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## The Potential Surfaces for the Lowest Singlet and Triplet States of Cyclobutadiene

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**Abstract:** The potential surfaces for the lowest singlet and triplet states of cyclobutadiene have been explored by ab initio MO calculations with full  $\pi$ -space, CI, using a basis set of STO-3G orbitals. The calculated force constants for distortion from  $D_{4h}$  symmetry are in excellent agreement with qualitative expectations, derived from an analysis in terms of second-order Jahn-Teller effects. A square geometry is found to represent a minimum for the triplet and a transition state between two rectangular geometries for the singlet. The rectangular minimum for the singlet has been located, and the energy difference between square and rectangular singlets is found to be 4.2 kcal/mol. Using a basis set of double  $\zeta$  quality, the calculated energy difference remains almost unchanged; but additional CI, involving the  $\sigma$  space, increases the difference to 8.3 kcal/mol. It is concluded from these calculations that the parent [4]annulene is not square or effectively square in its ground state, thus casting serious doubt on the interpretation of the IR spectrum of matrix isolated cyclobutadiene as belonging to a square molecule.

Although for several substituted cyclobutadienes a singlet ground state with a nonsquare equilibrium geometry has been indicated<sup>1</sup> or established,<sup>2</sup> the IR spectrum of the matrix isolated parent [4]annulene has been interpreted as belonging to a square molecule.<sup>3</sup> Not only have all attempts to detect an EPR signal from the matrix isolated species failed,<sup>4</sup> but also, one of us recently showed theoretically that the lowest singlet state of cyclobutadiene most certainly lies below the triplet, even at square geometries.<sup>5</sup> Kollmar and Staemmler have subsequently verified this theoretical result and have termed the interorbital electron correlation effect responsible for it "dynamic spin polarization",<sup>6</sup> a designation we find most appropriate in view of the previously demonstrated relationship between this effect in cyclobutadiene and the static spin polarization in radicals like allyl.<sup>5</sup>

Since dynamic spin polarization results in a singlet ground state for cyclobutadiene, even at square geometries, the IR of the matrix isolated molecule could reasonably be assigned to this state, *if* the lowest singlet state were expected to have a square equilibrium geometry, or if the potential surface for distortion away from a  $D_{4h}$  geometry were very flat. Although it has been argued that electron repulsion results in a rather flat potential curve for rectangular distortion in the singlet,<sup>5,7</sup> the ab initio calculations published at the time that we began the present theoretical study found the lowest energy square geometry to lie  $8^{3d}-11^8$  kcal/mol above the equilibrium rectangular one. One goal of this study was to examine the basis set dependence of the calculated energy difference between the rectangular and the square singlet and to see whether inclusion of correlation between the  $\sigma$  and  $\pi$  electrons would reduce the computed difference. In addition, we wanted to test the merit of suggestions in the literature that a rhomboidal geometry might be lower in energy than a square one<sup>9</sup> and that a trapezoidal carbon skeleton might have a smaller energy content than a rectangular one.<sup>7</sup> Thus, we did not confine ourselves to studying only the rectangle-square potential curve for the

singlet but set out instead to establish by ab initio MO calculations some of the important features of the complete potential surfaces for both the lowest singlet and triplet states of cyclobutadiene.

### Results and Discussion

**Square Cyclobutadiene.** As in our previous studies of the potential surfaces for other open-shell molecules,<sup>10,11</sup> we began by finding the optimum cyclobutadiene geometry of highest ( $D_{4h}$ ) symmetry and then considered distortions away from this square array of carbons. Unlike the case in trimethylenemethane<sup>10</sup> and the cyclopropenyl anion,<sup>11</sup> the lowest singlet state of square cyclobutadiene is nondegenerate ( $^1B_{1g}$ ). Square cyclobutadiene may be considered a diradical,<sup>12</sup> since in the lowest singlet state each of the degenerate ( $e_g$ ) nonbonding  $\pi$  MOs

$$\psi_2 = \phi_1 - \phi_3 \quad (1)$$

$$\psi_3 = \phi_2 - \phi_4 \quad (2)$$

contains one electron. Thus, the SCF wave functions for  $^1B_{1g}$  and the  $m_s = 0$  component of the lowest triplet ( $^3A_{2g}$ ) can be written

