

The ring opening of substituted cyclopropylidenes to substituted allenes: the effects of steric and long-range electrostatic interactions

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Received March 1, 1986; received in revised form August 30, 1990/Accepted September 15, 1990

Summary. It is shown that all stereospecific preferences found experimentally for the ring opening of substituted cyclopropylidenes are satisfactorily reproduced by adding steric and long-range electrostatic interactions to the cyclopropylidene reaction surface. The corresponding surface for dimethyl cyclopropylidene is mapped out in detail. The surface for 3-methyl- and 2-bromo-3-methyl-cyclopropylidene is explored around the transition region. From the success of this approach it is inferred that short-range covalent interactions are unlikely to be responsible for stereospecific preferences found in these systems.

Key words: Cyclopropylidene to allene (substituted) – Electrostatic interactions between substituents

1. Introduction

The ring opening of cyclopropylidene to allene presents a challenge to experimental and theoretical chemists. Because of the state of the art of their respective disciplines and by virtue of the nature of the chemical system, experimentalists have been constrained to deal only with the substituted species, while theoreticians have been limited, at least as far as rigorous *ab initio* calculations are concerned, to the unsubstituted molecule. A discussion of past work has been given in the introduction to the first paper of this series [16], in which we furthermore reported the results of a detailed *ab-initio* analysis for the energy surface of the unsubstituted reaction. Although they are believed to be quite accurate and in good agreement with other reliable theoretical data where available [3, 4, 13, 15] it remains true that, as yet, the observations made by the experimentalists have not been reproduced by the theorists. In particular, all existing experimental data [6–9, 17] substantiate stereospecificity in the course of the substituted reaction, while the theoretical results demonstrate the lack of stereospecificity for the unsubstituted reaction.

* Operated for the U.S. Department of Energy by Iowa State University under Contract No. 7405-ENG-82. This work was supported by the office of Basic Energy Sciences

An obvious explanation for this discrepancy would be that the introduction of substituents gives rise to steric hindrances which cause stereospecific preferences. This conjecture is, however, in contradiction to certain experiments of Jones and Krause [6] who showed that the stereospecificity found for 2,3-phenyl-*p*-methylphenyl-cyclopropylidene is substantially enhanced when the *p*-hydrogen is replaced by bromine in the phenyl substituent. In view of this situation a quantitative theoretical treatment of the ring opening of substituted cyclopropylidene appears desirable.

The results obtained in the first paper [16] suggest that covalent electronic interactions do not lead to stereospecific preferences in the system at hand. This leaves nonbonded interactions such as van der Waals forces and long-range electrostatic interactions as candidates for causing these preferences. It is the goal of the present investigation to explore whether such interactions can indeed explain the experimental findings.

Three substituted species are investigated: 2,3-dimethyl-cyclopropylidene, 2-methyl-cyclopropylidene, and 2-methyl-3-bromo-cyclopropylidene. For the first of these, a detailed study of the entire reaction surface is reported. For the second and third species, the reaction surface is examined only in the neighborhood of the transition state. A comparison between the second and third species leads to an understanding of the Jones-Krause experiments. Since in all cases our theoretical results agree with the experimental observations, we believe that the physical ideas advanced in this investigation furnish a credible theoretical basis for understanding the ring opening of substituted cyclopropylidenes.

2. Theoretical method

While a FORS MCSCF calculation of the reaction surface for the substituted species would be an obvious approach to the problem at hand, it suffers from two drawbacks: It would be prohibitively time-consuming and expensive, involving computations orders of magnitude larger than the ones reported in the first paper [16]. In addition, a nontrivial analysis of the roles of attractive and repulsive interactions in such calculations would be required in order to ascertain whether the introduction of substituents merely added steric effects or whether they changed the covalent bonding. It was therefore felt that a more useful approach would be to add steric energies and long-range electrostatic interactions to the *ab initio* MCSCF energy to the unsubstituted species.

Happily, expressions for additive nonbonded interaction effects have been developed in the field of molecular mechanics. Burkert and Allinger [2] have given an excellent account of the methods usually employed and of the reliability of the results obtained by many workers in the field. In the present case, there exist two kinds of interactions, namely steric effects, due to the size and nature of the substituents and possibly electrostatic interactions between polarized bonds already present.

Neutral, nonpolar parts of a molecule attract each other at large distances through induced electric moments, giving rise to London dispersion forces. According to Burkert and Allinger [2], the general form of this interaction is of the form:

$$V_{\text{disp}} = -c_6 r^{-6} - c_8 r^{-8} - c_{10} r^{-10} \dots \quad (1)$$

Usually only the r^{-6} term is kept, with the coefficient slightly adjusted to account for the neglected higher order terms. At short distances, nonbonded repulsions arise due to the Pauli exclusion effect. Their exact form is usually based on expediency. The total potential for neutral, nonpolar atoms or molecules is called the van der Waals interaction and its most common general form is that proposed by Lennard-Jones [11]:

$$V_{\text{VDW}} = \varepsilon \{ a(r_0/r)^n - b(r_0/r)^m \} \quad (2)$$

$$a = m/(n - m), \quad b = n/(n - m), \quad n > m > 0,$$

where ε is the depth of the potential and r_0 the position of the minimum. The latter is usually taken equal to twice the van der Waals radius. The exponent of the attractive potential, m , is usually set to 6 for the aforementioned reasons, however there is no compelling theoretical reason to choose any specific value for n , the exponent of the repulsive potential, as long as it is sufficiently greater than 6. When n is set to 12, the equation assumes the particularly simple form:

$$V_{\text{VDW}} = \varepsilon [(r_0/r)^{12} - 2(r_0/r)^6]. \quad (3)$$

This so-called 6-12 form of the Lennard-Jones potential fits the data for rare gases very well and has been the most used form of the potential for many years. More recently, it was however shown by Warshel and Lifson and others [18] that this potential is, in fact, too "hard" for hydrocarbons and they have proposed the use of a softer repulsive part. Such a 6-9 potential is given by Hagler et al. [4]:

$$V_{6-9} = \varepsilon [2(r_0/r)^9 - 3(r_0/r)^6]. \quad (4)$$

For noncharged *polar* molecules, or fragments thereof, the prevailing interaction energy is a dipole-dipole interaction term as given by the Jeans' formula (see, e.g., Lehn and Ourisson [10]):

$$V_{\text{dipole}} = \{ (\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j) / r^3 - 3(\boldsymbol{\mu}_i \cdot \mathbf{r})(\boldsymbol{\mu}_j \cdot \mathbf{r}) / r^5 \} / D, \quad (5)$$

where $\boldsymbol{\mu}_i, \boldsymbol{\mu}_j$ are the two dipoles and \mathbf{r} is the vector connecting their positions. The constant D is an effective dielectric constant which is unity in the present context.

The values for the parameters ε and r_0 in Eq. (4) for two interacting moieties X and Y are commonly derived from corresponding parameters $\varepsilon_X, \varepsilon_Y, r_X, r_Y$, characteristic for each species, by the combination rules:

$$\varepsilon(XY) = (\varepsilon_X \varepsilon_Y)^{1/2}, \quad r_0(XY) = (r_X + r_Y) / 2. \quad (6)$$

The quantitative values for these parameters as well as for the absolute values μ of the dipoles of Eq. (5) which are applicable to the moieties occurring in the present investigation were taken from the current literature. Their values, with appropriate references, are listed in Table 1.

