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THE ELECTROCYCLIC TRANSFORMATION OF CYCLOPROPYL TO ALLYL CATION, AN ALL VALENCE SCF MO TREATMENT

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Abstract—The transformation of cyclopropyl, to allyl cation has been investigated by the CNDO II SCF MO method. Energy differences for transformations involving planar and non planar cyclopropyl cations, have been considered in the ground state and three lowest energy excited singlet and triplet states. For the ground states the results are compared with those derived from Extended Hückel calculations.

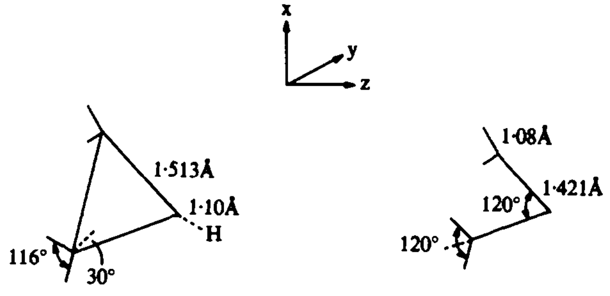
INTRODUCTION

THE original predictions,[1-3] concerning the stereochemistry of cyclopropyl-allyl transformations have been supplemented recently, for the cationic case, by more detailed Extended Hückel Theory (EHT) calculations.[4] These theoretical investigations have stimulated considerable research into the reactions of cyclopropyl derivatives and evidence is accumulating in support of the theoretical predictions.[5,6] However, for such an important theoretical concept the calculations which have been made are clearly unsatisfactory in several respects. Firstly the use of EHT in connection with charged species is theoretically unsound[7] and as far as charge distributions are concerned the results are unreliable.[8] Secondly EHT can make no predictions concerning excited states, although Longuet-Higgins and Abrahamson have presented a qualitative discussion in terms of state correlation diagrams. Thirdly the EHT investigations have only considered one intermediate configuration for each ring opening mode.

For some time now we have been investigating the application of a modified Pople–Segal CNDO II SCF MO[9-11] method to a variety of problems[12,13] and have found that the method gives a reasonable account of the electronic states of organic molecules. We present here the results of detailed calculations we have made by this method on the cyclopropyl-allyl cation transformation.

METHOD OF CALCULATION

The method of calculation has been fully described[12,13] and the parameters used here were identical to those employed in the treatment of the excited states of cyclopropane.[13] Configuration interaction between all singly excited states involving the four lowest unoccupied and four highest occupied orbitals has been included for each calculation. Fig. 1 shows the numbering system, coordinate axes bond angles and bond lengths used in the calculations for cyclopropyl and allyl cations. The geometry of the cyclopropyl system was assumed to be that of cyclopropane.[14] H-1 was located along a line at 58° and 0° to the plane of the ring for the transformations involving the non planar and planar cyclopropyl cation respectively. The carbon-carbon bond lengths in allyl cation were taken as the average of the C—C bond lengths in propylene.[14]



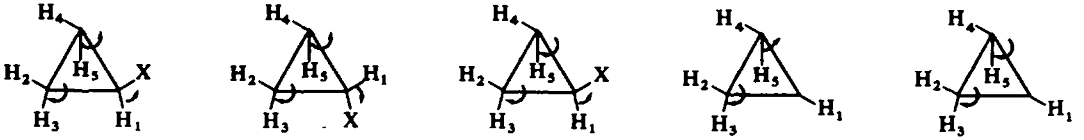
cyclopropyl

allyl

Fig. 1 Numbering system, coordinate axes, bond angles and bond lengths used in the calculations, for cyclopropyl and allyl cations.

The transformation of cyclopropyl to allyl is obviously quite a complicated motion. The H_2—C_2—H_3 (H_4—C_3—H_5) plane(s) is at 90° to the plane of the ring in cyclopropyl and initial rotation must be about an axis bisecting the C_1—C_2—C_3 (C_1—C_3—C_2) angles. However in the reverse process starting from allyl the axis of rotation initially lies along the appropriate C—C bond, hence as (H_2, H_3) and (H_4, H_5) are rotating the axis of rotation must be moving continuously. We have assumed that there is a continuous change in the bond angles, bond lengths and axes of rotation in going from cyclopropyl to allyl cation. For a concerted process there are three possible ring opening modes disrotatory 1, disrotatory 2 and conrotatory 1. This is shown in Fig. 2. Fig. 3 shows a scale drawing of cross sections of the envisaged reaction coordinate for one of the modes, disrotatory 2. As the group X departs H-1 moves into the plane of the ring.