$$^1B_{1g}, ^3A_{2g} = (| \dots \psi_1^2 \psi_2^\alpha \psi_3^\beta \rangle \mp | \dots \psi_1^2 \psi_2^\beta \psi_3^\alpha \rangle) / \sqrt{2} \quad (3)$$

where the upper sign gives the singlet wave function, the lower the triplet, and

$$\psi_1 = \phi_1 + \phi_2 + \phi_3 + \phi_4 \quad (4)$$

is the lowest energy ( $a_{2u}$ )  $\pi$  MO. Since  $\psi_2$  and  $\psi_3$  are confined to different sets of atoms, the exchange integral between them is expected to be small (zero when differential overlap is neglected).<sup>5</sup> Therefore, this set of nonbonding MOs is useful for understanding why  $^1B_{1g}$  and  $^3A_{2g}$  are nearly degenerate at the SCF level. Nevertheless, for considering all but rhomboidal

distortions from  $D_{4h}$  symmetry, it is more convenient to employ another set of nonbonding MOs,

$$\psi_2' = (\psi_2 + \psi_3)/\sqrt{2} \quad (5)$$

$$\psi_3' = (\psi_2 - \psi_3)/\sqrt{2} \quad (6)$$

Using the primed set of MOs, the wave function for the singlet takes the form<sup>12</sup>

$${}^1B_{1u} = (|\dots\psi_1^2\psi_2'^2\rangle - |\dots\psi_1^2\psi_3'^2\rangle)/\sqrt{2} \quad (7)$$

while in the triplet, of course, one electron occupies each of the primed nonbonding MOs.

The optimum C–C bond lengths for  ${}^1B_{1g}$  and  ${}^3A_{2g}$  were found, using an STO-3G basis set,<sup>13</sup> by carrying out a series of full  $\pi$ -space configuration interaction (CI) calculations for each state and assuming a quadratic potential around each minimum to interpolate the last significant figure. Throughout all the calculations reported in this paper the C–H bond lengths were fixed at 1.10 Å, and the C–H bonds were oriented so that they bisected the C–C–C bond angles. The unprimed set of  $\pi$  MOs in eq 1 and 2 were generated by restricted open-shell SCF calculations<sup>14</sup> in which  $D_{2h}$  symmetry, with two twofold axes oriented along the C–H bonds, was imposed on the MOs. As anticipated,<sup>12</sup> the same set of MOs were obtained from SCF calculations on both  ${}^1B_{1g}$  and  ${}^3B_{1g}$  ( ${}^1B_{1g}$  and  ${}^3A_{2g}$  in  $D_{4h}$ ). Also as expected,<sup>5</sup> the triplet was found to lie below the singlet by 2.7 kcal/mol at the SCF level. The primed set of MOs in eq 5 and 6 was generated by SCF calculations on  ${}^3B_{1g}$  ( ${}^3A_{2g}$ ), again with  $D_{2h}$  symmetry imposed on the MOs, but with two of the twofold axes bisecting pairs of C–C bonds. Whether the primed or unprimed MOs were employed for the CI calculations, the same CI energies were obtained.<sup>15</sup> The  ${}^1B_{1g}$  state was found to have its energy minimum at a C–C bond length of 1.453 Å with a calculated CI energy of  $-151.8409$  hartrees. The triplet was found to have almost the same optimum C–C bond length, 1.451 Å; and, as anticipated,<sup>5</sup> its CI energy was 18.0 kcal/mol above that of  ${}^1B_{1g}$ .