For the molecules considered here, where interactions between hydrogens and substituents such as CH_3 and Br are of interest, the inclusion of both the nonpolar and the polar terms is called for. While polar terms are negligible in the case of hydrocarbons and therefore usually omitted, neglecting them in the case of fragments such as $\text{C}-\text{Br}$, which exhibit a substantial polarization, would distort the results. Since these terms should therefore be included in some cases, it seems consistent to include them in all, leaving them to cancel out when negligible. The total molecular mechanics potential is therefore given by:

$$V_{\text{MM}} = V_{6-9} + V_{\text{dipole}}. \quad (7)$$

Table 1. Parameters for the nonbonded long-range interaction potential parameters

$\epsilon_{\text{H}} = 0.08^{\text{a}}$	$\epsilon_{\text{CH}_3} = 0.1^{\text{a}}$	$\epsilon_{\text{Br}} = 0.4^{\text{b}}$	kcal/mol
$r_{\text{H}} = 3.0^{\text{a}}$	$r_{\text{CH}_3} = 4.0^{\text{a}}$	$r_{\text{Br}} = 3.9^{\text{b}}$	Angstrom
$\mu_{\text{CH}} = 0.55^{\text{c}}$	$\mu_{\text{CCH}_3} = 0.06^{\text{d}}$	$\mu_{\text{CBr}} = 2.15^{\text{b}}$	Debye
$\text{C}^- - \text{H}^+ \text{ }^{\text{c}}$	$\text{C}^- - \text{C}^+ \text{H}_3^{\text{d}}$	$\text{C}^+ - \text{Br}^- \text{ }^{\text{b}}$	

^a From [4, 14, 19]

^b From [12, 14]

^c From [20]

^d From [21]

It may be noted that the steric repulsions are short-range, whereas the dipole-dipole interaction is long-range.

If one wishes to account for the effect of a substitution by means of such a potential, then the following procedure appears logical. Whenever a hydrogen is replaced by a substituent, one adds to the *ab-initio* energy of cyclopropylidene the difference:

$$\Delta V_{\text{MM}} = V_{\text{MM}}(\text{after substitution}) - V_{\text{MM}}(\text{before substitution})$$

for all interactions between the substituted moiety and the rest of the molecule. The sum total of all these difference potentials should therefore be incorporated into the *ab-initio* program of cyclopropylidene in the same manner as is done with the standard nuclear repulsions. A consistent calculation would then require the optimization of the twelve secondary internal coordinates for the entire space spanned by the reaction coordinates (Φ , δ_1 , δ_2) [16], using this modified energy program.

For the sake of expediency a more primitive avenue was followed in the present investigation. The geometries determined by the cyclopropylidene calculation were kept and used to calculate the difference potentials ΔV_{MM} . These were then added to the cyclopropylidene energies. In the spirit of this qualitative approach it seemed, moreover, appropriate to take into account only the nonpolar interactions between the partners in the substituent pairs 1-2, 1-2', 1'-2, and 1'-2', where the numbers represent the positions of the hydrogens in the unsubstituted species as given in Fig. 2 of the first paper [16]. The corresponding interactions for the pairs 1-1' and 2-2', i.e. between substituents bonded to the same atom, are omitted, since they remain essentially constant throughout the reaction because the C-H bond lengths and the H-C-H angles remain almost unchanged, as was seen in Sect. 5 of the first paper of the series [16]. For the same reasons the dipole-dipole interactions for the pairs of bonds (C₁-1)-(C₂-2), (C₁-1)-(C₂-2'), (C₁-1')-(C₂-2) and (C₁-1')-(C₂-2') are included and those for the pairs (C₁-1)-(C₁-1') and (C₂-2)-(C₂-2') are omitted. The dipoles are assumed to be located at the bond centers. It was felt that, in spite of its obvious shortcomings, this approach would serve to test the underlying physical concepts. If the results are in qualitative agreement with the experimental facts, then the fundamental point has been made.

In view of these simplifications we felt furthermore justified in using the energy surface of the unsubstituted reaction which was obtained with the STO-3G atomic orbital basis.

3. Dimethyl species

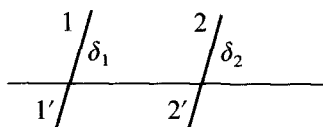
3.1. Reaction surface in the Φ , δ_1 , δ_2 space

Figures 1–7 show panels $\Phi = \text{constant}$ for the ring opening of 2,3-dimethylcyclopropylidene to 2,3-dimethylallene. As in the first paper [16], the total reaction surface is represented through a series of contour diagrams in terms of the variables δ_1 and δ_2 , for fixed values of Φ .

The diagrams are drawn in the same manner as those in Figs. 6–16 of the first paper [16]. Technical details of the method of display are explained in Sect. 3.1 and the color code is illustrated in Fig. 6 (top) of that paper. Very high energy areas are left grey and no contours are drawn within this area because the nonbonded interactions between the two methyl groups can become quite large, yielding indistinguishably close contours. Moreover, the areas of high energy are of little interest compared to those of low energy.

On any one panel, there appear both, *cis* and *trans* isomers, thus allowing a direct comparison between these two species. The *cis-trans* relationship between two hydrogen positions depends on the angles δ_1 and δ_2 . Specifically, one has in cyclopropylidene:

$\delta_1 \delta_2$	(H ₁ H ₂)	(H ₁ 'H ₂ ')	(H ₁ H ₂)	(H ₁ 'H ₂ ')
Same sign	<i>cis</i>	<i>cis</i>	<i>trans</i>	<i>trans</i>
Opposite sign	<i>trans</i>	<i>trans</i>	<i>cis</i>	<i>cis</i>



where the positions 1, 1', 2, 2' are those defined on Fig. 2 of the first paper [16]. In the sequel it is assumed that the methyl substituents are located at the positions of the hydrogens 1' and 2. This implies, e.g., that $(\delta_1, \delta_2) = (90^\circ, 90^\circ)$ and $(-90^\circ, -90^\circ)$ represent *trans*-disubstitutions, whereas $(\delta_1, \delta_2) = (90^\circ, -90^\circ)$ and $(-90^\circ, 90^\circ)$ represent *cis*-disubstitutions.

$\Phi = 59.5^\circ$, cyclopropylidene: Fig. 1 (top). The four distinct minima that were observed in Fig. 6 of the first paper [16] are no longer equivalent. Those located on the diagonal line $\delta_1 + \delta_2 = 0$ correspond to the *cis* case and are denoted by C. Those located on the lines $\delta_1 + \delta_2 = \pm 180^\circ$, correspond to the *trans* case and are denoted by T. The energy contours exhibit a number of differences between the *trans* regions and the *cis* regions, which are consequences of the obvious fact that the steric hindrance between the bulky methyl substituents causes stronger repulsions for the *cis* geometry than for the *trans* geometry. These differences are:

- (i) The *trans* compound is about 10 kcal/mol lower in energy than the *cis* compound.
- (ii) The *cis* minimum occurs at about $(\delta_1 = 85^\circ, \delta_2 = -85^\circ)$, showing that, here, the CH₃-C-H planes do not stand perpendicular to the CCC plane: the distance between the methyl substituents is longer than that between the hydrogens. By contrast, the *trans* minimum occurs for $(\delta_1 = 90^\circ, \delta_2 = 90^\circ)$, i.e., the CH₃-C-H planes are perpendicular to the CCC plane.

