adjusting the rubber belt which links the motor and the stirrer into its three different positions. For experiments in isotopic waters, the pH data were converted to concentrations using the glass-electrode correction given by Schowen.[11]

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On the Thermal Rearrangement of Methylenecyclobutane. An Exploration of the Potential Surface[1]

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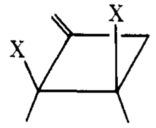
Abstract: An exploration of the potential surface for the thermal reaction of methylenecyclobutane is evaluated by the semiempirical MINDO/2 method and with inclusion of 3 × 3 configuration interaction between the ground state and single and double excited states. The optimization of structures in the transition state region of the hypersurface was carried out in 17 dimensions. The reaction proceeds through a biradical transition state with a flat energy profile. An energy analysis for the midpoint geometries casts doubt on the importance of electronic factors such as those described by Woodward and Hoffmann or Berson and Salem. According to a correlation diagram, quantitatively supported by the calculations, subjacent molecular orbital interaction in this 1.3-sigmatropic (nonpolar) reaction is symmetry allowed for a biradical triplet and symmetry forbidden for a biradical singlet. The quantum chemical study favors the recently given mechanistic interpretation of Gajewski: (a) a ring-opening pathway similar to that of other cyclobutane derivatives; (b) a flat energy profile in the transition state region.

The rules of orbital symmetry by Woodward and Hoffmann[2] have been a milestone in the development of theories about reaction mechanism. According to these rules, a 1.3-sigmatropic reaction should occur either with inversion of configuration at the migrating carbon center and including suprafacial participation of the allyl unit (is) or with retention of configuration at the migrating carbon center and including antarafacial participation of the allyl unit (ra).

However, only a few examples of 1,3-sigmatropic carbon shifts follow closely the concept set by the rules of orbital symmetry.[3] One reaction, presently poorly understood, is the thermal rearrangement of methylenecyclobutane. First predicted by Chesick[4] as automerization, it has been investigated in more detail by Doering and Gilbert,[5] by Doering and Fossel,[6] and by Baldwin and Fleming.[7] From the thermochemical data in comparison with the measured activation energy, one can conclude[5] that the reaction proceeds through a biradical transition state. Thus an aromatic transition state according to Dewar and Evans[8] can be excluded from these considerations.

The reaction is stereoselective: Doering and Fossel observed in the thermal rearrangement of **1** predominant retention of configuration at the migrating carbon center the outcome of stereochemistry in the products to be pressure dependent. Reduction of pressure in the gas phase pyrolysis to 1 mm alters the ratio[9] retention/inversion from 87/13 to 72/28. Baldwin and Fleming concluded from their experimental investigations that at least 77% of the reaction occurs with stereochemistry appropriate to an orbital symmetry allowed reaction,[10] including retention of configuration at the migrating carbon atom and antarafacial participation of the allyl unit. The same experimental observations have been recast recently by Gajewski[12] through a different mechanism. He concludes that the reaction occurs with 100% suprafacial participation of the allyl unit, partially with randomization of the migrating carbon stereochemistry. Therefore the interpretations of the mechanism for this reaction are divergent.



1, X = CO_2CH_3

The experimental observation that a 1,3-sigmatropic reaction can occur in contradiction with the requirements of orbital symmetry according to Woodward and Hoffmann has led Berson and Salem[13] to an important conclusion about the reversal of stereochemistry in 1,3-sigmatropic reactions. Their findings involve interaction of the p atomic orbital at the mi-

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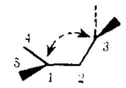
grating carbon atom and the "subjacent molecular orbital" of the allyl unit.

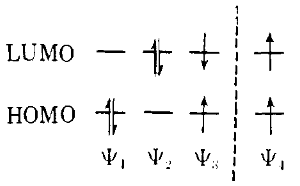
A most likely candidate for the Berson-Salem hypothesis is presented by the thermal rearrangement of methylenecyclobutane. The predominant retention of configuration at the migrating carbon center proposed by Doering et al.[5,6] and Baldwin and Fleming[7] can be accounted for by overlap of the p-AO at C_3 with the central position of the allyl unit, as schematically indicated below. Geometrical factors are most likely suitable for the interaction, since the participating orbitals are in close proximity to each other.