**Distortions from  $D_{4h}$  Symmetry. Theoretical Considerations.** Since  ${}^1B_{1g}$  is nondegenerate, it is not subject to a first-order Jahn–Teller effect. However, a distortion that destroys  $D_{4h}$  symmetry can mix  ${}^1B_{1g}$  with other states that have different symmetries in square cyclobutadiene. This mixing can be treated by second-order perturbation theory and has been called a second-order Jahn–Teller effect.<sup>16</sup> The alteration of the  ${}^1B_{1g}$  wave function by this mixing on distortion lowers the energy of the distorted molecule, relative to that of the distorted molecule with a frozen  ${}^1B_{1g}$  wave function. If the magnitude of the energy lowering caused by the mixing is greater than the increase in energy that results from the distortion with the wave function frozen, then molecular distortion will lead to a net decrease in energy. Thus, the second-order Jahn–Teller effect can, in principle, produce nonsquare equilibrium geometries for cyclobutadiene.

In order to assess qualitatively the relative probability that a distortion will lead to a net energy lowering, it must be established which states will mix under the influence of the distortion. In general, the closer the unperturbed states being mixed are in energy, the stronger will be their mixing and the more likely that a net energy lowering will result from distortion. The group theoretical rule for mixing of two states by a distortion is that the direct product of the representations to which they belong in the undistorted molecule must be the same as the representation of the vibration which produces the distortion.<sup>16</sup> Therefore, in cyclobutadiene it is possible to determine for each normal vibrational mode of the square molecule what states will be mixed. From the energetic proximity of these states, the relative likelihood that such a distortion will lead to an overall decrease in energy and, thus, to a nonsquare equilibrium geometry, can then be assessed.

A square array of four atoms has, in addition to a symmetrical stretch, which preserves  $D_{4h}$  symmetry, five other normal modes. The  $b_{1g}$  mode lengthens two opposite bonds and shortens the remaining two, thus leading to a rectangular distortion. This distortion mixes  $B_{1g}$  with states of  $A_{1g}$  symmetry. There is a very low lying singlet state of  $A_{1g}$  symmetry in square cyclobutadiene. At the square minimum we compute it to lie only 70 kcal/mol higher in energy than  ${}^1B_{1g}$ . Thus, its mixing into  ${}^1B_{1g}$  is anticipated to be strong and to lead, quite possibly, to an energetically favorable rectangular distortion. The physical reason why this mixing might favor distortion is apparent from the form of the  ${}^1A_{1g}$  SCF wave function,

$${}^1A_{1g} = (|\dots\psi_1^2\psi_2'^2\rangle + |\dots\psi_1^2\psi_3'^2\rangle)/\sqrt{2} \quad (8)$$

On mixing eq 8 into eq 7, it is seen that in the resulting wave function two electrons can be increasingly localized in the primed MO that is stabilized by rectangular distortion. Although a  ${}^3B_{2g}$  state can be mixed into  ${}^3A_{2g}$  by a  $b_{1g}$  mode, there is no low-lying triplet state of  $B_{2g}$  symmetry. A rectangular distortion, therefore, should be energetically costly for the triplet.

A second vibrational mode that destroys  $D_{4h}$  symmetry is  $b_{2g}$ , which involves only bond angle changes and distorts a square into a rhombus. This vibration mixes  ${}^1B_{1g}$  with  ${}^1A_{2g}$ . A singlet state of  $A_{2g}$  symmetry exists, but it differs from  ${}^1B_{1g}$  by the excitation of an electron from  $\psi_1$  to  $\psi_4$  ( $a_{2u} \rightarrow b_{1u}$ ), where  $\psi_4$  is the antibonding  $\pi$  MO,

$$\psi_4 = \phi_1 - \phi_2 + \phi_3 - \phi_4 \quad (9)$$

Since  ${}^1A_{2g}$  is, consequently, very high in energy, it is much less probable that  ${}^1B_{1g}$  cyclobutadiene will undergo a rhomboidal than a rectangular distortion. The same excitation is required to create a  ${}^3B_{1g}$  state, which can mix with  ${}^3A_{2g}$  upon a  $b_{2g}$  distortion; therefore, a rhomboidal triplet seems equally unlikely to represent an energy minimum.