If the cyclopropyl carbonium ion is formed prior to rearrangement the calculations show quite clearly that the local minimum for this species has H-1 in the plane of the ring so that two further modes were considered disrotatory (0) and conrotatory (0). For each mode we have carried out calculations corresponding to 15° intervals in the rotation of the H_2—C_2—H_3 (H_4—C_3—H_4) planes with respect to the plane of the ring.



dis. 1 dis. 2 con. 1 dis. 0 con. 0

Fig. 2 Ring opening modes considered for the transformation of cyclopropyl to allyl cation.

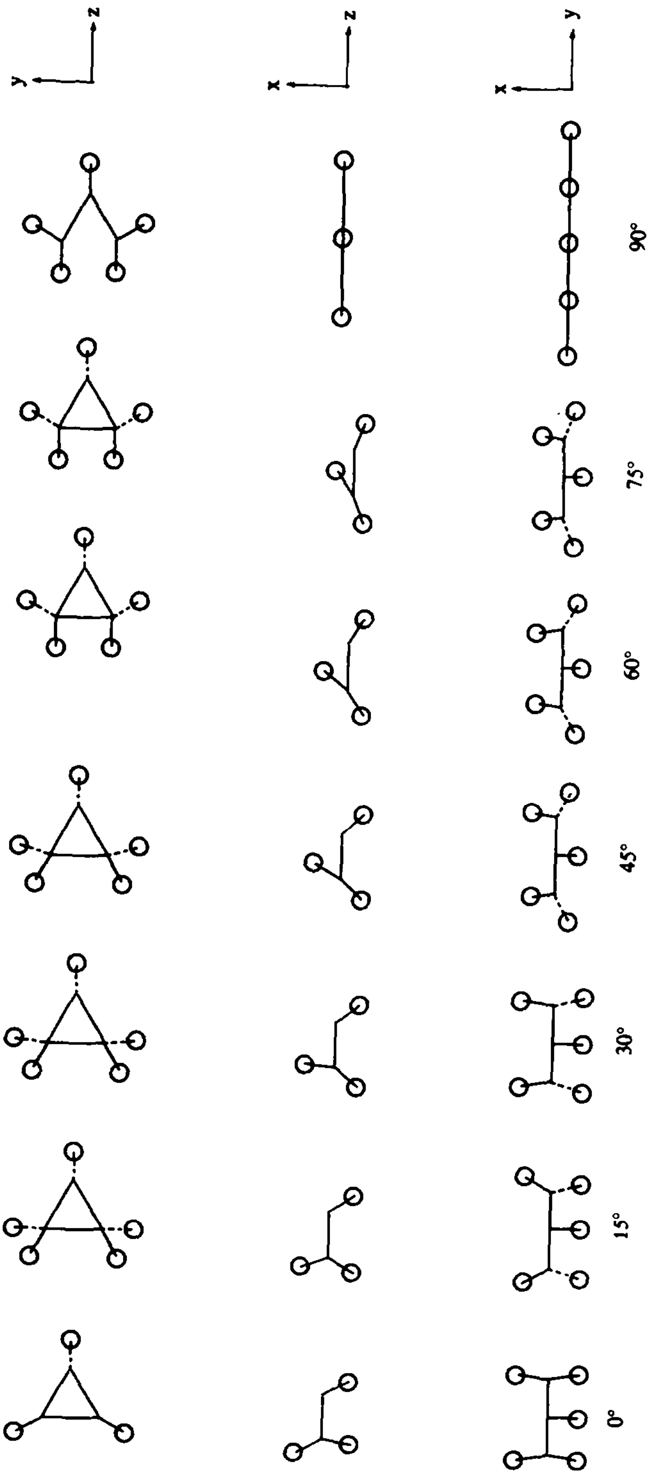


FIG. 3 Cross sections of the envisaged reaction coordinates for disrotatory mode 2.