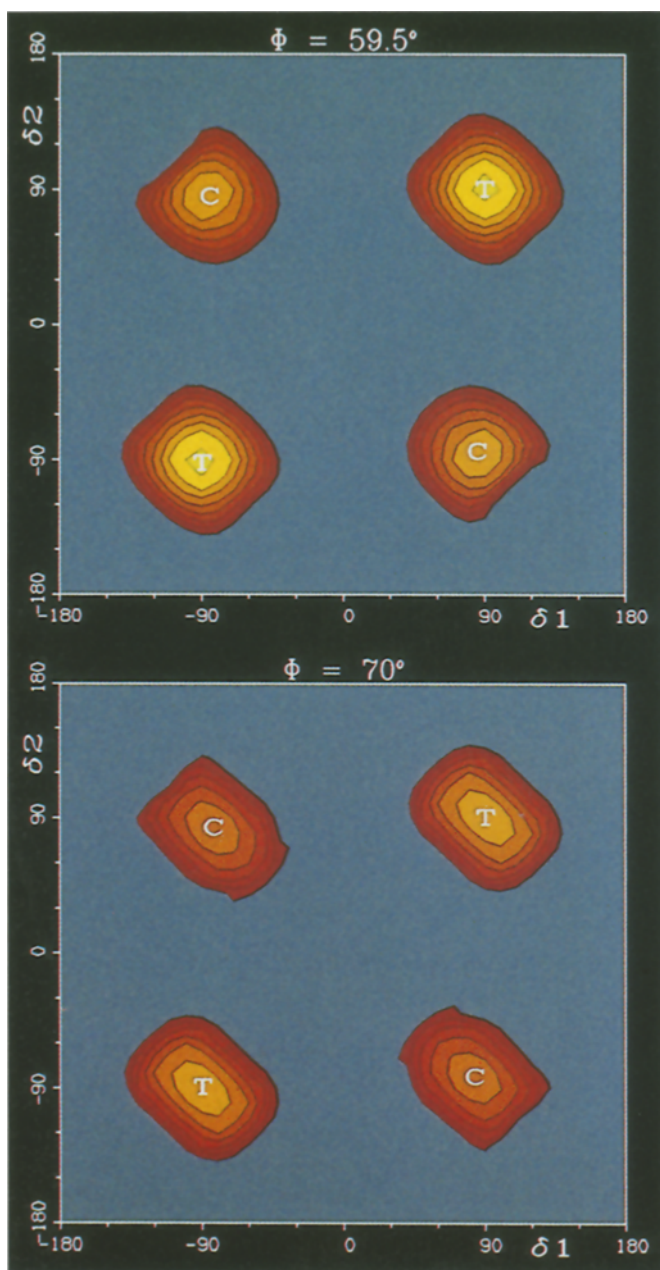


Fig. 1. Contours of $E(\phi, \delta_1, \delta_2)$ of dimethyl species for $\phi = 59.5^\circ$ (top) and for $\phi = 70^\circ$ (bottom). Color key: See end of Sect. 3.1 and Fig. 6 (top) of preceding paper

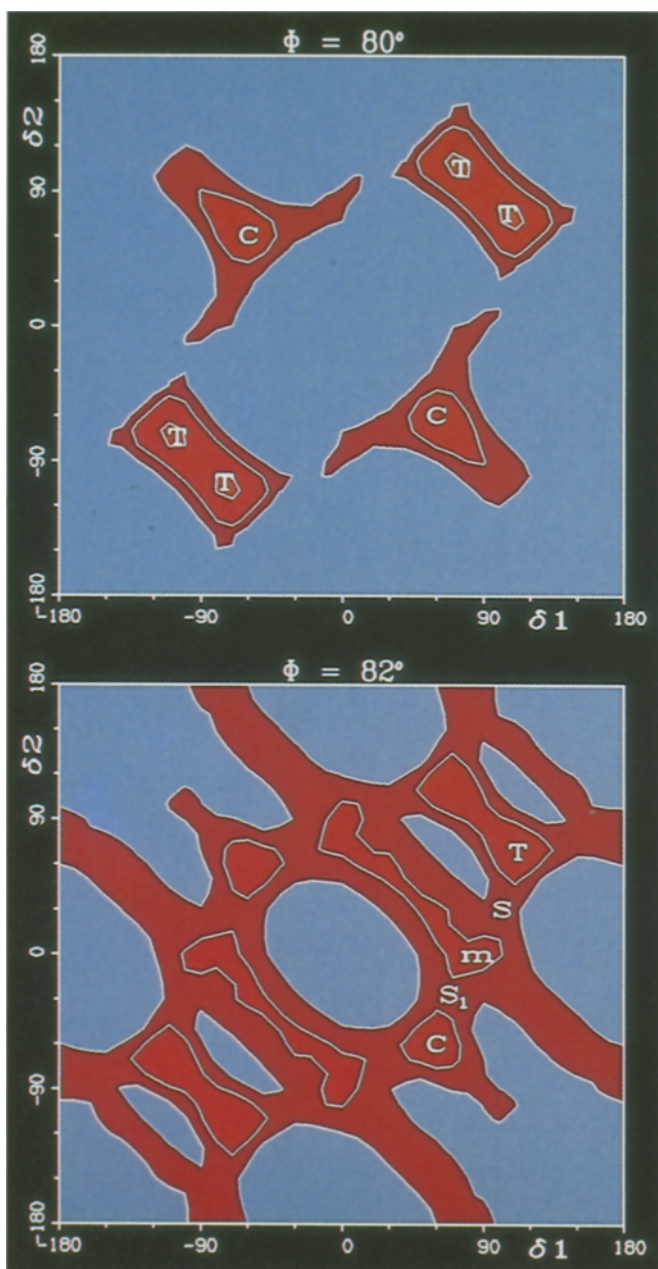


Fig. 2. Contours of $E(\Phi, \delta_1, \delta_2)$ of dimethyl-species for $\Phi = 80^\circ$ (top) and for $\Phi = 82^\circ$ (bottom)

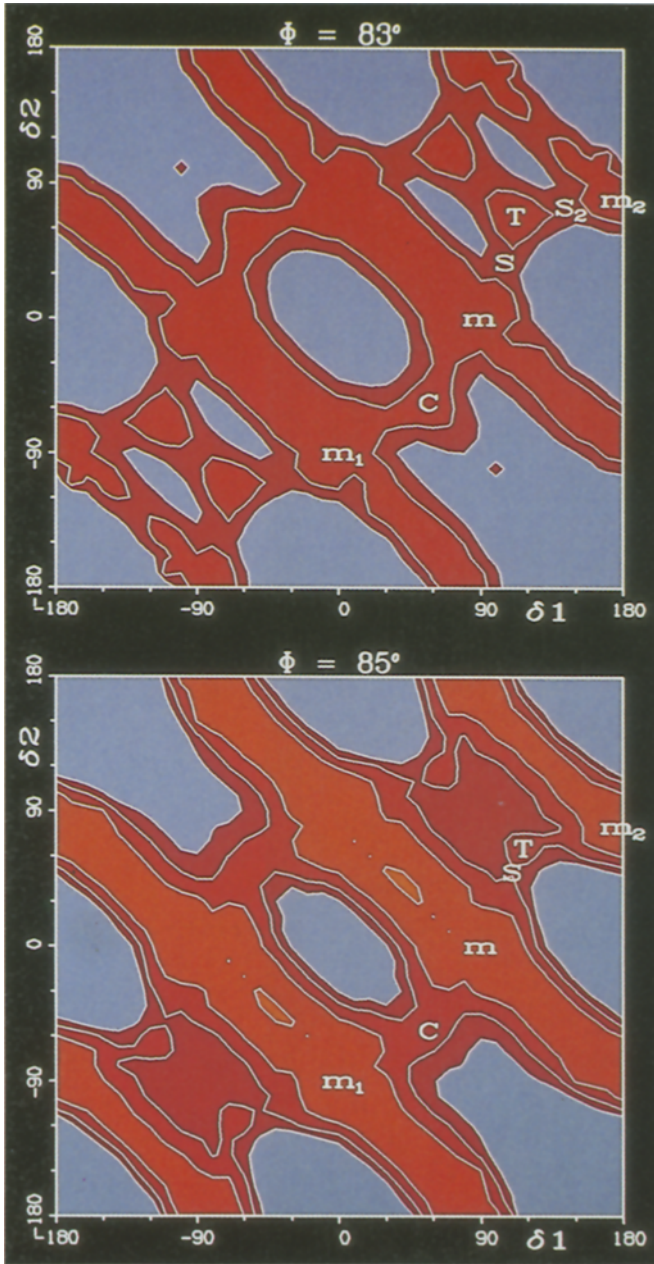


Fig. 3. Contours of $E(\Phi, \delta_1, \delta_2)$ of dimethyl species for $\Phi = 83^\circ$ (top) and for $\Phi = 85^\circ$ (bottom)