A  $b_{2g}$  distortion also mixes  $B_{2g}$  and  $A_{1g}$  states, and a singlet of  $B_{2g}$  symmetry is computed as being about 70 kcal/mol higher in energy than the excited  ${}^1A_{1g}$  state, discussed above. Mixing of  ${}^1B_{2g}$  into  ${}^1A_{1g}$  results in a  $D_{2h}$  wave function of the form

$${}^1A_g = c_1|\psi_1^2\psi_2^2\rangle + c_2|\psi_1^2\psi_3^2\rangle \quad (10)$$

where the configuration with the larger coefficient is the one in which two electrons occupy the MO that spans the two carbons along the long axis of the rhombus. Thus, this mixing not only occurs between states with an energy separation similar to that between  ${}^1B_{1g}$  and  ${}^1A_{1g}$ , but its effect is of the same type—the lower of the two  $\pi$  MOs, whose degeneracy is lifted by the distortion, has its occupation number increased. Nevertheless, since the nearest-neighbor  $\pi$  AO interactions, which are altered by a rectangular distortion, are substantially larger than the cross-ring interactions that are modified in going to a rhomboidal geometry, it can be predicted that  ${}^1B_{1g}$  is more apt to undergo a rectangular distortion than  ${}^1A_{1g}$  is a rhomboidal one.

In addition to an out-of-plane,  $b_{1u}$ , ring puckering distortion, whose effect we do not consider in this paper,<sup>17</sup> the remaining distortion modes of a square are a degenerate pair of  $e_u$  symmetry. They can each be represented as lengthening one C–C bond, shortening the one opposite it by the same amount, and leaving the remaining two unchanged in length. Thus, each of this pair of distortions leads to a trapezoidal geometry. These distortions mix the lowest singlet and triplet with states of  $E_u$  symmetry. Configurations with this symmetry have an odd number of electrons in the degenerate pair of  $e_g$  MOs. The lowest energy  $\pi$  configurations of this type are  $\{a_{2u}e_g^3\}$  and  $\{a_{2u}^2e_gb_{1u}\}$ , which, by the pairing theorem, have the same energy. There is a nonzero matrix element between these

**Table I.** Quadratic Force Constants (mdyn/Å) for Bond Length Changes in  $^1B_{1g}$  and  $^3A_{2g}$  States of  $D_{4h}$  Cyclobutadiene

	$k(^1B_{1g})$	$k(^3A_{2g})$
$a_{1g}$	8.2	8.1
$b_{1g}$	Negative	7.9
$e_u$	6.4	4.6

configurations, so two  $E_u$  states of different energy can be formed from linear combinations of these configurations. The lower of the two  $E_u$  states in both the singlet and triplet manifolds is the one that provides stabilization to the lowest state on trapezoidal distortion. The relevant  $^1E_u$  state is computed to lie 280 kcal/mol above  $^1B_{1g}$ , while the corresponding  $^3E_u$  is calculated as only 90 kcal/mol above  $^3A_{2g}$ .<sup>18</sup> Therefore, it can be predicted that  $^3A_{2g}$  should be more prone to trapezoidal distortion than  $^1B_{1g}$ .

**Computational Results.** Distortions of  $b_{1g}$ ,  $b_{2g}$ , and  $e_u$  symmetry were examined, starting from the optimized square geometry for  $^1B_{1g}$ . SCF orbitals, calculated with appropriate symmetry constraints for the lowest triplet, were used to form the CI matrices for both the singlet and triplet states, since near the square geometry SCF calculations on closed-shell singlet configurations led to overdistortion of the  $\sigma$  core.<sup>15</sup> To facilitate comparisons, the energies computed from the full  $\pi$  space CI calculations were fitted to quadratic potentials, and the resulting force constants for bond length distortions in  $^1B_{1g}$  and  $^3A_{2g}$  are displayed in Table I. For comparison, the force constants for  $a_{1g}$  bond stretching are included, because there is no second-order Jahn–Teller effect for this symmetrical mode.