RESULTS AND DISCUSSION

Ground state reactions

Since the effect of the leaving group X is not specifically taken into account a direct comparison between the energetics for a concerted or non concerted process cannot be made however for a given process the *relative* energies for each mode of transformation should be reliable.

(a) *Concerted process.* The transformation can proceed by three distinct modes, disrotatory modes 1 and 2 and conrotatory mode 1, and it is the *relative* energies of these three paths which are of interest. The theoretical results are therefore best represented in the form of energy difference diagrams. Fig. 4 shows the energy differences plotted as a function of angle of rotation for disrotatory 1 and conrotatory 1 modes compared with the lowest energy mode, disrotatory mode 2. The calculations have also been carried out using EHT and the results are essentially the same, as far as the energy differences are concerned, but the charge distributions show marked differences from the SCF results (Table 1).

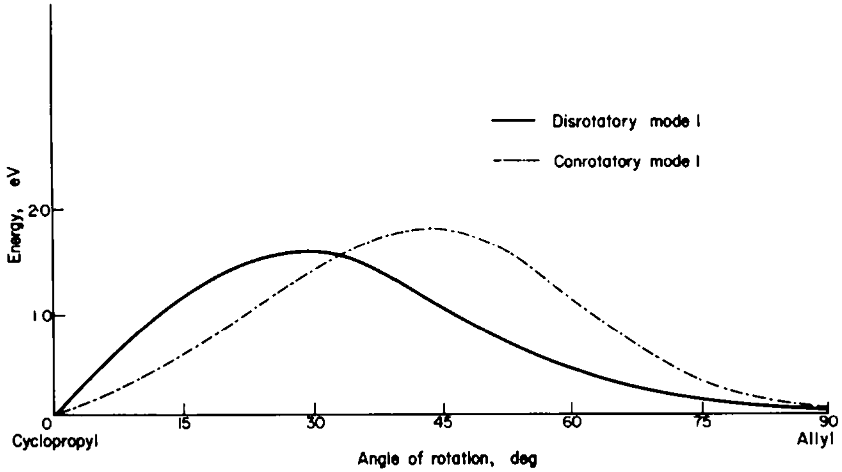


FIG. 4 Energy differences *vs* angle of rotation for disrotatory 1 and conrotatory 1 modes compared with the lowest energy mode, disrotatory mode 2.

The energy differences between the modes are almost certainly exaggerated since the two centre core integrals have been computed to give a reasonable account of the excited states.

There is now considerable experimental data in support of disrotatory mode 2 as the ring opening mode for the concerted transformation of cyclopropyl halides and tosylates into allyl cations and these have been discussed previously.[4–6, 15] There seem to be several points however worthy of further consideration. An interesting feature of Fig. 4 is that the main energy difference between the three modes occurs at low angles of rotation (<45°) and this suggests that the transition state for the transformation must also occur relatively early. There is ample experimental evidence

TABLE 1. A COMPARISON OF SCF MO AND EHT MO ATOMIC CHARGE DISTRIBUTIONS AS A FUNCTION OF ANGLE OF ROTATION FOR DISROTATORY MODE 2

Angle of rotation	Method	Atomic charges							
		H-1	H-2	H-3	H-4	H-5	C-1	C-2	C-3
0	SCF	0·1276	0·1279	0·1236	0·1279	0·1236	0·2950	0·0373	0·0373
	EHT	0·0690	0·0614	0·0587	0·0614	0·0587	0·4955	0·0977	0·0977
15	SCF	0·1185	0·1235	0·1346	0·1235	0·1346	0·2510	0·0570	0·0570
	EHT	0·0572	0·0626	0·0747	0·0626	0·0747	0·4172	0·1255	0·1255
30	SCF	0·1233	0·1250	0·1330	0·1250	0·1330	0·1833	0·0888	0·0888
	EHT	0·0598	0·0667	0·0785	0·0667	0·0785	0·3227	0·1635	0·1635
45	SCF	0·1292	0·1239	0·1256	0·1239	0·1256	0·1110	0·1310	0·1310
	EHT	0·0630	0·0649	0·0758	0·0649	0·0758	0·2372	0·2092	0·2092
60	SCF	0·1296	0·1172	0·1150	0·1172	0·1150	0·0401	0·1830	0·1830
	EHT	0·0596	0·0525	0·0693	0·0525	0·0693	0·1632	0·2669	0·2669
75	SCF	0·1217	0·1110	0·1040	0·1110	0·1040	−0·0161	0·2320	0·2320
	EHT	0·0481	0·0394	0·0608	0·0394	0·0608	0·1083	0·3216	0·3216
90	SCF	0·1058	0·1145	0·0960	0·1145	0·0960	σ 0·0191	−0·2732	−0·2732
							π − 0·0602	0·5300	0·5300
	EHT	0·0302	0·0447	0·0521	0·0447	0·0521	σ 0·0195	−0·1216	−0·1216
							π − 0·0791	0·4655	0·4655

