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# Non-Empirical LCAO-MO-SCF Calculations with Gaussian Type Functions on the Electrocyclic Transformation of Cyclopropyl to Allyl

## Part I. Cation Transformation

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Non-empirical molecular quantum chemical calculations have been performed on the electrocyclic transformation of planar and non-planar cyclopropyl cations, to allyl cations, in the LCAO-MO-SCF framework using gaussian type functions as atomic orbitals. Employing a total of 37 GTF, 3 disrotatory and 2 conrotatory modes of transformation have been considered. A total of 34 calculations have been carried out using this basis set; and to investigate the effect of increasing the $s$ basis set on carbon further calculations have been carried out using a basis set of 43 GTF. A detailed analysis of the energy terms involved show that there is little theoretical justification for the postulate that the mode of ring opening depends only on the symmetries of the highest occupied orbitals.

Nichtempirische SCF-MO-Rechnungen mit Gaußfunktionen (GF) für den Übergang des planaren und des unplanaren Cyclopropylkations zum Allylkation wurden vorgenommen. Mit einem Basissatz von 37 GF wurden 34 Rechnungen für 3 disrotatorische und 2 conrotatorische Arten des Übergangs durchgeführt. Um den Einfluß einer größeren Zahl von $s$-Funktionen am Kohlenstoff zu untersuchen, wurde auch mit einem Basissatz von 43 GF gerechnet. Die Analyse der Energieterme gibt wenig Anlaß zu der Annahme, daß die Art der Ringöffnung nur von der Symmetrie des obersten besetzten Orbitals abhängt.

Des calculs *ab-initio* en orbitales gaussiennes ont été effectués sur la transformation électrocyclique de cations cyclopropyliques plans et non plans en cations allyliques. Trois modes disrotatoires et deux modes conrotatoires ont été considérés en utilisant un total de 37 orbitales gaussiennes. Trente quatre calculs ont été effectués dans cette base; l'effet de l'augmentation de la base a été étudié en effectuant d'autres calculs avec une base de 43 orbitales gaussiennes. Une analyse détaillée des termes d'énergie impliqués montre qu'il y a peu de justification théorique pour le postulat selon lequel le mode d'ouverture du cycle dépend seulement de la symétrie de la plus haute orbitale occupée.

## 1. Introduction

In previous papers [1, 2] we have investigated the transformation of cyclopropyl to allyl systems for the particular cases of the cation and anion, employing a semi-empirical all valence SCFMO method. The main aim of this work has been to clarify the original predictions of Woodward and Hoffman [12] and Longuet-Higgins and Abrahamson [7], particularly for transformations involving excited state species.

For the ground state reactions the situation is still somewhat unsatisfactory. In the particular case of the cation, Extended Hückel Theory (EHT) results

[6, 12] indicate that energy differences between various modes can be largely ascribed to differences in particular orbital energy levels and that the mode of ring opening depends on the symmetry properties of a specific orbital. This seemingly simple result has been used qualitatively to rationalize a large body of experimental data [12]. However the fact remains that for charged species EHT is theoretically unsound and in any case it is implicit in EHT that the minimum in the sum of the orbital energies leads to a minimum in total energy as well. Clearly even if electron and nuclear repulsions are taken into account the latter may not be true, and hence any detailed conclusions drawn from EHT calculations should be regarded circumspectly. This in part has been the motivation for carrying out the semi-empirical all valence SCFMO calculations, however as we have indicated [1] an unsatisfactory feature of these calculations is the grossly exaggerated calculated energy difference between cyclopropyl and allyl cations. Although energy differences between various modes of transformation (which only involve conformational changes), seem quite reasonable by this type of calculation, a detailed interpretation of energy differences seems unwarranted.