For  $b_{2g}$  distortions of all four bond angles by  $5^\circ$ , the calculated energies of all the states remained essentially unchanged. For  $10^\circ$  distortions, however, there were substantial energy increases. Since the energy change was obviously not quadratic for  $b_{2g}$  distortions, the force constants for this mode do not appear in Table I. Nevertheless, as anticipated by the discussion in the previous section, the lowest singlet and triplet undergo nearly identical increases, 21.1 kcal/mol for the former and 21.7 kcal/mol for the latter on a  $b_{2g}$  distortion of  $10^\circ$ . Also as expected, the  $^1A_g$  state undergoes a rhomboidal distortion more readily than either the lowest singlet or triplet; its energy increases by 16.0 kcal/mol on a  $10^\circ$  distortion of all the bond angles. Based on an orbital symmetry analysis and semiempirical  $\pi$  electron calculations, it has been suggested<sup>9</sup> that a rhomboidal  $^1A_g$  state<sup>19</sup> might fall below the square  $^1B_{1g}$ , thus providing an “allowed” pathway for bond flipping in cyclobutadiene. Our results show that not only does the relevant  $^1A_{1g}$  state<sup>19</sup> start off more than 70 kcal/mol above  $^1B_{1g}$  at  $D_{4h}$ , but the energy of  $^1A_{1g}$  actually increases on a rhomboidal distortion. Thus, our data certainly provide no support for the suggestion<sup>9</sup> of an orbital symmetry allowed pathway for bond flipping in cyclobutadiene.

The results contained in Table I are in excellent agreement with the qualitative expectations based on the second-order

Jahn–Teller effect and discussed in the previous section. As would be anticipated from the fact that the lowest singlet and triplet have similar wave functions at square geometries, they have almost the same force constant for symmetrical ( $a_{1g}$ ) bond stretching. However, while the force constant for the triplet is nearly unchanged for rectangular ( $b_{1g}$ ) distortion, that of the singlet is actually negative, indicating that the square geometry represents an energy maximum for this mode. Also as expected, the triplet has a smaller force constant for trapezoidal ( $e_u$ ) distortion than the singlet, with both force constants being lower than those for  $a_{1g}$  bond stretching.

The most important findings of our study of distortions from  $D_{4h}$  symmetry in cyclobutadiene are that the singlet has a negative force constant for only a  $b_{1g}$  mode, while the triplet has no negative force constants. The first of these results implies that square  $^1B_{1g}$  cyclobutadiene is a transition state for interconversion, by double-bond flipping, of two equivalent rectangular singlets;<sup>20</sup> while the second shows that the triplet has its energy minimum at a square geometry.

#### Energy Difference between Rectangular and Square Singlets.

In order to locate the rectangular minimum for the singlet, we carried out additional full  $\pi$ -space CI calculations. As noted above, around the square minimum SCF calculations on  $^1A_g$  configurations led to overdistortion of the  $\sigma$  core and to higher CI energies than those calculated from the SCF MOs of the lowest triplet.<sup>15</sup> In contrast, near the rectangular minimum SCF MOs computed for the lower of the two singlet configurations in eq 7 gave better CI energies by 0.1 kcal/mol than did the SCF MOs of the triplet. The rectangular minimum had C–C bond distances of 1.369 and 1.539 Å and a CI energy of  $-151.8477$  hartrees, 4.2 kcal/mol below that of the square singlet. The force constants for trapezoidal distortion from the rectangle were found to be 5.3 and 9.3 mdyn/Å. One of these is smaller and one larger than the degenerate pair for the singlet in the square geometry, since in the rectangle the force constants correspond, respectively, to altering the lengths of essentially single and double bonds, rather than to distorting the partial double bonds in the square molecule. The positive force constants show that the lowest singlet prefers a rectangular to a trapezoidal geometry, in contrast to the results of a previous semiempirical study.<sup>7</sup>

In order to test to what extent our calculated energy difference between the rectangular and square singlet was basis set dependent, we carried out full  $\pi$  space CI calculations at the optimized geometries, using a double  $\zeta$  quality basis consisting of 9s and 5p Huzinaga orbitals<sup>21</sup> on carbon, contracted to 4s and 2p using Dunning's scheme,<sup>22</sup> and 5s orbitals on hydrogen, contracted to 3s by Davidson's method.<sup>23</sup> As with the STO-3G calculations, the SCF orbitals for full  $\pi$ -space CI were generated for the square singlet from the  $^1B_{1g}$  wave function in eq 3 and for the rectangular singlet from the lower of the two configurations in eq 7. The results at both the SCF and CI levels are given in Table II, along with those for the