for this. Depuy *et al.*[15] have investigated the rates of solvolysis of various phenyl substituted cyclopropyl tosylates. Rho(ρ) was found to be $\sim -4{\cdot}0$ for 1 substituted compounds and $\sim -2{\cdot}0$ for the 2 substituted compounds. From Table 1 it can be seen that the charge at C-1 becomes less than that at C-2 and C-3 for angles of rotation greater than 45°, whereas the rho values indicate a larger charge density at C-1 than C-2 or C-3. The charge on the H atoms H-2 (H-4) *trans* to the leaving group is greater than that on the *cis* hydrogens H-3 (H-5), and this suggests that replacement of hydrogen by a good electron donor such as phenyl should have a different effect depending on the relative disposition of the leaving group and the phenyl.

The solvolytic behaviour of *exo* and *endo* 6 tosyl bicyclo [3.1.0] hexanes is particularly interesting, the relative rates of acetolysis at 100°C being[6] *k endo*/*k exo* $> 2{\cdot}5 \times 10^6$. This indicates the large difference in energy between the two disrotatory modes. For the endo and exo isomers the expected favoured mode (disrotatory 2) produces *cis* and *trans* double bonds respectively in a 6-membered ring. The latter is obviously energetically very unfavourable, however the concerted reaction for the exo isomer could proceed by disrotatory mode 1. The solvolytic inertness of the *exo* isomer indicates that the energy difference between the two disrotatory modes is large, as indicated by the calculations. The recent results[6] concerning the exo bicyclo [*n*.1.0] tosylates ($n > 3$) deserve special consideration and we shall return to this point later on.

(b) *Non concerted process.* If the rearrangement is preceded by the formation of a free cyclopropyl cation, our calculations show that the energetically most favourable configuration has H-1 in the plane of the ring. There are then two possible modes of

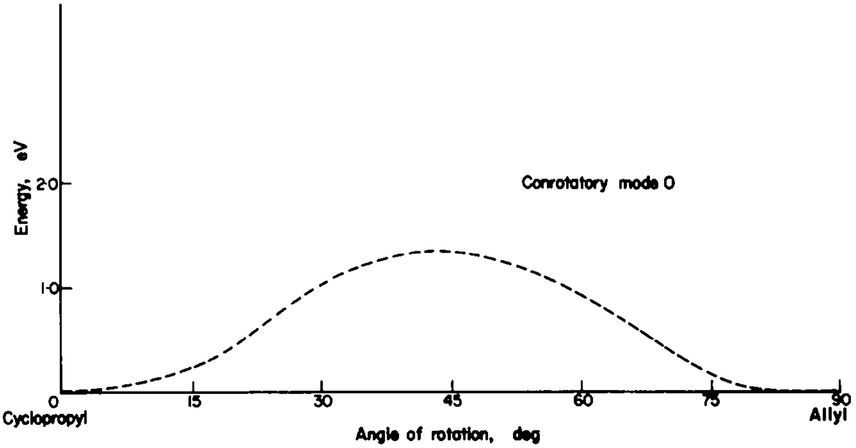


Fig. 5 Energy difference *vs* angle of rotation for conrotatory mode 0 compared with the lowest energy mode disrotatory mode 0.

transformation disrotatory (0) and conrotatory (0). Fig. 5 shows the energy difference diagram for the two modes. The disrotatory mode as expected is energetically much more favourable. The EHT results are essentially the same although again there is a difference between the charge distributions. For the disrotatory mode (0) this is shown in Table 2.