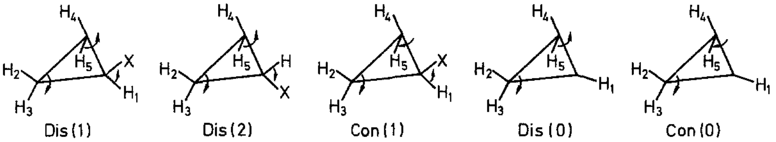

Fig. 1

In this paper we consider the transformation of both planar and non planar cyclopropyl cation to allyl cation by a non-empirical LCAO SCFMO treatment with gaussian type functions. In a subsequent communication we shall deal with the anionic species.

Fig. 1 shows the various modes and their designations which we have considered. Modes Dis(0) and Con(0) refer to the disrotatory and conrotatory transformations respectively of an initially planar cyclopropyl cation; prototype for a non-concerted transformation of a substituted cyclopropane precursor. Dis(1), Dis(2) and Con(1) refer to transformations of an initially non planar cyclopropyl cation, prototype for a concerted transformation of a substituted cyclopropane precursor.

## 2. Method of Calculation

The calculations performed in this work were carried out using the POLYATOM system [3, 4] tailored to make use of the extensive disc handling facilities of the Northumbrian Universities IBM 360/67 Multiple Access Computer (NUMAC). As we have previously indicated, [1, 2] if one is to draw meaningful conclusions from calculations on reaction co-ordinates, it is imperative to take a sufficient number of points. Fig. 1 shows the five modes of transformation of cyclopropyl to allyl, which we have investigated, and for each, calculations have been carried out corresponding to 15° intervals in the rotation of the $H_2$–$C_2$–$H_3$-

($H_4$–$C_3$–$H_5$) planes with respect to the plane of the ring. Fig. 2 shows the numbering system, co-ordinate 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 [11]. H–1 was located along a line at 58° and 0° to the plane of the ring of the transformation 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 [11]. We have assumed that there is a continuous change in the bond angles, bond lengths and axes of rotation of the $H_2$–$C_2$–$H_3$($H_4$–$C_3$–$H_5$) planes in going from cyclopropyl to allyl cation. Time limitations, particularly for charged species where convergence tends to be slow, and the number of calculations involved, dictated that a medium size basis set of 37 GTF be used. This consisted of 3*s* and 6*p* (2 each for the $p_x$, $p_y$ and $p_z$ orbitals), GTF for each carbon and 2*s* for each hydrogen. The *s* and *p* GTF exponents for carbon are those reported in Ref. [4], while the exponents of GTF on the H atoms were taken from Ref. [5].

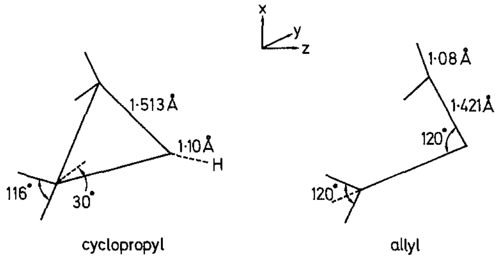

Fig. 2

A total of 34 calculations have been carried out using a basis set of 37 GTF. A further 4 calculations on planar cyclopropyl cation, allyl cation and the Dis(0) and Con(0) modes at 45° have been investigated with enlarged basis set of 43 GTF consisting of 5*s* and 6*p* on each carbon to obtain more reliable estimates of the cyclopropyl-allyl cation energy difference and ensure that conclusions concerning inner shell electrons were not a result of using a relatively small *s* basis set. To put the time element in proper perspective, for allyl cation which has considerable symmetry the 37 GTF calculation took 50 min, increasing the basis set to 43 GTF extended the time to 95 min, illustrating the dependence of $t$ on $\sim n^4$ and showing the difficulty of using larger basis sets.