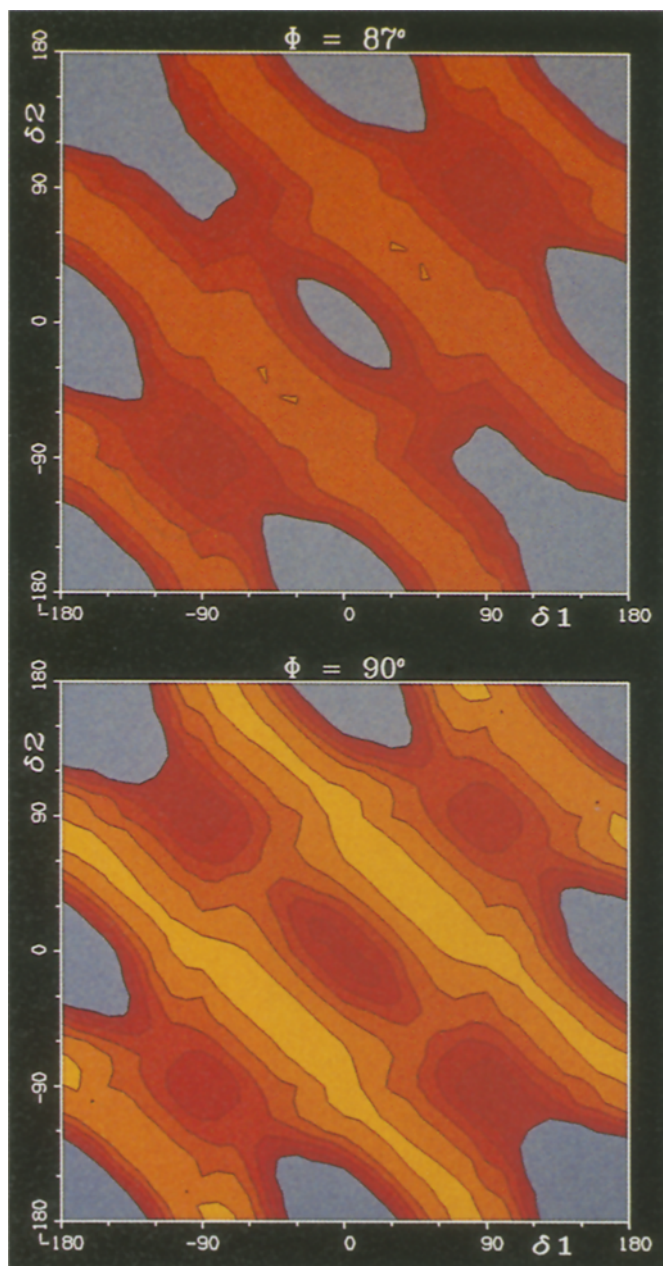


Fig. 4. Contours of $E(\Phi, \delta_1, \delta_2)$ of dimethyl species for $\Phi = 87^\circ$ (top) and for $\Phi = 90^\circ$ (bottom)

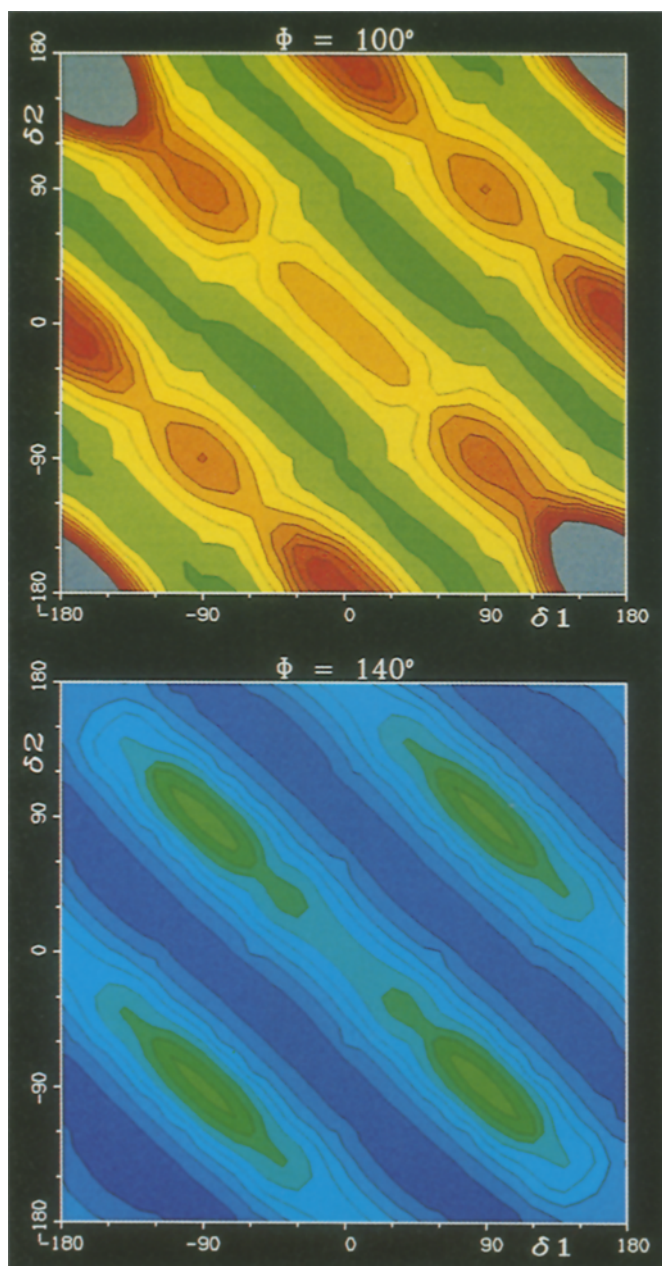
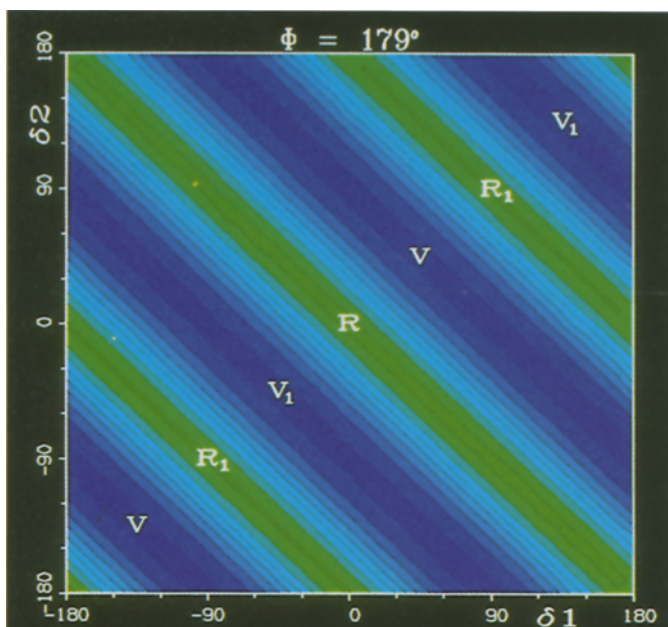
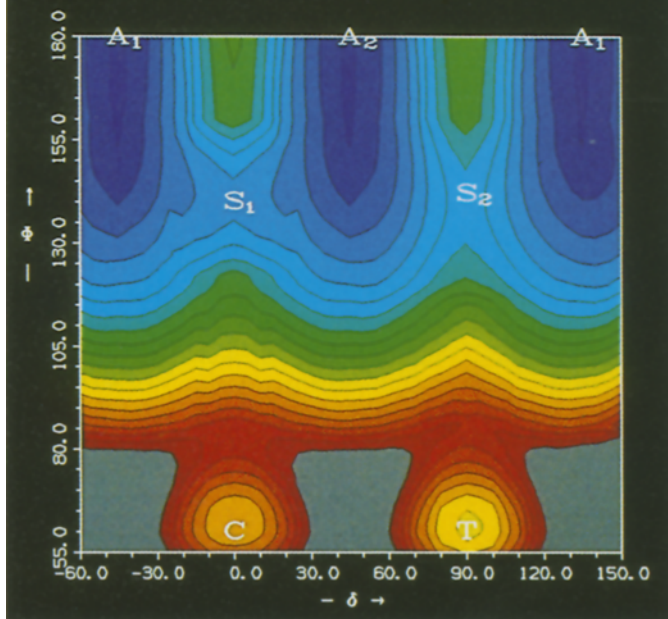