In this paper we wish to report on a theoretical study of the complete resolved potential surface of this reaction. Our study has a bearing on the following mechanistic aspects of this reaction: (a) the importance of the different electronic theories, such as those of Woodward-Hoffmann or Berson-Salem, which treat conditions of orbital symmetry as the driving force for the stereoselectivity observed in this reaction; (b) the diverging interpretations for this thermal 1,3-sigmatropic reaction.

Theoretical Procedure

For the MO calculations, we used the semiempirical MINDO/2 method, extensively developed by Dewar and coworkers.[14,15] For the computation of the electronic properties of biradical structures we included minimal configuration interaction. For a singlet state this corresponds to CI between the ground state Ψ_1, the double excited state Ψ_2, and the singlet excited state Ψ_3. For completeness we also included a triplet state Ψ_4 in our considerations. This type of minimal configuration interaction as a necessary prerequisite for the proper description of biradical structures has been stressed previously by Salem and Rowland.[16] The three routes which yield from the CI procedure correspond to one biradical and two zwitterionic configurations for the singlet states. The energies for these configurations are of increasing energy in the same order. Minimal configuration interaction (3 × 3 CI) has proven sufficient for a number of thermochemical reactions studied so far, such as the isomerization of cyclopropane[17] and of cyclobutane.[18] However, the account of configuration interaction of higher order is essential if low-lying configurations of like symmetry can be constructed. This has been nicely illustrated for the case of trimethylenemethane.[19]



For the computation of the 3 × 3 CI matrix we started with a single excited configuration, which was determined by the method of fractional electrons.[20,21]

At an INDO level of sophistication, the total electronic energy can be partitioned into one- and two-center energy contributions. This method of energy partitioning originally suggested by Pople and Segal for the CNDO method[22] and applied to closed shell systems[23] was extended for our 3 × 3 configuration interaction mixture. Mathematical details for the introduction of 3 × 3 configuration interaction as well as the extension of energy partitioning to the open shell configuration will be presented elsewhere.[24] Our procedure, i.e., partitioning of energy for the open shell configuration, makes it possible to analyze quantitatively through bond and through space orbital interactions[25] in terms of energy for biradical, photochemically, and zwitterionic species. On this basis also, a stringent test can be conducted on the applicability of the Berson-Salem hypothesis as the driving force for the stereochemistry in the thermal reaction of methylenecyclobutane.

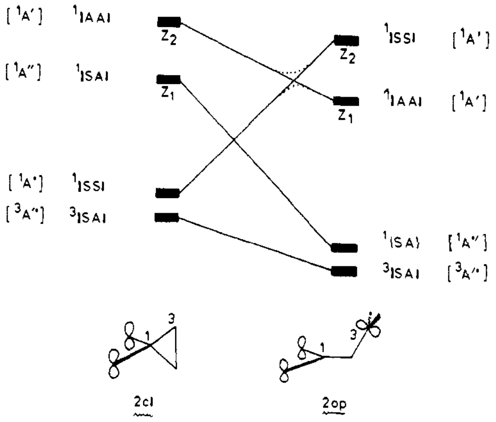
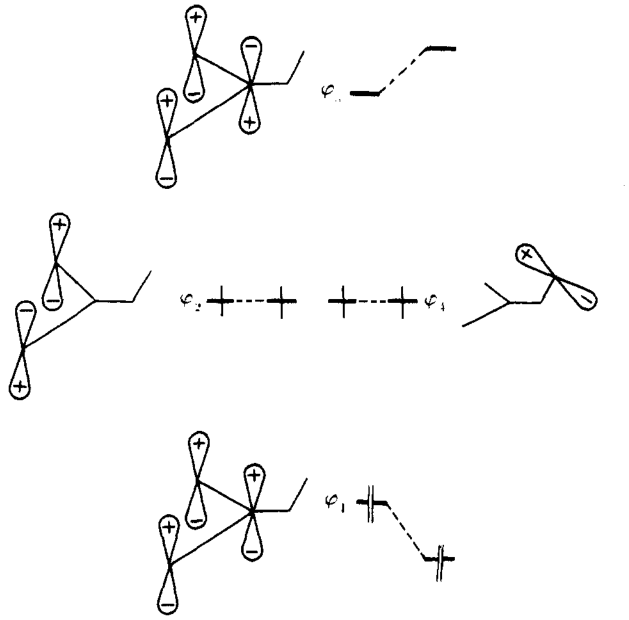


Figure 1. Correlation diagram for the formation of pericyclic bonding according to Berson and Salem in the midpoint geometry for the automerization of methylenecyclobutane. Electronic configurations are classified in respect to a symmetry plane P ($C_1C_2C_3$) as C_s symmetry.