## 3. Results and Discussion

### 3.1. Bond Length Variation in Allyl Cations

The molecular geometries indicated in Fig. 2 are those used previously in the semi-empirical all valence SCF-MO treatment [1]. However as a check we have carried out calculations on allyl cation varying the C–C bond length with the C–H bond length fixed at 1.08 Å. Fig. 3 shows the derived potential energy curve with a calculated minimum at 1.37 Å. Experience has shown that with basis sets of this size bond lengths are of the order of 5—10% too small, and thus our initial estimate of 1.42 Å must be close to the actual bond length.

By fitting a parabola to the potential energy curve, a force constant for the symmetric stretching vibration of the C–C bonds of 22.8 m.dyne $Å^{-1}$ was obtained. This is almost certainly too large and a considerable increase in the size of the basis set would be required to give a more realistic estimate.

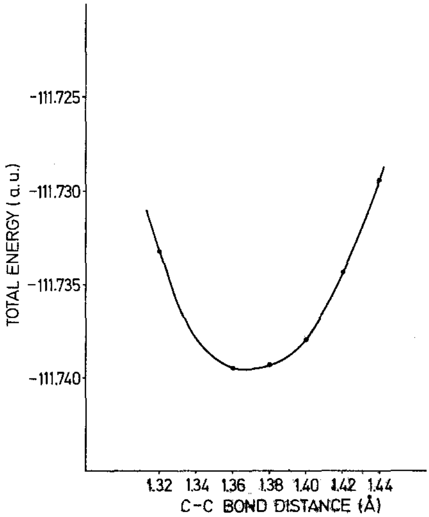

Fig. 3. Potential curve of the allyl cation as a function of the C–C bond length

### 3.2. *Energies for Bent and Planar Cyclopropyl and Allyl Cations*

Table 1 shows the energies and symmetries of the occupied and two lowest energy virtual orbitals for bent and planar cyclopropyl and allyl cations.

For allyl cation the lowest unoccupied orbital is of $\pi$ symmetry with a node through C 1, whilst the corresponding orbital for planar cyclopropyl cation might be designated as a pseudo $\pi$ orbital, constructed from the $2p_x$ orbitals on carbon and an appropriate anti-symmetric combination of hydrogen $1s$ orbitals. Applying Koopman's theorem the electron affinity of these cations, equal to the negative of the ionization potentials of the corresponding radicals are calculated to be 6.66 eV, 7.75 eV and 6.46 eV, for planar, non planar cyclopropyl and allyl respectively. The experimental ionization potentials are 8.05 eV [8] and 8.16 eV [9] respectively for cyclopropyl and allyl radicals. There is little to be drawn from the fact that the calculated ionization potentials for cyclopropyl [planar and bent (H 1 58° out of plane)], are greater than that for allyl, the reverse of that found experimentally, since in all probability the cyclopropyl radical will be bent but with the angle of bending being quite small ($\leqslant 58°$).

The calculations indicate that a free cyclopropyl cation adopts a planar configuration about C–1. The energy difference with respect to a bent cyclopropyl cation obtained from a cyclopropane precursor in an adiabatic process amounts to 0.06317 a.u. (39.64 Kcals/mole), the dominant feature being the much lower nuclear energy for the planar species.

Table 1. *Energies and symmetries of the occupied and two lowest energy virtual orbitals for bent and planar cyclopropyl and allyl cations (energies in a.u.)*

