. E. Bertie, *Can. J. Chem.*, **54**, 2679 (1976); (g) S. Masamune, T. Machiguchi, and M. Aratani, *J. Am. Chem. Soc.*, **99**, 3524 (1977).
(3) (a) S. Masamune, N. Nakamura, M. Suda, and H. Ona, *J. Am. Chem. Soc.*, **95**, 8481 (1973); (b) G. Maier and A. Alzerreca, *Angew. Chem., Int. Ed. Engl.*, **12**, 1015 (1973).
(4) (a) L. T. Delbaere, M. N. G. James, N. Nakamura, and S. Masamune, *J. Am. Chem. Soc.*, **97**, 1973 (1975); (b) H. Irngartinger and H. Rodewald, *Angew. Chem., Int. Ed. Engl.*, **13**, 740 (1974).
(5) M. D. Newton in "Methods of Electronic Structure Theory", H. F. Schaefer III, Ed., Plenum Press, New York, N.Y., 1977, p 223.
(6) R. C. Haddon and G. R. J. Williams, *J. Am. Chem. Soc.*, **97**, 6582 (1975).
(7) H. Kollmar and V. Staemmler, *J. Am. Chem. Soc.*, **99**, 3583 (1977).
(8) W. T. Borden, E. R. Davidson, and P. Hart, *J. Am. Chem. Soc.*, **100**, 388

(1978). We are grateful to these authors for making available a preprint prior to publication.

(9) (a) Several recent semiempirical studies have also been reported.[9b-e] (b) M. J. S. Dewar and H. W. Kollman, *J. Am. Chem. Soc.*, **97**, 2933 (1975); (c) M. J. S. Dewar, *Pure Appl. Chem.*, **44**, 767 (1975); (d) M. J. S. Dewar and A. Komornicki, *J. Am. Chem. Soc.*, **99**, 6174 (1977); (e) E. A. Halevi, F. A. Matsen, and T. L. Welsher, *ibid.*, **98**, 7088 (1976).

(10) (a) R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, **48**, 354 (1968); (b) *J. Am. Chem. Soc.*, **91**, 4342 (1969).

(11) G. Herzberg, "Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra of Polyatomic Molecules", Van Nostrand, Princeton, N.J., 1945.

(12) E. Wasserman and R. S. Hutton, *Acc. Chem. Res.*, **10**, 27 (1977); *J. Am. Chem. Soc.*, **95**, 8481 (1973).

(13) G. Herzberg, "Electronic Spectra and Electronic Structure of Polyatomic Molecules", Van Nostrand, New York, N.Y., 1967.

(14) (a) P. C. Hariharan, W. A. Lathan, and J. A. Pople, *Chem. Phys. Lett.*, **14**, 385 (1972); P. C. Hariharan and J. A. Pople, *ibid.*, **16**, 217 (1972); P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, **28**, 213 (1973). Smaller commonly used bases are the STO-3G[14b] and 4-31G[14c] sets. (b) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969); (c) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).

(15) (a) W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **97**, 6941 (1975); (b) J. S. Binkley, J. A. Pople, and W. J. Hehre, *Chem. Phys. Lett.*, **36**, 1 (1975).

(16) (a) C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 179 (1960); (b) W. J. Hunt, W. A. Goddard, and T. H. Dunning, Jr., *Chem. Phys. Lett.*, **6**, 147 (1970); (c) W. J. Hunt, P. J. Hay, and W. A. Goddard III, *J. Chem. Phys.*, **57**, 738 (1972); (d) J. S. Binkley, J. A. Pople, and P. A. Dobosh, *Mol. Phys.*, **28**, 1423 (1974); (e) J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, **22**, 571 (1954). (f) The open-shell restricted Hartree–Fock (RHF) SCF calculations reported here were carried out using the computer program written by the authors of ref 16b. The other SCF calculations (closed-shell RHF and open shell unrestricted Hartree–Fock (UHF)[16e]) employed the GAUSSIAN 70 program, written by W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, QCPE 236, Quantum Chemistry Program Exchange, Indiana University, Newsletter 43, Bloomington, Ind. 47401, November, 1973.

(17) (a) J. L. Whitten and M. Hackmeyer, *J. Chem. Phys.*, **51**, 5584 (1969). The CI calculations reported here were carried out with the computer program written by these authors. (b) Typically 5–10 reference configurations were sufficient for generating all the desired configurations.

(18) See, for example, J. L. Whitten, *J. Chem. Phys.*, **56**, 5458 (1972).