Orbital Interaction in the Midpoint Geometries

For a 1,3-sigmatropic reaction, the subjacent molecular orbital interaction according to Berson and Salem[13] can be viewed in the following MO diagram. The interaction of the p-AO φ_4 with the πMO's of the allyl unit lowers the bonding MO φ_1 in its energy and raises that of the corresponding antibonding MO φ_3. Since both effects are equal but opposite in magnitude, the p-AO φ_4 will not be affected.



Does subjacent molecular orbital interaction occur in the thermal reaction of methylenecyclobutane? As has been noted before, in the midpoint geometry of this reaction the p-atomic orbital at C_3 is most suitably oriented for overlap with the facing p-AO at C_1. We therefore first investigated plausible transition states with retention and inversion of configuration at the migrating carbon center and corresponding to the midpoint geometries for the reaction.

A qualitative answer to the question of subjacent molecular orbital interaction (in the following abbreviated as SMO in-

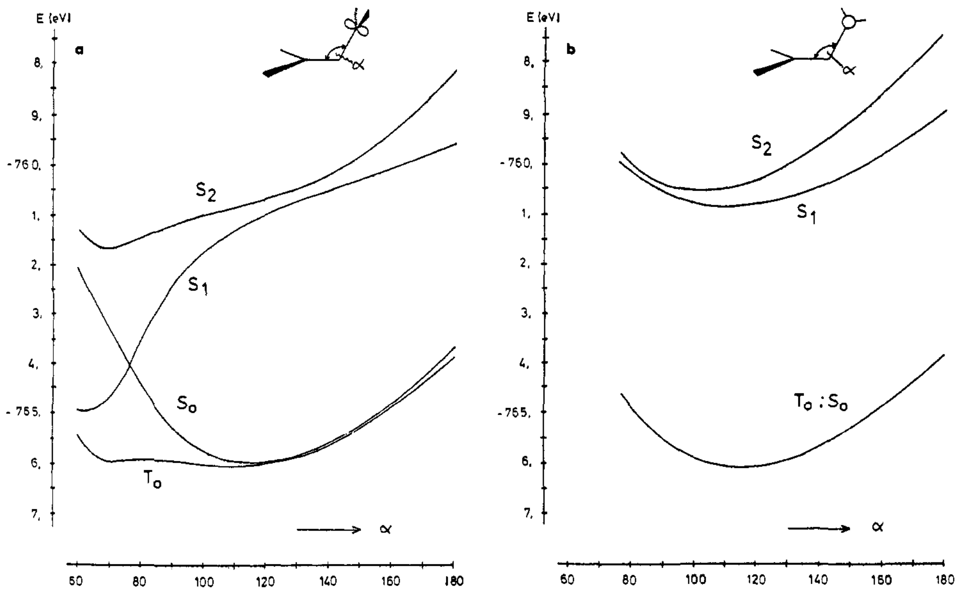


Figure 2. Energies (in eV) of the midpoint geometries for the three singlet states and for a triplet state as a function of the valence angle α with (a) retention or (b) inversion of configuration at the migrating carbon atom C_3. Configurations are in reference to C_s symmetry.

teraction) is provided by construction of a correlation diagram presented in Figure 1.

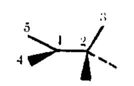
The formation of pericyclic bonding between the AO's at C_1 and C_3 leads from the conformation $\mathbf{2}_{op}$ (open) to conformation $\mathbf{2}_{cl}$ (closed). In other words, $\mathbf{2}_{cl}$ represents a bonding situation with maximum SMO interaction in the midpoint geometry $\mathbf{2}_{op}$.