| | Cyclopropyl cation | | Allyl cation |
|---|---|---|---|
| | *Bent* | *Planar* | |
| Virtual orbitals | $-0.0068\ A''\ 13\sigma^*$ | $0.0388\ B2\ 13\sigma^*$ | $-0.0230\ B1\ 13\pi^*$ |
| | $-0.2849\ A'\ 12\sigma^*$ | $-0.2446\ B1\ 12\sigma^*$ | $-0.2374\ A2\ 12\pi$<br>(non bonding) |
| | $-0.6551\ A'\ 11\sigma$ | $-0.7288\ A1\ 11\sigma$ | $-0.6643\ B1\ 11\pi$ |
| | $-0.7596\ A''\ 10\sigma$ | $-0.7441\ B2\ 10\sigma$ | $-0.7729\ A1\ 10\sigma$ |
| | $-0.8058\ A''\ 9\sigma$ | $-0.7723\ A2\ 9\sigma$ | $-0.8117\ B2\ 9\sigma$ |
| | $-0.8816\ A'\ 8\sigma$ | $-0.9239\ A1\ 8\sigma$ | $-0.8762\ B2\ 8\sigma$ |
| | $-0.9374\ A'\ 7\sigma$ | $-0.9251\ B1\ 7\sigma$ | $-0.9306\ A1\ 7\sigma$ |
| | $-1.0648\ A'\ 6\sigma$ | $-1.0832\ B2\ 6\sigma$ | $-1.0220\ A1\ 6\sigma$ |
| | $-1.1047\ A''\ 5\sigma$ | $-1.0846\ A1\ 5\sigma$ | $-1.1870\ B2\ 5\sigma$ |
| | $-1.4225\ A'\ 4\sigma$ | $-1.4586\ A1\ 4\sigma$ | $-1.3321\ A1\ 4\sigma$ |
| | $-11.1753\ A''\ 3\sigma$ | $-11.1717\ B2\ 3\sigma$ | $-11.1362\ A1\ 3\sigma$ |
| | $-11.1755\ A'\ 2\sigma$ | $-11.1725\ A1\ 2\sigma$ | $-11.2040\ B2\ 2\sigma$ |
| | $-11.3048\ A'\ 1\sigma$ | $-11.3007\ A1\ 1\sigma$ | $-11.2041\ A1\ 1\sigma$ |
| Electronic energy | −179.99028 | −179.66239 | −175.97704 |
| Nuclear energy | 68.42081 | 68.02974 | 64.24261 |
| Total energy | −111.56947 | −111.63264 | −111.73443 |

For the transformation of planar cyclopropyl to allyl cation the calculated energy change is 0.1018 a.u. (63.87 Kcals/mole). This is a much more reasonable estimate than the CNDO-SCF-MO result [1]. A rough estimate of ~25 Kcals/mole for the experimental value may be obtained from electron impact data [8]. This is fortuitously close to the CNDO-SCF-MO result obtained with a modified nuclear energy which we have reported previously [1].

### 3.3. *Analysis of Energy Terms for the Disrotatory and Conrotatory Modes of Transformation for a Free Cyclopropyl Cation*

The calculations indicate that a free cyclopropyl cation adopts a planar configuration about C 1 and we have studied the transformation of this species to allyl cation via Dis(0) and Con(0) modes. Fig. 4 shows a plot of energy versus reaction co-ordinate for the two modes. The salient features are as follows:

(1) The favoured transformation Dis(0) involves no activation barrier.

(2) The transformation involving Con(0) involves a substantial activation barrier of 0.07364 a.u. (46.21 Kcals/mole).

According to Woodward and Hoffmann [12] the energy differences between the two modes of transformation are determined by the energies of the highest occupied orbitals, and it is the purpose of this paper to examine this proposal in detail. Fig. 5 shows a plot of the orbital energies for both the occupied and two lowest energy virtual orbitals for the Dis(0) and Con(0) modes. A striking feature evident in Fig. 5 is the variation in energy of the "inner shell" carbon *s* orbitals; this has been noted for other compounds by Preuss and Diercksen [10]. Throughout the transformations the Dis(0) mode retains a plane of symmetry (*xz*) whilst