Fig. 5. Contours of $E(\Phi, \delta_1, \delta_2)$ of dimethyl species for $\Phi = 100^\circ$ (top) and for $\Phi = 140^\circ$ (bottom)



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Fig. 6. Contours of $E(\Phi, \delta_1, \delta_2)$ of dimethyl species for $\Phi = 179^\circ$

Fig. 7. Contours of $E(\Phi, \delta)$, where $\delta = (\delta_1 + \delta_2)/2$ for dimethyl species. *Cis*-cyclopropylidene: C; *trans*-cyclopropylidene: T; allenes: A_1, A_2 . Allene isomerization transition states: S_1, S_2

(iii) The energy contours of the *cis* species are asymmetric in the *disrotatory* direction, i.e. along the line $\delta_1 + \delta_2 = 0^\circ$. The energy goes up much faster when the two methyl groups are brought closer together than when they move farther apart. The *trans* species exhibits no such asymmetry since, initially, the two opposite disrotatory motions are for them completely equivalent. A further difference is that the *trans* species are chiral, and the two depicted minima are each others' stereoisomers. The *cis* species, on the other hand, are not chiral and the two depicted minima are related to each other either by a reflection or by a rotation of the molecule.

The discussion of the subsequent panels pertains to the progression of the *trans* minimum located at $(\delta_1, \delta_2) = (90^\circ, 90^\circ)$ and to that of the *cis* minimum located near $(\delta_1, \delta_2) = (-85^\circ, 85^\circ)$.

$\Phi = 70^\circ$: Fig. 1 (bottom). As in the case of the unsubstituted compound, one observes an elongation of the area around the minima. As in the preceding panel, and for the same reasons, the area around the *trans* minimum is symmetric along the disrotatory direction, whereas that around the *cis* minimum is not. Moreover, because of the steric hindrance, the *trans* regions T are less elongated than in the unsubstituted case, while the *cis* regions C are as elongated as the unsubstituted species in the favorable disrotatory direction, but not at all in the opposite direction. This is because there is no steric hindrance to the two methyl groups moving farther apart from one another, while the molecule strongly resists their being brought closer together. The *trans* minimum is still significantly lower in energy than the *cis* minimum. The energies of all minima have increased.

$\Phi = 75^\circ$. This panel, which is not shown, looks similar to the preceding one. The *trans* species is still lower in energy than the *cis*, while both are higher than the corresponding values found for $\Phi = 70^\circ$.

$\Phi = 80^\circ$: Fig. 2 (top). As in the unsubstituted system, the ring opening has reached the point of the first bifurcation in the reaction path for the *trans* species. The *cis* species can, as we have seen, move in only one direction, the other being sterically obstructed. The behavior of the surface in the allowed direction of the *cis* ring opening is remarkably similar to that for the unsubstituted compound. The behavior of the *trans* compound is becoming increasingly similar to that of the unsubstituted compound because, as the opening angle increases, so does the distance between the methyl groups and hence the steric hindrance decreases. The differences in energy between the *trans* species T, which is still lower, and the *cis* species C is less than before, presumably due to the lessening role of the steric hindrances. Both the *trans* and the *cis* molecules are moving uphill on their reaction paths.

$\Phi = 82^\circ$: Fig. 2 (bottom). The energies of both the *cis* and *trans* isomers have increased with respect to those of the previous panel. But they now have almost the same values. The new alternate minimum m near $(\delta_1 = 90^\circ, \delta_2 = 0^\circ)$, which for the unsubstituted species appeared only at $\Phi = 83^\circ$, has already appeared here. The access from T or C to m is however still blocked by the saddle points S and S_1 .

$\Phi = 83^\circ$: Fig. 3 (top). The saddle point separating the former *cis* minimum from the new minimum m near $(\delta_1 = 90^\circ, \delta_2 = 0^\circ)$ has now disappeared, leaving the *cis* species free to move downhill. The *cis* species has thus reached its transition state

somewhere between a Φ angle of 82° and 83° . It is also apparent that there exists a non-preferential bifurcation of the reaction path in that the *cis* molecule is equally likely to move down to the alternate new minimum m_1 near ($\delta_1 = 0^\circ$, $\delta_2 = -90^\circ$) which is stereoisomeric to the minimum m . While, in the unsubstituted compound, the two stereoisomers m and m_1 could only be distinguished by the theoretical numbering of the atoms, in the present case the corresponding species are different molecules which can be experimentally distinguished.

The *trans* minimum T , on the other hand, is still separated by the saddle point S from the new minimum m . There is furthermore an additional new minimum m_2 near ($\delta_1 = 180^\circ$, $\delta_2 = 90^\circ$) which is separated from T by the saddle S_2 . The *trans* species has therefore not yet reached the transition state. Even though the *trans* configuration for $\Phi = 83^\circ$ is slightly lower in energy than the *cis* configuration C for the same Φ , the *cis* species will actually have moved to a lower energy because it has already passed its transition state.

$\Phi = 84^\circ$ (not shown). This panel looks similar to the preceding one. The *cis* species is well on its way downhill on the reaction path, while the *trans* species T , has not yet reached its transition state. However, as was already apparent in the $\Phi = 83^\circ$ panel, the two saddle points S and S_2 which separate this minimum from the two adjacent energy valleys with the respective minima m and m_2 , are no longer equivalent: One barrier is clearly higher than the other, i.e., the $\delta_1 + \delta_2 = 180^\circ$ line containing the *trans* minima is no longer a line of "local C_s symmetry". This is due to the fact that to move in the direction of one saddle, the molecule would have to go through a geometry where a methyl group would be situated between carbons 1 and 2, while in moving towards the other saddle the methyl groups stay away from the three-carbon ring.

$\Phi = 85^\circ$: Fig. 3 (bottom). There is very little to be said, anymore, about the *cis* species, since from this point on it behaves essentially like the unsubstituted compound.