The different electronic configurations can easily be constructed from the frontier orbitals in the previous interaction diagram and ordered according to increasing energy. The HOMO and LUMO of $\mathbf{2}_{op}$ are the nonbonding MO of the allyl unit (φ_2) and the p-AO at C_3 (φ_4). In respect to a symmetry plane formed by the atoms C_1. C_2, and C_3, these orbitals are antisymmetric (A) or symmetric (S), respectively. The HOMO and LUMO of $\mathbf{2}_{cl}$ are given by a bonding combination (S) or antibonding (A) combination of the p-AO's at C_4 and C_5.

On this basis the geometry $\mathbf{2}_{op}$ has the electronic configuration ^{1}(SA) lowest in energy. The configurations ^{1}(SS) and ^{1}(AA) correspond to the zwitterionic states Z_2 and Z_1. In contrast to $\mathbf{2}_{cl}$, the configuration ^{1}(SS) is lowest in energy, and ^{1}(SA) and ^{1}(AA) correspond to zwitterionic states.

Increase of bonding between the atoms C_1 and C_3 can be. according to these considerations (Figure 1). visualized as a process leading from the ground state of $\mathbf{2}_{op}$ to the excited state of $\mathbf{2}_{cl}$. On the other hand the lowest singlet ^{1}(SS) of $\mathbf{2}_{cl}$ correlates with a zwitterionic configuration of $\mathbf{2}_{op}$ of like symmetry. The surface crossing thus revealed is allowed because the electronic configurational state symmetries are different.[26] In contrast to the two zwitterionic states, the crossing is avoided.

For a quantitative substantiation of the bonding situation in the midpoint geometries. calculations were performed assuming the following structures and including planarity of the atoms of the allyl unit with the adjacent hydrogen atoms. As noted before, the plane formed by the atoms $C_1C_4C_5$ was assumed to be orthogonal to the plane formed by the atoms $C_1C_2C_3$. Calculations were carried out for geometries with



$C_1C_2 = 1.480$ Å: $C_2C_3 = 1.480$ Å: $C_1C_4 = C_1C_5 = 1.370$ Å

$\angle C_4C_1C_5 = 120°: \angle C_1C_2C_3 = \alpha$

various angles for α from 60 to 180°. The results of these computations are recorded in Figure 2.

For the lowest singlet states as well as the triplet state, the calculations indicate a most likely geometry in which $\alpha \sim 110°$. Thus the equilibrium geometries of both transition states are relaxed. The same holds true for the equilibrium geometries referring to retention (Figure 2a) or inversion (Figure 2b) of configuration at the migrating carbon center. For the geometries corresponding to inversion of configuration at C_3, the energy curves for the lowest singlet ^{1}(SA) and the triplet ^{3}(SA) are identical.[27]

A quantitative assessment of bonding between the atoms C_1 and C_3 emerges from an energy analysis of the 3 × 3 configuration interaction mixture and is collected in Figure 3. According to the scheme of energy partitioning,[22-24] the total electronic energy is the sum of one-center and two-center energy contributions:

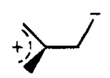
$$E = \sum_{A} E_A + \sum_{A \neq B}\sum E_{AB}$$

The quantity E_{AB} is a measure of bond strength. If it is becoming more negative, the bond will become stronger.

In the extended geometries ($\alpha \geq 110°$) bonding between the atoms C_1 and C_3 is negligible. It comes to the fore only by decreasing the valence angle α. In the zwitterionic states Z_1 and Z_2 the attraction of positive and negative charge between C_4 (C_5) and C_3 yields a negative quantity to the two-center energy.

Charge densities which are not recorded here indicate that in the lower zwitterionic singlet, Z_1. negative charge is mostly localized in the allyl unit. The order of charge localization is reversed in the upper zwitterionic singlet Z_2. In both zwitterionic configurations (Figure 2b) a geometry is preferred in which the valence angle α is smaller (compared to the corresponding equilibrium structure of the singlet state lowest in energy). The increase in angle strain resulting from the smaller value of α is, to a certain extent, offset by the coulombic attraction of positive and negative charges in the zwitterionic states.