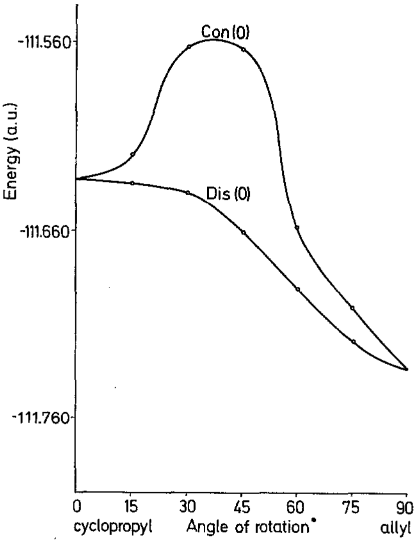

Fig. 4. Energy (a.u.) versus angle of rotation° for Dis(0) and Con(0) transformation of cyclopropyl to allyl cation

the Con(0) mode retains an axis of symmetry ($C_2(z)$), so that orbitals may be classified in the point groups $C_s$ or $C_2$ respectively. For the disrotatory mode the highest energy occupied orbitals is of $A$ symmetry for all angles of rotation. However the highest occupied orbital of $A$ symmetry for cyclopropyl correlates with

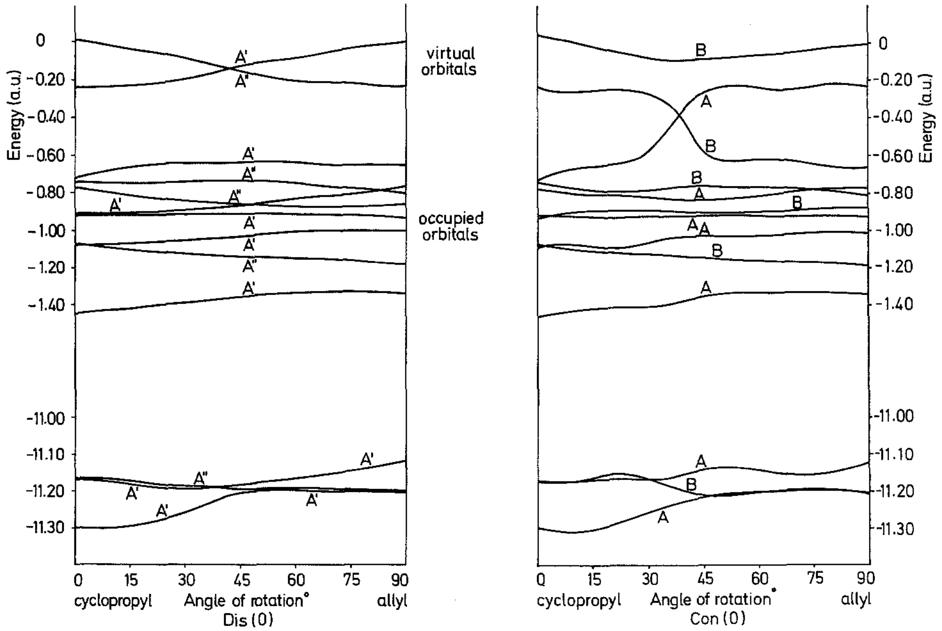

Fig. 5. Orbital correlations for Dis(0) and Con(0) modes of transformation of planar cyclopropyl to allyl cation

the lowest unoccupied orbital of allyl cation for the conrotatory mode, and hence for angles of rotation $> \sim 35°$ the highest orbitals is of $B$ symmetry. This may be visualized as follows. The highest occupied orbital of cyclopropyl cation has considerable bonding character between C2 and C3 and in the disrotatory mode, this orbital correlates with the $\pi$ bonding orbital of allyl, whilst for the conrotatory mode the correlation is with the $\pi$ non bonding orbital of allyl with a node through C1. Superficially this lends considerable support to Woodward and Hoffmann's arguments [12]. However it is not clear that this is the major factor contributing to the lower energy of the disrotatory modes, since there are differences in other orbital energies, and electron repulsion terms have not been considered.