Table 2. A comparison of SCF MO and EHT atomic charge distributions as a function of angle of rotation for disrotatory mode (0)

Angle of rotation	Method	Atomic charges							
		H-1	H-2	H-3	H-4	H-5	C-1	C-2	C-3
0	SCF	0·1471	0·1353	0·1353	0·1353	0·1353	0·3417	−0·0150	−0·0150
	EHT	0·0811	0·0763	0·0763	0·0763	0·0763	0·6004	0·0066	0·0066
15	SCF	0·1364	0·1360	0·1562	0·1360	0·1562	0·3561	−0·0385	−0·0385
	EHT	0·0701	0·0788	0·1065	0·0788	0·1065	0·5885	−0·1450	−0·0145
30	SCF	0·1456	0·1314	0·1513	0·1314	0·1513	0·2480	0·0210	0·0210
	EHT	0·0760	0·0758	0·1053	0·0758	0·1053	0·4323	0·0648	0·0648
45	SCF	0·1480	0·1266	0·1338	0·1266	0·1338	0·1310	0·1000	0·1000
	EHT	0·0774	0·0688	0·0894	0·0688	0·0894	0·2777	0·1642	0·1642
60	SCF	+0·1393	0·1184	0·1175	0·1184	0·1175	0·0450	0·1720	0·1720
	EHT	0·0673	0·0540	0·0742	0·0540	0·0742	0·1740	0·2512	0·2512
75	SCF	0·1244	0·1112	0·1047	0·1112	0·1047	−0·0155	0·2297	0·2297
	EHT	0·0501	0·0397	0·0619	0·0397	0·0619	0·1100	0·3183	0·3183
90		As in Table 1							

Our EHT results confirm those of Kutzelnigg,[4] that for large angles of rotation (>45°), a small out of plane bending of H-1 lowers the energy of the disrotatory mode. However the SCF calculations do not show this behaviour and for all angles of rotation the species with H-1 in the plane of the ring is the lower in energy although for angles of rotation >60° the difference is extremely small. Fig. 6 shows the energy

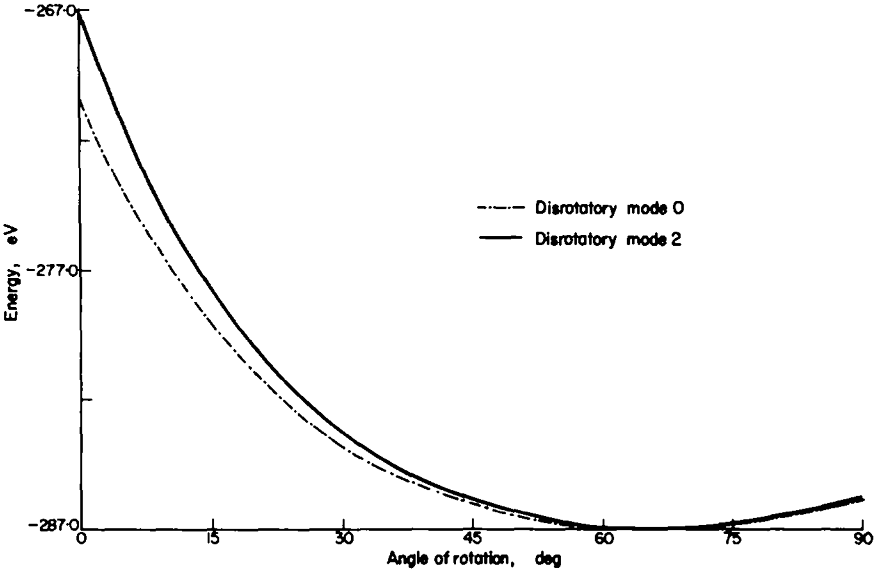


FIG. 6 Energy variations for disrotatory mode 2 and 0 as a function of angle of rotation.*