Z_1



Z_2

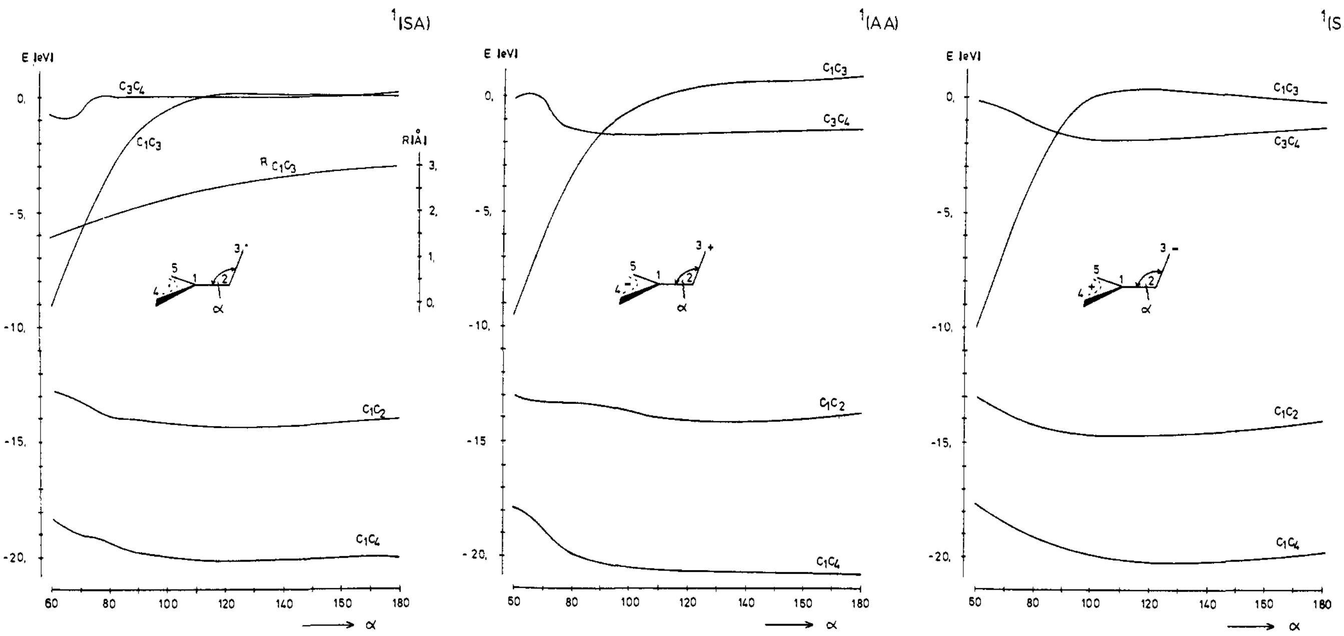


Figure 3. Energy analysis (two-center energies) for the three singlet configurations. The geometries refer to retention of configuration at the migrating carbon atom C_3.

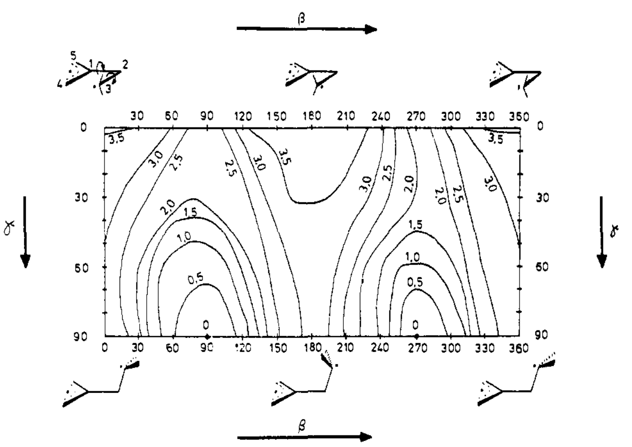


Figure 4. Contour map of the potential energy for the transition state region. Energies (in kcal/mol) are related to the point lowest in energy.

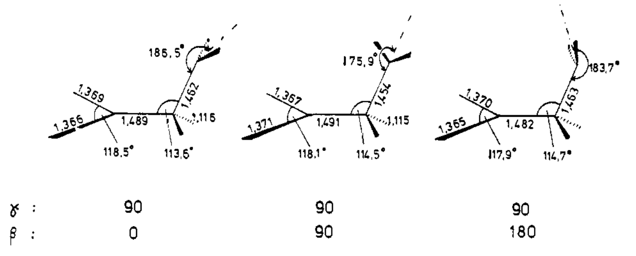


Figure 5. Totally optimized midpoint geometries. Bond lengths are in Ångström units, and bond angles are in degrees.