It is convenient to divide the total energy into three components, Eq. (1)

$$E_{\text{Total}} = E_1 + E_2 + E_3 \tag{1}$$

where with the usual notation

$$E_1 = \sum_i \varepsilon_i \text{ summation of occupied orbital energies,}$$

$$E_2 = -\sum_{\text{pairs } rs} (J_{rs} - K_{rs}) \text{ summation of electron repulsion terms,}$$

$$E_3 = V_{nn} \text{ the nuclear repulsion energy.}$$

For EHT the rhs of (1) reduces to the first term.

Table 2 gives an analysis of the various energy terms for the Dis(0) and Con(0) modes and also energy difference between the modes. Also included are the contributions to the orbital energy term arising from the highest occupied orbitals.

It is evident from Table 2 that the energy differences between the modes are largely determined by the electronic energy differences $\Delta(E_1 + E_2)$, the nuclear energy differences $\Delta E_3$ being much smaller and in each case favouring the conrotatory mode. A plot of $\Delta\varepsilon_{\text{HOC}}$ against $\Delta E_{\text{Total}}$ produces a reasonable straight line as required by the Woodward-Hoffmann hypothesis [12]. However this correlation is illusory and arises from a fortuitous balance of the factors contributing to $\Delta E_{\text{Total}}$. For angles of rotation of 15°, 30° and 75°, $\Delta E_1 > \Delta\varepsilon_{\text{HOC}}$, whilst for angles of rotation of 45° and 60° $\Delta E_1 < \Delta\varepsilon_{\text{HOC}}$. Thus there is little direct correlation between differences in the summation of orbital energy terms and the particular term in the summation arising from the highest occupied orbitals. Furthermore the relationship between $\Delta E_1$ and $\Delta E_{\text{Total}}$ is by no means simple. For example for a 75° angle of rotation the lower energy of the disrotatory mode is determined by $\Delta E_2$ although for lower angles of rotation there is some correlation between $\Delta E_1$ and $\Delta E_{\text{Total}}$.

To sum up, these calculations clearly indicate that the Dis(0) transformation of planar cyclopropyl to allyl cation is the energetically preferred mode. The analysis indicates that this arises largely as a result of the lower electronic energy for this mode. However the evidence presented here is that the simple type of relationship presented by Woodward and Hoffmann [12] and suggested by EHT calculations [6, 12], is not reproduced by the more sophisticated *ab initio* treatment. This points to the danger of using too simple an analysis for what is obviously a complex situation, and suggests strongly that for charged species at any rate the results of an EHT analysis should be regarded with due caution.

Table 2. *Detailed comparison of energy terms for* Dis(0) *and* Con(0) *modes (all energies in a.u.)*

| Angle of rotation and mode | | Electronic energy | | | Nuclear energy | Energy differences Dis(0)–Con(0) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $E_1$ | $E_2$ | $E_1+E_2$ | $E_3$ | $\Delta E_1$ | $\Delta E_2$ | $\Delta(E_1+E_2)$ | $\Delta\varepsilon_{HOC}$[a] | $\Delta E_3$ | $\Delta E_{Total}$ |
| 0 | Dis(0)<br>Con(0) | −82.7310 | −96.9314 | −179.6624 | 68.02974 | 0 | 0 | 0 | 0 | 0 | 0 |
| 15 | Dis(0) | −82.5938 | −95.5008 | −178.0946 | 66.4590 | −0.0298 | +0.0109 | −0.0189 | −0.0438 | 0.0040 | −0.01503 |
| | Con(0) | −82.5640 | −95.5117 | −178.0757 | 66.4550 | | | | | | |
| 30 | Dis(0) | −82.5274 | −94.5473 | −177.0747 | 65.4341 | −0.0798 | −0.0069 | −0.0867 | −0.1290 | 0.0100 | −0.07678 |
| | Con(0) | −82.4476 | −94.5404 | −176.9879 | 65.4241 | | | | | | |
| 45 | Dis(0) | −82.4020 | −94.0358 | −176.4378 | 64.7764 | −0.2068 | +0.0970 | −0.1098 | −0.1466 | 0.0120 | −0.09787 |
| | Con(0) | −82.1952 | −94.1328 | −176.3280 | 64.7644 | | | | | | |
| 60 | Dis(0) | −82.2958 | −93.6248 | −175.9206 | 64.2293 | −0.1096 | +0.0690 | −0.0406 | −0.0572 | 0.0085 | −0.03208 |
| | Con(0) | −82.1862 | −93.6938 | −175.8800 | 64.2208 | | | | | | |
| 75 | Dis(0) | −82.2718 | −93.6463 | −175.9181 | 64.1981 | +0.0950 | −0.1032 | −0.0081 | −0.0028 | 0.0027 | −0.00546 |
| | Con(0) | −82.3668 | −93.5431 | −175.9099 | 64.1954 | | | | | | |
| 90 | Dis(0)<br>Con(0) | −82.2822 | −93.6948 | −175.9770 | 64.2426 | 0 | 0 | 0 | 0 | 0 | 0 |