The *trans* species, on the other hand, has just passed its transition state, and it is stereospecific. Indeed, it is manifest that a barrierless path has opened from T to one of the adjacent minimum valleys, namely the one containing m_2 , while there is still a barrier S in the way towards the other adjacent valley containing m . The reasons for this difference are the same as those outlined in the discussion of the preceding panel. Although the barrier is only of the order of a few kcal/mol, it will direct the molecule preferentially towards one stereoisomer rather than the other. As was the case for the *cis* species, the two stereoisomeric valleys m and m_2 are experimentally distinguishable. Some reflection will also show that the valleys containing the minima m_1 and m_2 are in fact equivalent.

$\Phi = 86^\circ$ (not shown). There is little difference between this panel and the one for $\Phi = 85^\circ$, except that the remaining barrier S_2 from T towards m_2 is becoming smaller and is close to disappearing.

$\Phi = 87^\circ$ to 140° : Figs. 4 and 5. The barrier S between T and m has now disappeared, i.e., the *trans* species has passed the second transition state and it, as well as the *cis* species, can now move downhill towards both final products. Noteworthy is the gradual restoration of the "local" (but not global!) C_s symmetry about and along the axis $\delta_1 + \delta_2 = 180^\circ$, as the Φ angle increases. By the time $\Phi = 140^\circ$ is reached, this symmetry is almost completely restored. The reason for this symmetry restoration is the fact that as the opening angle Φ increases, the

distance between the methyl groups increases also, and the corresponding nonbonded interactions decrease.

We also note the isomeric isoenergetic valleys ($\delta_1 + \delta_2 = \pm 90^\circ$) implying free, synchronized, cogwheel-like, disrotatory rotations of the two $\text{CH}_3\text{—C—H}$ planes, which are entirely analogous to those found in the unsubstituted compound.

$\Phi = 179^\circ$, *allene*: Fig. 6. As in the case of the unsubstituted allene, we again have a series of nearly perfectly straight valleys V and ridges R, corresponding to a rigid rotation of the entire molecule around the CCC axis. There are, however, the following differences:

(i) The valleys denoted by V are equivalent (i.e., they represent the same molecular species); and so are the valleys denoted by V_1 . However, the valleys V represent the molecular species which is the stereoisomer of that represented by the valleys V_1 . The analogous statements hold for the ridges R and R_1 .

(ii) The valleys are somewhat narrower, because steric effects, albeit weak ones, come into play when the D_{2d} symmetry is broken.

(iii) More importantly, the ridge situated at $\delta_1 + \delta_2 = 0^\circ$ is slightly higher than the ridge at $\delta_1 + \delta_2 = 180^\circ$, showing that the CHCH_3 groups would prefer to internally rotate relative to one another in one direction rather than the other. The reasons are again steric, i.e., rotation in one direction brings the two methyl groups closer together while rotation in the opposite direction brings them farther apart.

In summary, on the basis of the analysis of the various $\Phi = \text{constant}$ panels, it is apparent that the chosen theoretical model for adding substituents yields the experimentally observed stereospecificity.

3.2. The reduced reaction surface in the Φ, δ space

In order to get a comprehensive picture, it is again helpful to reduce the 3-dimensional surface (Φ, δ_1, δ_2) to a 2-dimensional one, as was done for the case of the unsubstituted molecule. This condensation is accomplished by the same method as that employed in Sect. 5.3 of the first paper [16]. There is however a difference. In order to obtain reaction paths which are continuous in the sense that no discontinuities are generated with respect to the optimized internal coordinates in general and $\delta_- = (\delta_1 - \delta_2)/2$ in particular, we must restrict the search for the minimum along the lines $\delta = (\delta_1 + \delta_2)/2 = \text{constant}$ to the area enclosed by the lines $\delta_- = 90^\circ$ and $\delta_- = -90^\circ$. This is necessary in order to maintain the difference between the valley along the diagonal $\delta_1 + \delta_2 = 90^\circ$ and the valley along the diagonal $\delta_1 + \delta_2 = 270^\circ$, which accounts for the stereoisomeric asymmetry in the descent from T. The new surface will again be a plot of the energy as a function of $\delta = (\delta_1 + \delta_2)/2$ and Φ .

The results are shown in Fig. 7. In contrast to the corresponding plot for the unsubstituted system we now display a wider range of δ values in order to cover the areas corresponding to the various isomeric species. It is apparent that the surface possesses translational symmetry in the δ direction with a period of 360° . It is also apparent that the surface exhibits reflection symmetry with respect to the lines $\delta = 0^\circ$ and 180° , but *not* with respect to the lines $\delta = -90^\circ$ and 90° . Points on the plot which are mirror images with respect to the lines $\delta = 0^\circ, 180^\circ$

correspond to molecular geometries which are chiral images of each other and are distinguished by their optical activities. Molecular geometries corresponding to the points on the lines $\delta = 0^\circ, 180^\circ$, etc. show no such activity, because they are their own mirror images.

For $\Phi = 59.5^\circ$ we have the cyclopropylidene isomers. The *trans* isomers T occur for $\delta = -90^\circ$ and 90° . Although the energy at these points is the same, the isomers at 90° and -90° are each other's chiral images and experimentally distinguishable by their optical activities. The *cis* isomers C occur for $\delta = 0^\circ, 180^\circ$. The energies at these points are the same (and different from the *trans* isomers) and the isomers at 0° and 180° differ from each other merely by a rotation of the whole molecule. They are thus experimentally indistinguishable. The surfaces around these points, although locally symmetric, differ from each other at large distances, corresponding to two different paths from *cis* to *trans*.

For $\Phi = 180^\circ$ we have the allene isomers A_1 and A_2 all of which have the same energy. The isomer A_1 occurs for $\delta = -45^\circ, 135^\circ$ etc., whereas the isomer A_2 occurs for $\delta = -135^\circ, 45^\circ$ etc. The isomers A_1 and A_2 are each others mirror images and chiral.

As before we note that the *trans* dimethyl-cyclopropylidene species is lower in energy than the *cis* molecule. As the C_1-C_2 bond breaks and the ring starts to open, the molecules (*cis* and *trans*) move upwards towards their respective transition states. The *cis* species continues to be higher in energy than the *trans* all through this ascent. It will, however, reach its transition state *first* (at a Φ angle of around 82.5°). The *trans* species does not reach its transition state until about 84.5° . As soon, therefore, as the *cis* molecule arrives at the top of its own energy curve, it will start descending towards the final products and, for a while at least, it will be lower in energy than the *trans* compound with the same Φ ring-opening angle. But there is a more important difference between the two transition states. While the *cis* transition state is similar to that of the unsubstituted species in being a perfectly symmetrical, valley-to-ridge bifurcation region, leading to two distinct allene stereoisomers with exactly equal probability, the *trans* transition state is clearly asymmetrical. It is apparent that, when the molecule reaches the transition region, it will find it energetically advantageous to move to the right instead of to the left. And while this advantage is only of the order of a few kcal/mol, it is enough to bias the reaction in one direction rather than the other, i.e., to make it partially stereospecific.

It is also of interest to note that there exists no reasonable path that leads from *cis*-dimethyl-cyclopropylidene to the *trans* molecule, or vice versa. At first glance, it may seem to be trivially obvious that one has first to break the C_1-C_2 bond in order to achieve the internal rotation necessary for the stereoisomerization. The preceding statement implies more, however, namely: even after the C_1-C_2 is broken, there exists no low energy path for this isomerization before the transition states are reached. A low energy path from the *cis* region to the *trans* region is manifestly available only *after* the transition states have been passed. At that point the descent to allene is however overwhelmingly preferred. It is apparent that this feature is not a consequence of having the methyl substituents, it existed already for the unsubstituted species (Fig. 16 of the first paper [16]). There, however, it was impossible to experimentally distinguish between the *cis* and the *trans* isomers.