The energy analysis in Figure 3 has indicated that in the biradical singlets of the midpoint geometries (equilibrium structures) electronic factors which favor pericyclic bonding according to Woodward and Hoffmann or Berson and Salem should be negligible.[28] Although both plausible transition states in their equilibrium geometries are, in conformity with our calculations, almost equal in energy, quantitative conclusions regarding the energy differences for the two transition states suffer from the failure of semiempirical SCF methods to yield reliable energies. More precise conclusions about the energy differences must await better calculations.[15]

The Biradical Region of the Transition State

In the next step we quantitatively computed the biradical region of the transition state for the reaction of methylenecyclobutane. The contour map shown in Figure 4 was determined by optimizing bond lengths and bond angles in 17 dimensions. The horizontal and vertical axes respectively represent the rotations of the methylene group around the bond C_2C_3 (β) and around the bond C_1C_2 (γ). According to our calculations there are rotational barriers for both degrees of freedom. However, these barriers are very small and within the accuracy limit of the quantum mechanical procedure.[30]

Totally optimized structures for the midpoint geometries in the automerization of methylenecyclobutane are reported in Figure 5. The structures confirm the previously derived conclusions reached by Salem and co-workers in their study of the isomerization of cyclopropane.[17] The methylene group of the migrating carbon atom is canted. The energy differences for the various conformations reported in Figure 5 are very small (see Figure 4). The optimization of the geometries also yields planarity for the allyl unit at all points of the hypersurface in the biradical transition state. These conclusions are also borne out by comparison of experimental observations to thermochemical data.[5]

According to the energy analysis of the midpoint geometries reported in Figure 3, bonding interaction between the atoms C_1 and C_3 is not substantial in the extended geometries ($\alpha \geq 110°$). Since for all points of the hypersurface for the biradical region the optimization of structures always yields relaxed geometries, SMO interaction is also negligible in the optimized biradical transition state geometries.

The Ring Opening

Quantum mechanical calculations on the ring opening of cyclobutane[18,31] indicate that the bond-breaking process occurs with simultaneous torsion of the four-membered ring.

Does methylenecyclobutane open in the same fashion?

We have computed a contour map for the process of bond breaking by assuming a simplified model with constant bond lengths. This simplified model in the study of the ring opening process is justified by the related studies on cyclobutane. A more elaborate optimization and hence a more accurate determination of the contour map plotted in Figure 6 seems

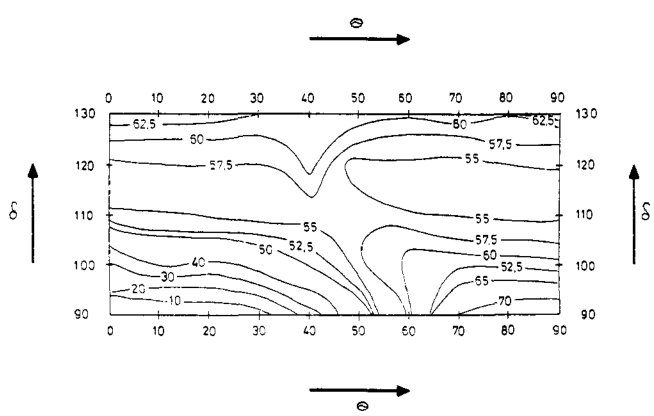
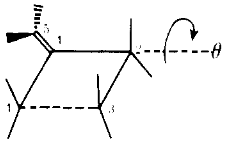


Figure 6. Contour map of the potential energy for the process of bond breaking. Energies (in kcal/mol) are related to the point lowest in energy.

hardly worthwhile because semiempirical SCF methods in general fail to properly reproduce the amount of ring strain.