* A feature clearly evident in Fig. 6 is the exaggerated energy difference between cyclopropyl and allyl cations. Although energy differences are calculated to be in good agreement with experiment by the CNDO method, when conformational changes are involved (i.e. bond lengths remain the same), the same does not apply to situations where the bond lengths are changed. This has been noted previously.[10] A large part of the discrepancy almost certainly arises from an incorrect estimate of the *nuclear* repulsion energy. In the original papers[9–11] this term was assumed to be of the form

$$\sum_{i>j} \frac{Z_iZ_j}{rij}$$

corresponding to the interaction of point charges located at the nuclei. However the repulsion between two unit positive charges located on nuclei v and μ should be the same as that between two electrons, i.e. $\gamma_{\mu v}$. Hence the nuclear repulsion energy in this approximation may be written

$$\sum_{i>j} Z_iZ_j\gamma_{ij}$$

Also the nuclear charges Z_i for carbon have been taken to be +4, however this assumes complete screening of the nucleus by the 1s electrons. Allowing for this incomplete screening ($Z = 4{\cdot}1$), gives an energy difference between cyclopropyl and allyl cation of 1·1 eV, with allyl being the lower in energy, and this is probably very close to the experimental value.

The important points we wish to bring out are that the energy *differences* between the two disrotatory modes should be quite reasonable and that for all angles of rotation the dis 0 mode is the lower in energy. It is obviously of considerable interest to know the absolute energy differences involved in the transformation and we are currently studying the transformation using Gaussian type functions in an ab initio treatment.

variations for disrotatory modes 2 and 0 as a function of angle of rotation. The SCF results seem the more reasonable. The most significant features evident in Fig. 6 are that the energies of the two modes are virtually identical at angles of rotation >60° that there are minima for both modes at ~60°. This implies that a carbonium ion with a significant lifetime is likely to be formed en route to allyl cation. As yet there appear to be no experimental data pertaining to the nonconcerted transformation, however the results discussed above have a direct bearing on the solvolysis of the *exo*-bicyclo [*n*.1.0] alkyl tosylates reported by von Schleyer *et al.*[6] On the basis of relative rates of reaction and products formed in the solvolysis of *exo*-bicyclo [*n*.1.0] alkyl tosylates (where $n = 3, 4, 5$ and 6) von Schleyer *et al.* proposed that the reactions proceed by a concerted disrotatory 2 ring opening to produce a carbonium ion of finite lifetime. Our calculations support this interpretation. For the exo tosylates disrotatory mode 2 produces initially a product with a *trans* double bond, and as *n* increases the strain involved in this process decreases. For a 60° angle of rotation the tosylate group will have almost completely departed and bonding to the remaining cation should be weak. The calculations show that the cation should be in an energy minimum, the energies of the configurations with H-1 in the plane or out of the plane of the ring being almost the same. In such a situation, the cation can either ring open, and the energy for this process will obviously decrease as the flexibility of the bridge increases (i.e. as *n* increases); or react with any nucleophilic species present.

For $n = 3$ and 4 where the strain in the resultant allylic species is high the intermediate cation will almost certainly correspond to <60° rotation and hence relative to the $n = 5$ and 6 compounds the charge density at C-1 will be much higher than at C2 and C3. Thus for $n = 4$ attack on the intermediate cation by acetate from the least hindered side at C-1 results in the *exo*-acetate, whilst attack at C-2 (C-3) results in *trans*-cyclohexenyl acetate which under the reaction conditions reacts further with acetic acid to produce a 1,3-diacetate. For $n > 4$ the intermediate cation has now advanced further along the reaction coordinate so that the charge densities are now much larger at C-2 (C-3) and the ring opening transformation is much lower in energy. Under conditions of thermo dynamic control the products, *cis*-cycloalkenyl acetates and cycloalkyl diacetates are formed from the initially formed *trans*-cycloalkenyl acetates. The latter arise from nucleophilic attack of acetate at C-2 (C-3), either directly on the intermediate cation or the allylic cation arising from the transformation.

Excited state reactions

Longuet-Higgins and Abrahamson[2] have given a qualitative discussion of the non-concerted ring opening modes of cyclopropyl cation in various excited states. We have previously investigated the excited states of cyclopropane, ethylene oxide and ethylenimine by this method and found it to give a reasonable interpretation of the electronic spectra of these compounds.[13] There is little experimental evidence to compare with theory for the cationic species except for allyl cation, the electronic spectrum of which has been tentatively assigned to a species produced on dissolution of allyl alcohol in concentrated sulphuric acid.[16,17] Table 3 shows the calculated excited states (energy <6·0 eV) and oscillator strengths for the cyclopropyl cation (H-1 pyramidal and planar conformations) and allyl cation.