With the molecules moving past their respective transition states towards the final products, one notes that the ridge following the *trans* transition region is steeper, with the valleys on either side somewhat more pronounced than the

respective *cis* valleys. This will have the effect of further enhancing the stereospecificity, because once a trajectory starts falling down one side of the ridge, it is less likely that it will recover and go the other way.

When analyzing the $\Phi = \text{constant}$ panels in the preceding section, it was noted that, due to steric reasons, it was more favorable for the allene stereoisomers to internally rotate one way rather than the other when going into each other. From the surface in Fig. 7 it is seen that the preferential transition state S_1 for the allene isomerization occurs at ($\delta = 0^\circ$, $\Phi = 141^\circ$) involving a concerted bending and twisting. The alternative route over the saddle S_2 at ($\delta = 90^\circ$, $\Phi = 139^\circ$) involves a twist in the opposite direction and has a higher barrier by about 6 kcal/mol. It is interesting to note that the opposite is true for the twisting isomerization *without* simultaneous bending: The barrier at ($\delta = 0^\circ$, $\Phi = 180^\circ$) is about 15 kcal/mol higher than that at ($\delta = 90^\circ$, $\Phi = 180^\circ$)! It is indeed easily seen that, in the case of $\Phi = 180^\circ$, the two methyl substituents approach each other more closely when $\delta = 0^\circ$, whereas, in the case $\Phi \approx 140^\circ$, they approach each other more closely when $\delta = 90^\circ$.

4. Asymmetrically disubstituted species

4.1. The experimental problem

The study of 2,3-dimethyl-cyclopropylidene and its conversion to 2,3-dimethylallene has given satisfactory explanations of the experimentally observations in terms of purely nonbonded interactions. There remains an unresolved question, however. This is the observation by Jones and Krause [6] that *cis*-2-*p*-bromophenyl-3-*p*-methyl-phenyl-cyclopropylidene gave an allene of *higher* optical activity and the *same* relative configuration as *cis*-2-phenyl-3-*p*-methylphenyl-cyclopropylidene, even though bromine is larger than hydrogen, so that purely steric arguments would tend to predict the *opposite* result. On the basis of these experiments, these authors argue that the substituents must be able to promote or retard the rotation of one group relative to the other during the ring-opening process by "electronic" effects. They use Borden's [1] suggested mechanism (where only one CX_2 group is supposed to rotate, with the other remaining fixed) in their arguments and suggest that the relative electron-donating or electron-withdrawing potential of the two groups will determine which of the two will rotate. With respect to these arguments we note that, in light of the results presented in the first paper [16] Borden's mechanism does not seem to be the correct one. Moreover, the suggestion that a bromine substituent in *para* position on the phenyl substituent of one of the carbons connected to the carbene carbon would have an electronic effect on the carbene center sufficient to influence the outcome of the reaction seems somewhat difficult to imagine.

A much simpler possibility, which was not considered by Jones and Krause, is that the observed changes are due to the fact that the C-Br bond is highly polar and can therefore be expected to interact via nonbonded dipole-dipole interactions with such bonds as C-H. Although the latter are considerably less polar, the interactions may nevertheless be sufficiently strong to be nonnegligible. In view of the opposing polarity of the C-Br and C-H bonds, this dipole-dipole interaction is in most cases attractive. If it is greater than the relevant nonpolar steric repulsion, then it might explain the results observed by Jones and Krause, without recourse to arguments about electronic effects. In this context, it should

be pointed out that covalent effects are "short-range" because they are related to exponentially decaying overlap integrals. By contrast, dipole-dipole interactions are "long-range" effects (see Eq. (5)) and therefore can be effective at the relatively large distances which are relevant in the Jones and Krause experiment.

4.2. Theoretical treatment of a model reaction

In order to test the validity of the aforementioned conjecture, we consider and compare the following two separate reactions. First, the case where only the hydrogen H_1 of cyclopropylidene is substituted by a methyl group and, second, the case where, in addition, a bromine atom is substituted for the hydrogen H_2 . We consider in particular geometries in the neighborhood of $(\delta_1, \delta_2) = (90^\circ, -90^\circ)$ where the methyl is *cis* to the bromine position (see Sect. 3.1).

The general features of the energy surfaces for the ring opening of these two molecules are quite similar to those of the previously considered dimethyl compound, the main difference being that the reaction of the *cis* species now exhibits stereospecificity because of the dissimilarity of the two *cis* substituents. (The asymmetry of the reaction surface for methyl cyclopropylidene could of course be observed *experimentally* only by replacing the *cis* hydrogen with deuterium.) The calculated asymmetries on the *cis* part of this reaction surface are, however, considerably smaller than those found for the *trans* species in the preceding section. It would, therefore, serve little purpose to exhibit the complete results for every $\Phi = \text{constant}$ panel. Instead we merely examine an enlargement of the area around the intersection of the reaction path with the $\Phi = 83^\circ$ panel, which happens to be right before the transition state. The minima denoted as m_1 lie in the entrance channels coming from the reactants. The minima denoted by m lie in the exit channels going to the products. For a slightly larger value of Φ , the minima m , will disappear and we are at the transition states. They occur for $\delta_1 \approx 60^\circ$, $\delta_2 \approx -60^\circ$.

Figure 8 shows two such enlargements. Figure 8a corresponds to the 3-methyl species, while Fig. 8b corresponds to the 2-bromo-3-methyl species. It should be noted that in both cases, a progression from the entrance minimum m_1 towards the exit minimum m in the lower left-hand corner corresponds to a *conrotatory* motion with the methyl group moving *towards the outside* of the three-carbon ring, while a progression towards the upper right-hand corner corresponds to a *conrotatory* motion with the methyl group moving *nearer to the inside* of the ring. According to steric considerations one would therefore expect the former rotation to be more facile for the methyl compound than the latter and, indeed, the energy surface of Fig. 8a exhibits such a bias in that there exists an open pathway from the reactant-side minimum m_1 towards the left, leading to the product-side minimum m , while there still exists a saddle point S barring the way to the right. The height of this barrier is about 1–2 kcal/mol. Since Br is at least as large as CH_3 , one would expect it to resist being moved over the ring at least as much as CH_3 , if steric effects were dominant. Since Br and CH_3 are *cis* to each other, one would then expect the energy surface in Fig. 8b to exhibit no bias or possibly even an opposite bias, i.e., to the right. In fact, however, the surface in Fig. 8b exhibits an even greater bias to the left than the surface in Fig. 8a. A closer examination shows that there exists a strong dipole-dipole attraction between the CBr bond (in the position denoted by C_2H_2 in Fig. 1 of the first paper [16]) and the C_1H_1 bond.