**Table II.** Calculated Energies of Singlet Cyclobutadiene at Square<sup>a</sup> and Rectangular<sup>b</sup> Geometries

	STO-3G $\pi$ space CI	Double $\zeta$ $\pi$ space CI	STO-3G $\sigma$ - $\pi$ CI
Square SCF energy <sup>c</sup>	-151.7442	-153.5871	-151.7442
Rectangular SCF energy <sup>c</sup>	-151.7363	-153.5845	-151.7363
$\Delta^d$	-5.0	-1.6	-5.0
Square correlation energy <sup>c</sup>	-0.0967	-0.0735	-0.2731
Rectangular correlation energy <sup>c</sup>	-0.1114	-0.0825	-0.2943
$\Delta^d$	+9.2	+5.6	+13.3
Square total energy <sup>c</sup>	-151.8409	-153.6606	-152.0173
Rectangular total energy <sup>c</sup>	-151.8477	-153.6670	-152.0306
$\Delta^d$	+4.2	+4.0	+8.3

<sup>a</sup> Optimized C–C bond length = 1.453 Å. <sup>b</sup> Optimized C–C bond lengths 1.369 and 1.539 Å. <sup>c</sup> Energy in hartrees. <sup>d</sup> Energy in kcal/mol.

STO-3G basis set. The double  $\zeta$  basis set gives a somewhat smaller singlet-triplet gap (14 kcal/mol) at the square geometry than the minimal one, and the magnitude of both the SCF and correlation energy<sup>24</sup> differences between rectangular and square singlets decreases. However, since the SCF energy difference favors the square, while the  $\pi$  correlation energy difference favors the rectangle,<sup>25</sup> and the changes are of nearly the same magnitude, the computed difference in total energy between rectangle and square alters by only 0.2 kcal/mol in going from the STO-3G to the double  $\zeta$  basis set.

We next studied what effect inclusion of  $\sigma$ - $\pi$  correlation would have on this energy difference. We anticipated that dynamic spin polarization of the  $\sigma$  electrons on inclusion of  $\sigma$ - $\pi$  correlation would strongly stabilize the square singlet. On the other hand, the closed-shell  $\pi$  wave function for the rectangular singlet has more ionic character than the diradical wave function for the square, where the two nonbonding electrons occupy separate MOs that have no atoms in common. Since  $\pi$  wave functions with ionic character are significantly stabilized by  $\sigma$ - $\pi$  correlation,<sup>26</sup> this effect was expected to preferentially lower the energy of the rectangular singlet. Which of the two effects would dominate and, thus, whether the energy difference between rectangular and square cyclobutadiene would increase or decrease on inclusion of CI in the  $\sigma$  space, could not be predicted in advance of actually carrying out the calculations.

Using the STO-3G basis set, SCF calculations were performed at the optimized square and rectangular geometries to obtain the primed set of MOs. These MOs were used to form CI matrices that included all single and double excitations from  $|\dots\psi_1^2\psi_2^2\rangle$  and  $|\dots\psi_1^2\psi_3^2\rangle$  that contributed more than  $10^{-5}$  hartree to the second-order perturbation energy. This resulted in a CI matrix for the square singlet containing 1186 configurations and a CI matrix for the rectangular singlet with 1253 configurations. The resulting CI energies are shown in Table II. The inclusion of CI involving the  $\sigma$  space lowers the CI energy by roughly 0.18 hartree at both geometries. However, the magnitude of the correlation energy change is slightly greater for the rectangle, so the energy difference between square and rectangular geometries for the singlet is increased to 8.3 kcal/mol.