The electronic spectrum of allyl alcohol in concentrated sulphuric acid exhibits a weak band at ~273 mμ and a strong band with maximum ~200mμ. There is also

TABLE 3. CALCULATED EXCITED STATES (<6·0 eV) OF CYCLOPROPYL CATION (H-1 IN AND OUT OF PLANE) AND ALLYL CATION

State Nos. (in Figs 7 and 8)	Cyclopropyl cation						Allyl cation		
	H-1 (in plane) C2v			H-1 (pyramidal arrangement) Cs			C2v		
	Singlet	f	Triplet	Singlet	f	Triplet	Singlet	f	Triplet
I	A_2 2·157	0	A_2 2·491	A'' 1·713	0·0036	A'' 1·587	B_1 3·092	0	B_1 3·092
II	B_1 3·505	0·0015	B_1 3·494	A' 2·667	0·019	A' 2·298	A_2 3·831	0	A_2 3·831
III	B_2 5·815	0·021	B_2 5·652	A'' 4·834	0·020	A'' 4·712	B_2 5·637	0·191	B_2 4·031

evidence for a very weak band at ~363 mμ. These absorption bands have been assigned to the allyl cation and on the basis of PPP SCF MO calculations[18] the band at ~273 mμ has been tentatively assigned to the $^1B_2 \leftarrow {}^1A_1$ ($\pi^* \leftarrow \pi$) transition. However this assignment is almost certainly incorrect since the oscillator strength is too small and also the observed frequency shifts on methyl substitution are inconsistent with this assignment.[16, 17] Rosenbaum and Symons[16] have therefore proposed that the $\pi^* \leftarrow \pi$ transition corresponds to the absorption at ~200 mμ, and the band at ~273 mμ is then assigned to a ($\pi^* \leftarrow \sigma$) involving the C—H bonding electrons. Our calculations fully support this assignment. The $^1B_1 \leftarrow {}^1A_1$ (3·092 eV, 401 mμ) and $^1A_2 \leftarrow {}^1A_1$ (3·831 eV, 324 mμ) transitions are both $\pi^* \leftarrow \sigma$, and although the oscillator strengths are calculated to be zero, by coupling with vibrations of appropriate symmetry the transitions can become vibronically allowed. The $^1B_2 \leftarrow {}^1A_1$ ($\pi^* \leftarrow \pi$) transition is calculated to occur at 5·637 eV (220 mμ) in reasonable agreement with experiment. An analogous transition is predicted to occur in the planar cyclopropyl cation at 5·815 eV the transition in this case may be designated as "pseudo" ($\pi^* \leftarrow \pi$), the orbitals involved being "pseudo" π orbitals constructed from 2px orbitals on carbon and anti symmetric combinations of the appropriate hydrogen 1S orbitals.

(a) *Concerted process.* Throughout the transformation from cyclopropyl to allyl disrotatory modes 1 and 2 both maintain a plane of symmetry, and hence the excited states may be classified as either A′ or A″ in the point group C_s. The conrotatory mode however for angles of rotation ϕ ($0° < \phi < 90°$) possesses no symmetry elements other than the identity operation. Fig. 7 shows the energy difference diagrams for the three lowest energy singlet states and the corresponding triplet states. The overall

TABLE 4. PREDICTED RING OPENING MODES FOR NON CONCERTED PROCESS FOR THE THREE LOWEST ENERGY SINGLET AND TRIPLET STATES OF CYCLOPROPYL CATION

	Excited state	Favoured mode
I	Singlet and triplet	disrotatory
II	Singlet and triplet	conrotatory 1
III	Singlet and triplet	conrotatory 1

prediction concerning the mode of ring opening is essentially the same for both singlet and triplet states, and are shown in Table 4. Transitions to the corresponding states in a mono-substituted cyclopropane (point group C_s) are all symmetry allowed. However unless the substituent contains a conjugating chromophore these states will almost certainly have energies corresponding to absorption in the vacuum UV region