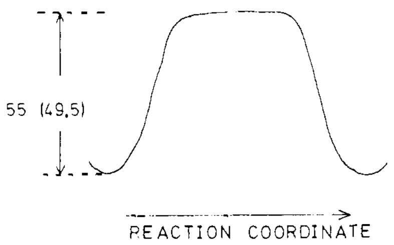


$$C_1C_2 = 1.450\ \text{Å};\ C_2C_3 = 1.500\ \text{Å};\ C_1C_4 = 1.450\ \text{Å};$$
$$C_1C_5 = 1.350\ \text{Å}$$
$$\angle C_1C_2C_3 = \angle C_4C_1C_2 = \delta;\ \angle[(C_4C_1C_2)(C_1C_2C_3)] = \theta$$

From Figure 6 it can be easily seen that the hypersurface compares to that of the bond-breaking process in cyclobutane.[18,31] On this basis torsion required to open the four-membered ring is also of importance in the ring opening of methylenecyclobutane.

A profile of the potential energy along the reaction coordinate lowest in energy can be constructed by combination of Figures 4 and 6. The thermal reaction of methylenecyclobutane passes through a transition state rather than an intermediate. The reaction may be compared with quantum mechanical studies on cyclobutane[18,31] and methylenecyclopropane,[32] where an intermediate has been invoked.

The computed activation energy for the reaction amounts to 55 kcal/mol in contrast to 49.5 kcal/mol measured for the reaction of dideuteriomethylenecyclobutane.[5] Thus the problem is that methylenecyclobutane is too stable on the computed hypersurface, since semiempirical SCF methods tend to overestimate the stability of strained ring systems. On departure from the strained ring structures, this problem vanishes. As a consequence the energies in the left corner of the above scheme tend to be too low compared to the rest of the hypersurface. However, this general pitfall of semiempirical SCF methods does not invalidate the conclusions reached in this study that neither orbital symmetry considerations according to Woodward–Hoffmann nor to Berson–Salem are operative.



Conclusions

The results of our investigations into the thermal reaction of methylenecyclobutane indicate that electronic factors are least likely to be the cause of the observed stereospecificity in this reaction. Moreover, our study reveals a similarity between the reaction of cyclopropane and cyclobutane with that of methylenecyclobutane. All these reactions pass a biradical transition state (or intermediate in the case of cyclobutane[18]) which is not bound by large rotational barriers. The conclusions reached in this study give, moreover, strong support to a recent reinterpretation of the mechanism for this reaction.[12]

Acknowledgment. I am grateful to Professor Werner Kutzelnigg for his lasting encouragement.

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(27) The energy difference is less than 1 kcal/mol, the triplet being below the singlet.

(28) The recognition that the Berson–Salem hypothesis is not operative in the rearrangement of methylenecyclobutane contradicts with the conclusions reached by Epiotis[29] for nonpolar substituent effects on SMO control in 1,3-sigmatropic reactions. Our type of analysis presented here goes far beyond the conclusions reached by Epiotis because (a) all valence electrons are taken into consideration, (b) configuration interaction is included, and (c) a quantitative assessment of pericyclic bonding is made by an energy

analysis. Moreover, on the basis of the conclusions reached, it is necessary to discuss the Berson–Salem hypothesis in terms of electronic configurations rather than one-electron energies. The forbidden crossing of the ground state configurations in Figure 1, which is only facilitated in the triplet configuration, could be removed by placing one zwitterionic state (of $\mathbf{2}_{op}$ or of $\mathbf{2}_{cl}$) below the biradical singlet.

(29) N. D. Epiotis, R. L. Yates, and F. Bernardi, *J. Am. Chem. Soc.*, **97**, 4198 (1975).

(30) The 3 × 3 CI procedure within the MINDO/2 approximation overestimates the importance of C–H hyperconjugation probably due to the neglect of overlap.[24] For the case presented here the conformation with $\beta = 90°$, $\gamma = 90°$ tends to be too low in energy compared to the conformation with $\beta = 0°$, $\gamma = 90°$. Because of this failure the rotational barrier of our procedure comes out too large. A reasoning will be given elsewhere.[24]

(31) R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *J. Am. Chem. Soc.*, **92**, 7091 (1970).