The finding that inclusion of CI involving the  $\sigma$  space increases the energy difference between square and rectangular singlet cyclobutadiene indicates that the 4 kcal/mol, calculated with only  $\pi$ -space CI, represents a minimum value for this difference. Indeed, the increase suggests that with the inclusion of CI involving the  $\sigma$  space, the optimized rectangular geometry might be found to be even more distorted from the square, so that 8.3 kcal/mol could, therefore, represent a minimum value for the energy difference.<sup>27</sup>

## Conclusions

The most important result of this theoretical study is that a square geometry represents a transition state for bond flipping in singlet cyclobutadiene. Minimal basis set calculations, including CI in both the  $\pi$  and the  $\sigma$  space, and full  $\pi$ -space CI calculations with a basis set of double  $\zeta$  quality give no indication that a square geometry represents an energy minimum for the singlet or that the barrier between rectangular geometries is so low that cyclobutadiene could behave dynamically on the IR time scale as if it were effectively square. Although we find that triplet cyclobutadiene does prefer a square geometry, this state is calculated to lie well above the lowest singlet at all geometries that we have explored, in agreement with previous theoretical considerations<sup>5</sup> and the absence of an EPR signal from the matrix isolated molecule.<sup>4</sup> Therefore, on the basis of MO calculations we must conclude that, like derivatives which have been studied,<sup>1,2</sup> the matrix

isolated parent [4]annulene is not square. Since the IR spectrum obtained from it has been shown to have too few bands for even a square molecule,<sup>3c,f</sup> the assignment of a square geometry now rests only on the premise that the  $1240\text{-cm}^{-1}$  absorption represents the excitation of an allowed  $e_u$  skeletal vibration in a  $D_{4h}$  species.

After this theoretical study was essentially complete, the cyclobutadiene calculations of Kollmar and Staemmler were published.<sup>6</sup> Although the two studies differ in the basis sets used and the methods employed for including electron correlation, both come to the same qualitative conclusions regarding the relative energies of square and rectangular singlet cyclobutadiene and also those of the square singlet and triplet. This agreement should lend credence to the results obtained by both groups, which cast doubt on the interpretation of the IR spectrum of cyclobutadiene as being that of a square molecule.

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- (17) A nondegenerate state with U symmetry in the  $\pi$ -space cannot be constructed with four  $\pi$  electrons.
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- (19) Before  $\pi$ -space CI the  ${}^1B_{2g}$  and the  ${}^1A_{1g}$  states start off nearly degenerate, with the  ${}^1B_{2g}$  lower in energy. Thus, Halevi, Matsen, and Welsher<sup>9</sup> predicted that  ${}^1B_{2g}$  would be strongly stabilized by rhomboidal distortion. The distinction between  ${}^1A_{1g}$  and  ${}^1B_{2g}$   $D_{4h}$  states vanishes on rhomboidal distortion, since both becomes  ${}^1A_g$  in  $D_{2h}$ , which is why they mix. The symmetry labels for the two singlet states on the right-hand side of Figure 4 in the paper by Halevi, Matsen, and Welsher<sup>9</sup> should be interchanged.
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- (24) Using a double  $\zeta$  basis set, instead of a minimal one, the number of  $\pi$  configurations increases dramatically. For instance, with a minimal basis set there are three  ${}^1B_{1g}$   $\pi$  configurations in square and seven  ${}^1A_g$   $\pi$  configurations in rectangular cyclobutadiene. With a double  $\zeta$  basis set the number of configurations becomes respectively 48 and 74 for the square and rectangle. Nevertheless, as shown in Table II, the correlation energy calculated from full  $\pi$ -space CI decreases on going to the double  $\zeta$  basis set. At least some of the reduction with a more flexible basis probably

- comes from the fact that the two lowest energy  $\pi$  electrons occupy an MO composed of more contracted AOs than do the remaining pair of  $\pi$  electrons, so interorbital electron repulsion is smaller at the SCF level.
- (25) The SCF wave function for the square singlet (eq 7) consists of two configurations, when the MOs appropriate for describing the rectangle are used. The fact that only a one-configuration SCF wave function was employed for the rectangular singlet essentially guaranteed that the rectangular geometry would have the larger correlation energy.
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## The Lowest Energy Excited Singlet States and the Cis-Trans Photoisomerization of Styrene