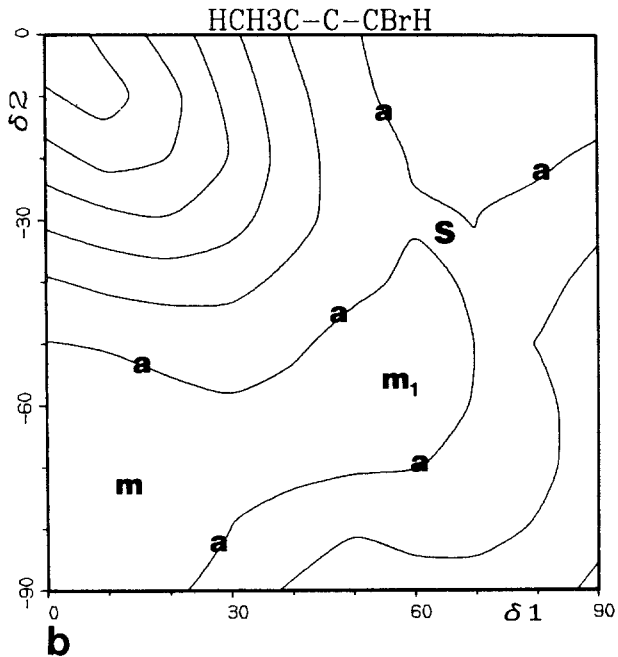
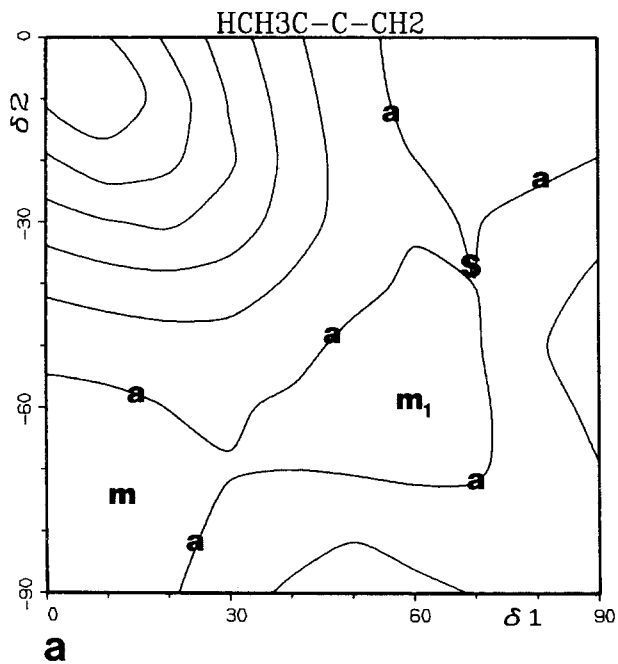


Fig. 8. Enlarged view of the area near the transition state on the plane $\Phi = 83^\circ$ for 3-methyl-allene (a) and *cis*-2-bromo-3-methyl-allene (b). The lowest energy contour is denoted by (a) and has the same energy on both panels ($E = -114.31638$). The increment between adjacent contours is 0.01 hartree

This attraction favors a motion of Br *towards* the ring. We believe that a similar attraction exists for the Br which is introduced in the Jones–Krause experiment [6]. Indeed, in the case considered *here* the dipole attraction has to overcome the not insubstantial steric concomitant hindrances of the Br atom. In the case of the Jones and Krause experiment, on the other hand, where the bromine is further away from the C₃ ring, one would hardly expect the bromine substitution to alter the short-range *steric* effects substantially, whereas the long-range *dipole-dipole* interaction would *not* be much weaker at the relevant distances. Hence, one would expect an even more pronounced enhancement of the stereospecific preference.

In view of this result it would seem unnecessary to assume that the introduction of substituents causes major changes in the short-range covalent binding interactions.

5. Critical energies

In view of the approximate nature of the employed procedure there are reasons to regard the values obtained for the critical energies with caution. Because of the omission of the geometrical relaxation of the substituent positions, one could expect a quantitative overestimate of the nonbonded effects and this is borne out by the results listed in Table 2. The first column in this table repeats the values obtained by the STO-3G calculation for unsubstituted cyclopropylidene of the first paper [16]. The subsequent columns list the differences between the critical energies found here for the ring opening of various substituted molecules and the corresponding values in the first column. In agreement with the discussion in the preceding sections all values have the correct sign. The relatively large values of opposite signs and nearly identical magnitude found for the barrier and reaction energies of the *cis* compounds are a consequence of the fact that the energy of the reactant has increased due to the steric hindrances. As explained above this increase is overestimated.

Table 2. Critical energies (kcal/mol)

	Unsubstituted values	Changes with respect to unsubstituted values			
		Dimethyl		Mono methyl	Methyl-bromo <i>Cis</i>
		<i>Cis</i>	<i>Trans</i>		
Ring-opening barrier	40	-15.3	-3.5 (favored) 2.5 (disfavored)	-8.2	-22.2
Reaction energy	65	16.3	6.5	9.9	24.7
Allene isomerization energy	42	-7	-18.8		

6. Conclusions

The description of substituents by grafting the simply calculated nonbonded interactions of the short-range steric and long-range electrostatic kind onto the

ab initio reaction surface of cyclopropylidene qualitatively reproduces the experimental observations made to date on the substituted moiety. The dimethyl-substituted *trans* species exhibits clear stereospecificity in the correct direction, while the corresponding *cis* compound exhibits stereospecificity. Both results agree with experiment and with chemical intuition. The calculations on the methyl-bromo species reveal that long-range dipole-dipole interactions can be more important than steric effects in inducing stereospecificity and in determining its direction. This finding explains previously puzzling experimental observations and should be kept in mind for future qualitative reasoning regarding substituent effects.

It is difficult to deduce detailed quantitative conclusions from the present calculations. On the one hand, the approximations (described at the end of Sect. 2) limit the quantitative rigor of the theoretical results. On the other hand, experimental uncertainties exist as to the degree of the stereospecificity in these reactions. However, the order of magnitude of the barriers, energy differences, etc., fall within the range expected from the experimental observations.

In view of the satisfactory explanation of the experimental observations by the present approach, there exists no evidence that would require the postulate of a covalent electronic origin of the observed stereospecificities. It seems therefore likely that the ring-opening reaction of cyclopropylidene to allene is covalently essentially nonstereospecific and that the stereospecific preferences are caused by nonbonded interactions, partly steric and partly long-range electrostatic between the substituents.

References

1. Borden WT (1967) *Tetrahedron Lett* 5:447 and a widely quoted private communication
2. Burkert U, Allinger NL (1982) *Molecular mechanics*, American Chemical Society, Washington, D.C., and references therein
3. Honjou N, Pacansky J, Yoshimine M (1984) *J Am Chem Soc* 106:5361
4. Hagler AT, Huler E, Lifson S (1974) *J Am Chem Soc* 96:5319
5. Johnson RP (1985) Private communication
6. Jones WM, Krause DL (1971) *J Am Chem Soc* 93:551
7. Jones WM, Walbrick JM (1969) *J Org Chem* 34:2217
8. Jones WM, Wilson JW, Jr (1965) *Tetrahedron Lett* 21:1587
9. Jones WM, Wilson JW, Jr, Tutwiler FB (1963) *J Am Chem Soc* 85:3309
10. Lehn JM, Ourisson G (1963) *Bull Soc Chim Fr*. 1113
11. Lennard-Jones JE (1924) *Proc R Soc London, Ser. A* 106:463
12. Meyer AY, Allinger NL (1975) *Tetrahedron* 31:1971
13. Pasto DJ, Haley M, Chipman DM (1978) *J Am Chem Soc* 100:5272
14. Pauling LC (1960) *The nature of the chemical bond*, 3rd ed, Cornell University Press, Ithaca, NY
15. Rauk A, Bouma WJ, Radom L (1985) *J Am Chem Soc* 107:3780
16. Valtazanos P, Elbert ST, Xantheas S, Ruedenberg K (1991) *Theor Chim Acta* 78:287 (Paper 1)
17. Walbrick JM, Wilson W, Jr, Jones WM (1968) *J Am Chem Soc* 90:2895
18. Warshel A, Lifson S (1970) *J Chem Phys* 53:582
19. Wertz DH, Allinger NL (1974) *Tetrahedron* 30:1579
20. Wiberg KB, Wendolowski JJ (1976) *J Am Chem Soc* 98:5465
21. Wodarczyk FJ, Wilson E (1972) *J Chem Phys* 56:166