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Characterization of the Anomalous Phosphorescence of *p*-Chlorobenzaldehyde in Polycrystalline Methylcyclohexane at 4.2 K[1a]

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Abstract: Shpol'skii-type quasi-line phosphorescence spectra of *p*-chlorobenzaldehyde (PCB), and its deuterated derivatives, are studied in methylcyclohexane polycrystalline matrix at 4.2 K. The phosphorescence is composed of two subspectra at 44 cm^{-1} separation in PCB-h_5, a low-energy short-lived one ($\tau \sim 1$ ms) and a higher-energy long-lived one ($\tau \sim 12$ ms). Aldehyde group deuteration leads to the disappearance of the short-lived emission, while ring deuteration leads to changes in energies and relative quantum yields of the two emission systems. Thermal population of an upper state, aggregation, and different host crystalline modifications are excluded as origins of the multiple emissions. A two-site model is not directly ruled out experimentally but appears to require an abnormally large intermolecular contribution to the deuterium isotope effect on radiationless relaxation processes if the isotope effects on the spectra are to be explained. A two-state model involving an unrelaxed upper excited state is proposed. The salient features of this model are: large geometric dissimilarity between the two emitting states, and small efficiency for relaxation of the upper state through the lattice phonons. The main difficulty with this model is in the latter feature, requiring a weak host-guest interaction so that PCB in methylcyclohexane acts nearly like a relaxed free molecule. The deuteration effects are then explained by varying degrees of coupling between the two states as modulated by the isotope-dependent energy gap. Thermalization experiments and the details of the phosphorescence of PCB in MCH-d_{14} qualitatively support the model. Either the two site or the two-state model illustrate the inadequacy of current theories of radiationless transitions in molecules with closely spaced states in describing intermolecular contributions to electronic relaxation processes.

The effects of interstate coupling on photophysical properties of the lowest triplet states of aromatic aldehydes and ketones have attracted attention[1b-8] to the vibronic spectra[1b,6,7] and magnetic properties[2-5] involving such states. These and photochemical reactivity[8] are found to depend on $^3n\pi^*$-$^3\pi\pi^*$ interaction and hence in general terms on the energy separation $\Delta E(^3n\pi^*$-$^3\pi\pi^*)$.

An example of the sensitivity of triplet state properties to $^3n\pi^*$-$^3\pi\pi^*$ energy spacing is found in the simple aromatic aldehyde *p*-chlorobenzaldehyde (PCB). The phosphorescence vibrational structure[2] and magnetic properties[4] of this molecule show dependence on the energy gap. These properties can be explained by interstate mixing that increases inversely with the gap.

In this paper we report the phosphorescence spectra of *p*-chlorobenzaldehyde and its deuterated derivatives in methylcyclohexane (MCH) at 4.2 K. The purpose is to investigate the effect of a solid environment on radiationless processes in a molecule with closely spaced states.

In MCH, the lowest energy phosphorescences of PCB can be assigned as originating from a predominantly $^3n\pi^*$ state (vide infra). Very closely separated from this phosphorescence origin, at 44 cm^{-1} to higher energy, another phosphorescence origin is observed with attendant vibronic structure and lifetime indicating considerable interstate mixing between the $^3n\pi^*$ state and a closely spaced $^3\pi\pi^*$ level. The phosphorescence pattern is very sensitive to intramolecular deuteration. The short-lived $^3n\pi^*$-like emission disappears upon aldehyde group deuteration and is regained upon ring deuteration.

We examine the spectra of selectively deuterated *p*-chlorobenzaldehydes, e.g., PCB-d_1 (aldehyde hydrogen deuterated), PCB-d_4 (ring hydrogens deuterated) and PCB-d_5 (perdeuterated), to elucidate the origin of the deuterium isotope dependent multiple phosphorescence. We establish that the two phosphorescence spectra do not originate from thermal population of upper states, aggregation, different PCB ground state conformations, or different crystalline phases in the matrix. Thus a two site or a single-site two-state model interprets the multiple phosphorescence. However, neither is found satisfactory in terms of present theories of radiationless transition.

Experimental Section

PCB (Matheson Coleman and Bell) was vacuum sublimed twice and then zone refined (50 passes, 3 cuts, repeated twice). Deuterated derivatives were synthesized[9-11] by Dr. Ronald Ruden and were purified by multiple recrystallizations from *n*-hexane followed by vacuum sublimation. A gift of PCB-d_1 was also received from Professor D. S. Tinti, of the University of California at Davis, and was found to give identical results.[12] NMR, Raman, and mass spectral analyses of PCB-d_1 revealed isotopic purity greater than 99.5%. NMR analyses of PCB-d_4 reveals 2.5% PCB-d_3 distributed approximately equally between the two mono ring hydrogen isotopes. There are no detectable