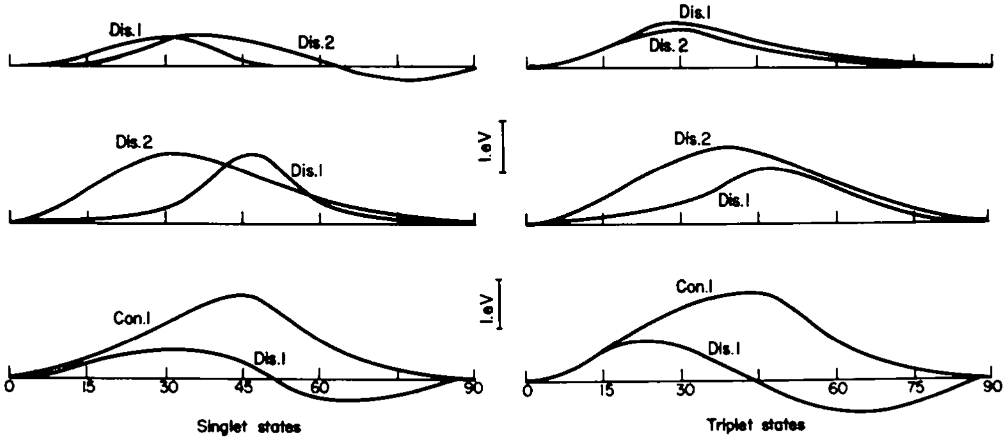


FIG. 7 Energy differences between the various concerted ring opening modes of cyclopropyl cation, for the three lowest energy singlet and triplet states, as a function of angle of rotation.

of the spectrum. From the published UV spectra[19] there is little doubt that there is considerable electronic interaction between the cyclopropyl and phenyl groups in phenyl cyclopropane, and it seems likely that with the appropriately substituted phenyl cyclopropane at least some of the excited state transformation to the allylic system should be possible, in the UV region of the spectrum.

(b) *Non concerted reaction.* Previously we have shown that if the transformation involves an initially formed cyclopropyl carbonium ion, the local minimum for this

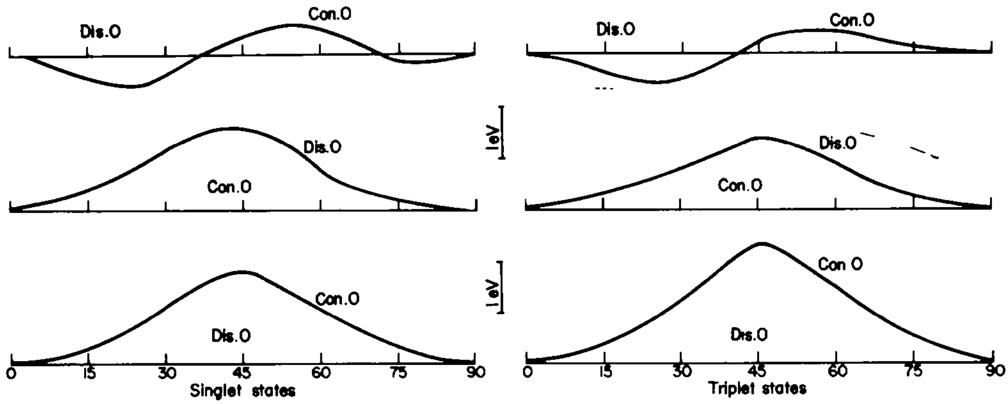


FIG. 8 Energy differences between the disrotatory 0 and conrotatory 0 modes of ring opening of cyclopropyl cation, for the three lowest energy singlet and triplet states, as a function of angle of rotation.

species has H-1 in the plane of the ring. In the particular excited states under consideration this is still the case and the species planar at H-1 is a local minimum with respect to bending H-1 out of the plane for both disrotatory 0 and conrotatory 0 modes. For angles of rotation ϕ ($0° < \phi < 90°$) the states arising from disrotatory mode 0 may be classified as A′ or A″ (point group C_s) whilst those arising from conrotatory mode (0) may be classified as A or B (point group C_2). The energy difference diagrams for the three lowest energy singlet and triplet states is shown in Fig. 8. The results indicate that transformations involving the first two excited states are likely to be stereospecifically disrotatory and conrotatory respectively. For the third excited state however the situation is not clear cut, and suggests that the photochemical cyclization of allyl cation by excitation of the $\pi^* \leftarrow \pi$ transition is unlikely to be stereospecific.

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