(19) CI calculations for the $^1B_{2g}$ state of the square demonstrated little sensitivity to whether the MO's were taken from the $^3A_{2g}$ or $^1B_{1g}$ SCF calculations: e.g., at the large π electron CI level, the total energies differed by $<10^{-4}$ au. Even at the 2-configuration level, the difference is quite small (1.8 kcal/mol). Direct SCF calculations for the $^1B_{2g}$ (or ^1A_g for rhomboid geometry) state are discussed in section IIIB.

(20) See, for example, the discussion given in ref 5. The general formalism is given in ref 21.

(21) (a) R. G. Pearson, *J. Am. Chem. Soc.*, **91**, 4947 (1969); (b) R. F. W. Bader, *Can. J. Chem.*, **40**, 1164 (1962); (c) L. Salem, *Chem. Phys. Lett.*, **3**, 99 (1969).

(22) A somewhat smaller value (~3.1 mdyn/Å) was obtained for the trapezoidal distortion of the long single bonds of the equilibrium rectangular singlet, based on a RHF (single configuration) calculation (6-31G* basis).

(23) J. Cizek and J. Paldus, *J. Chem. Phys.*, **47**, 3976 (1967).

(24) The ϕ_2' and ϕ_3' MO's are not totally confined to nonadjacent centers because of the small contributions (≤ 0.01 electron) of 3d basis functions to the centers lying in the modal planes.

(25) The CI results for both square and rhomboid structures were based on MO's obtained from SCF calculations for the ground state singlets (i.e., $^1B_{1g}$).

(26) In spite of the role of ψ_C and ψ_D in increasing the separation of ψ_A and ψ_B, it should be noted that this separation is still well within the "rule of thumb" upper limit of ~100 kcal/mol, below which stable nonsymmetric distortions are typically observed.

(27) The mixing is even greater (~50–50%) when the 2-configuration wave function is obtained self-consistently (i.e., the MO's are calculated directly for the lowest ^1A_g state), as discussed in section IIIB.

Electronic Structure of Cyclopentadienylthallium(I)

Carl S. Ewig, Roman Osman,[1] and John R. Van Wazer*

Contribution from the Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235. Received December 16, 1977

Abstract: An SCF calculation based on the recently developed theory of effective potentials has been carried out for gaseous cyclopentadienylthallium(I) in its experimental equilibrium conformation. In this compound, the thallium atom is found to be nearly neutral with an overall electron distribution of $s^{1.75}p^{0.45}d^{0.71}$ as obtained from a Mulliken population analysis. The overlap population of 0.47 e between thallium and the cyclopentadienyl ring is about half of each C–C overlap in the ring. Bonding is principally due to the highest filled molecular orbital pair of E_1 symmetry based primarily on pd^2 of Tl and p of the C atoms interacting in π symmetry with respect to the C_5 axis of the molecule. A lesser contributor is the second highest a_1 orbital dominated by Tl sp interaction with the carbon p's that are again π with respect to the ring plane. The electronic basis for the half-sandwich structure of C_5H_5Tl is discussed.

The compound C_5H_5Tl, discovered by Fischer[2] in 1957, is a highly insoluble crystalline substance that sublimes to a monomeric vapor around 80 °C. The solid has found wide laboratory application as a donor of the cyclopentadienyl moiety. The chemical properties of solid C_5H_5Tl led Fischer to think that the compound was a half-sandwich rather than a structure exhibiting a Tl–C σ bond.

By X-ray diffraction,[3] the solid form of cyclopentadienylthallium has been shown to have a chain structure consisting of alternating C_5H_5 rings and Tl atoms with the center of each ring being equidistant from the nearest thalliums and a 137° bend in the chain at each Tl atom. Raman spectroscopy[4] did not show bands in the region where metal–ring frequencies are usually observed. Microwave spectra[5] of the vapor of monomeric C_5H_5Tl demonstrated C_{5v} symmetry and provided a partial molecular geometry, while a full molecular structure[6] was obtained by electron diffraction for the related compound C_5H_5In, which has the same symmetry. An interesting feature of the C_5H_5In structure is the fact that the C–H bonds are

pushed 4.5° out of the plane of the carbon ring by the indium atom.

The large core-electron structure of the thallium atom of pentadienylthallium has thus far precluded a full SCF calculation on this interesting molecule. However, the recent advances[7,8] in effective potential theory and its application have made it feasible to study the electronic structure of the gaseous monomer of this compound by a nonempirical SCF method, and such calculations are reported below.

Computational Procedure

Our NOCOR theory of molecular effective potentials and pseudopotentials has been described previously.[7,8] The resulting SCF equations are of the form

$$F\chi_v^i = \epsilon_v^i \chi_v^i \qquad (1)$$

where χ_v^i is the ith valence pseudo-wave function; ϵ_v^i is the valence orbital energy; and F, the effective Fock operator, has the form