[a] $\varepsilon_{HOC}$ orbital energy term arising from highest occupied orbital.

### *3.4. Calculations Using an Enlarged s Basis Set for Carbon Atoms*

Table 3 shows the orbital energies, and total energies for planar cyclopropyl, Dis(0) and Con(0) 45° and allyl cations using a basis set of 43 GTF. The increase in size of the carbon *s* basis set results in a substantial lowering in the absolute energies of the cations. The cyclopropyl-allyl cation energy difference is calculated to be 35.27 Kcals/mole (0.0562 a.u.) in very reasonable agreement with the estimated experimental value. The energy difference between the Dis(0) and Con(0) modes at 45° is calculated to be 59.10 Kcals/mole (0.0942 a.u.) compared with 61.44 Kcals/mole (0.0979 a.u.) obtained with the basis set of 37 GTF, whilst for the cyclopropyl cation – Con(0) 45° energy difference the corresponding figures are 52.47 Kcals/mole and 43.29 Kcals/mole (0.0690 a.u.).

As expected the largest changes in orbital energies on increasing the basis set is for the inner shell electrons. However the energy differences within the group of three 1*s* orbitals is almost identical to those calculated with the smaller basis set, which strongly indicates that these differences are both real and significant.

Table 3. *Energies and symmetries of the occupied and two lowest energy virtual orbitals for planar cyclopropyl,* Dis(0) *and* Con(0) *45° and allyl cations (energies in a.u.)*

| | Planar cyclopropyl | 45° | | Allyl |
|---|---|---|---|---|
| | | Dis(0) | Con(0) | |
| Virtual orbitals | 0.0358 *B*2 | −0.1322 *A′* | −0.0806 *B* | −0.0127 *B*1 |
| | −0.2234 *B*1 | −0.1541 *A″* | −0.2421 *A* | −0.2260 *A*2 |
| | −0.7120 *A*1 | −0.6249 *A′* | −0.5551 *B* | −0.6507 *B*1 |
| | −0.7200 *B*2 | −0.7249 *A″* | −0.7434 *B* | −0.7682 *A*1 |
| | −0.7555 *A*2 | −0.8461 *A″* | −0.8287 *A* | −0.7969 *B*2 |
| | −0.9017 *A*1 | −0.8595 *A′* | −0.8789 *B* | −0.8635 *B*2 |
| | −0.9200 *B*1 | −0.9049 *A′* | −0.8961 *A* | −0.9204 *A*1 |
| | −1.0991 *B*2 | −1.0490 *A′* | −1.0407 *A* | −1.0347 *A*1 |
| | −1.1048 *A*1 | −1.1683 *A″* | −1.1731 *B* | −1.2063 *B*2 |
| | −1.4718 *A*1 | −1.3912 *A′* | −1.3793 *A* | −1.3685 *A*1 |
| | −11.5801 *B*2 | −11.6122 *A′* | −11.5606 *A* | −11.5613 *A*1 |
| | −11.5806 *A*1 | −11.6126 *A″* | −11.6249 *B* | −11.6237 *B*2 |
| | −11.7122 *A*1 | −11.6187 *A′* | −11.6253 *A* | −11.6238 *A*1 |
| Total energy | −115.08853 | −115.09909 | −115.00491 | −115.14474 |