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**Abstract:** Potential energy curves, as functions of the torsional angle around the ethylenic bond, were obtained for the ground and for a few singlet excited states of styrene by ab initio configuration interaction methods and an STO/3G minimal basis set of Gaussian atomic orbitals. Limited and more extended CI computations were performed to investigate the stability of the computed potential energy curves with respect to the size of the CI expansion and to the inclusion of  $\sigma\pi^*$  and  $\pi\sigma^*$  electronic configurations. The computed level ordering and oscillator strengths are in agreement with the available experimental data and the first excited state is predicted to have a potential curve with a minimum at  $\theta = 0^\circ$  (planar geometry). The inclusion of doubly excited configurations and the variation of the C-C bond lengths in the vinyl group during internal rotation are found to affect significantly the shape of the potential energy curves. The relevance of the theoretical results to the theory of the cis-trans isomerization is briefly discussed.

A number of spectral properties of diphenylpolyenes have been recently determined.<sup>4-5</sup> In particular, the fluorescence lifetimes of these molecules were found to be much larger than the values estimated from the measured absorption intensities. Moreover, the apparent origins of the absorption and of the emission spectra of diphenylpolyenes are not coincident and have different shifts in solution. All these properties suggest that in these molecules the emission originates from an optically forbidden state lying just below the allowed state responsible for absorption.

Experimentally, direct evidence for the existence of such a forbidden state has been found for diphenyloctatetraene<sup>4</sup>, diphenylbutadiene,<sup>6</sup> and the visual chromophore retinal.<sup>5</sup>

Theoretically, Pariser-Parr-Pople type computations on the first members of the polyene series, i.e., butadiene, hexatriene, and octatetraene,<sup>7</sup> support this assignment. In fact, when doubly excited (DE) configurations are included in the configuration interaction (CI) treatment, a singlet state of  $A_g$  symmetry, with dominant contributions from DE configurations, is predicted to be the lowest singlet state and to lie just below the optically active singly excited (SE)  $B_u$  state. Nonempirical computations on butadiene<sup>8</sup> and benzene<sup>9</sup> also gave a similar sequence for the singlet states.

Subsequently, DE states were proposed to play an important role in the photoisomerization reaction of stilbene.<sup>10</sup> According to this model, in analogy with the results of van der Lugt and Oosterhoff on the butadiene photocyclization,<sup>11</sup> the DE  $^1A_g$  state, which in this molecule arises from an electronic excitation mainly localized in the ethylenic fragment, has higher energy than the lowest  $B_u$  state for planar geometry but lower energy for twisted geometries, thus becoming instrumental in the process of direct photoisomerization.

In order to verify this hypothesis and to investigate the role of DE configurations in determining the order of the excited states, we have performed CI computations on styrene and obtained theoretically the potential energy curves for torsion around the double bond for the ground and for the lowest excited singlet states. Styrene was chosen rather than stilbene, since this molecule, being smaller, makes it possible to examine the main features of the cis-trans isomerization by more accurate theoretical procedures.

### Method of Computation

The bond lengths of the benzene ring and all bond angles were fixed to standard values ( $R_{CC} = 1.397 \text{ \AA}$ ,  $R_{CH} = 1.084 \text{ \AA}$ ,  $\angle CCC = \angle HCC = 120^\circ$ ). The torsional coordinate  $\theta$  of the methylene around the double bond and the C-C ( $R_s$ ) and C=C ( $R_d$ ) bond distances<sup>12</sup> in the vinyl group were allowed to vary by taking

$$\begin{aligned} \theta &= 0, 40, 80^\circ \\ R_s &= 1.467 \text{ \AA} - \Delta R \\ R_d &= 1.344 \text{ \AA} + \Delta R \\ \Delta R &= 0, 0.04, 0.08 \text{ \AA} \end{aligned} \quad (1)$$

The three  $\Delta R$  values are appropriate respectively to the ground, to the first SE state,<sup>12</sup> and to the DE state of ethylenic type, where the molecule is better described as  $\text{Ar}::\text{CH}::\text{CH}_2$ . The molecular orbitals (MOs) were expressed as linear combinations of STO/3G atomic orbitals.<sup>13</sup> CI energies of two levels of accuracy were next computed for nine molecular geometries in order to obtain two-dimensional sections of the potential energy surfaces of the ground and lowest excited