### *3.5. Analysis of Energy Terms for the Disrotatory and Conrotatory Modes of Transformation for a Bent Cyclopropyl Cation, Analogue for a Concerted Reaction Process*

Most of the experimental data concerns transformations in which the generation of the cation and ring opening to allyl are synchronous in a concerted process [1]. As we have indicated there are three modes of transformation to be considered, Dis(1), Dis(2) and Con(1) and these are illustrated in Fig. 1. Ideally of course one would like to calculate the reaction co-ordinate for a particular leaving group X starting from a substituted cyclopropane and finishing with allyl cation and $X^-$. However this would be fraught with difficulties since the wavefunctions for the state $CH_2{=\!=}\overset{+}{C}H{=\!=}CH_2X^-$ corresponds to an excited state. Hence calculations would be required not only on the ground states but on the excited states as well, for each mode of transformation in order to construct the correct state correlation diagrams. Instead we have considered the process whereby $X^-$ is removed from the substituted cyclopropane in an adiabatic process, and the resulting cation is allowed to relax to allyl cation. This is in line with previous analyses based on EHT and CNDO-SCF-MO calculations [1, 6, 12]. Thus the effect of the leaving group X is not explicitly taken into account and in the discussion we make the reasonable assumption that this will be similar for all modes of transformation.

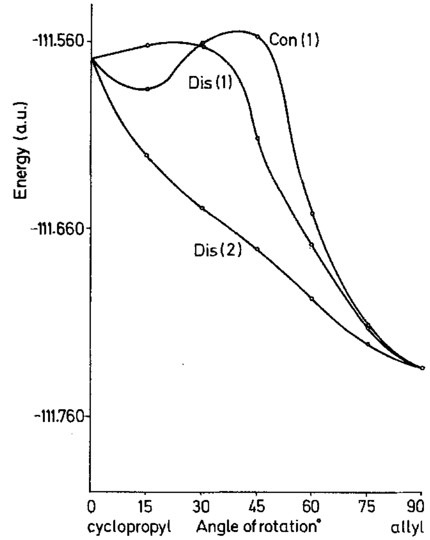

Fig. 6. Energy (a.u.) versus angle of rotation° for the Dis(1), Dis(2) and Con(1) transformation of bent cyclopropyl to allyl cation

Fig. 6 shows a plot of energy versus reaction co-ordinate for the three modes. The Dis(2) mode is quite clearly the favoured mode of ring opening, the other two modes being much higher in energy. This is in accord with an overwhelming body of experimental evidence [1]. It is interesting to note that for the initially "bent" cyclopropyl cation both the Dis(1) and Con(1) modes go through activation barriers of ~6 Kcals/mole and ~9 Kcals/mole respectively. This incidentally points to the danger of taking too few points on the reaction co-ordinate. For example drawing a curve through the three points corresponding to 0°, 45°, and 90° for the Dis(1) mode, the activation barrier would be completely missed cf. Ref. [6].

Fig. 7 shows a plot of orbital energies for both the occupied and two lowest energy virtual orbitals for the Dis(1), Dis(2) and Con(1) modes. Throughout the transformation the disrotatory modes retain a plane of symmetry ($xz$), whilst the conrotatory mode has no symmetry elements other than the identity. As for the transformation involving the planar cyclopropyl cation, the highest occupied orbital for bent cyclopropyl correlates with the lowest unoccupied orbital of allyl, for the conrotatory mode. The close similarity in energy of the Dis(1) and Con(1) modes evident in Fig. 6 dispels any doubt that the mode of ring opening is

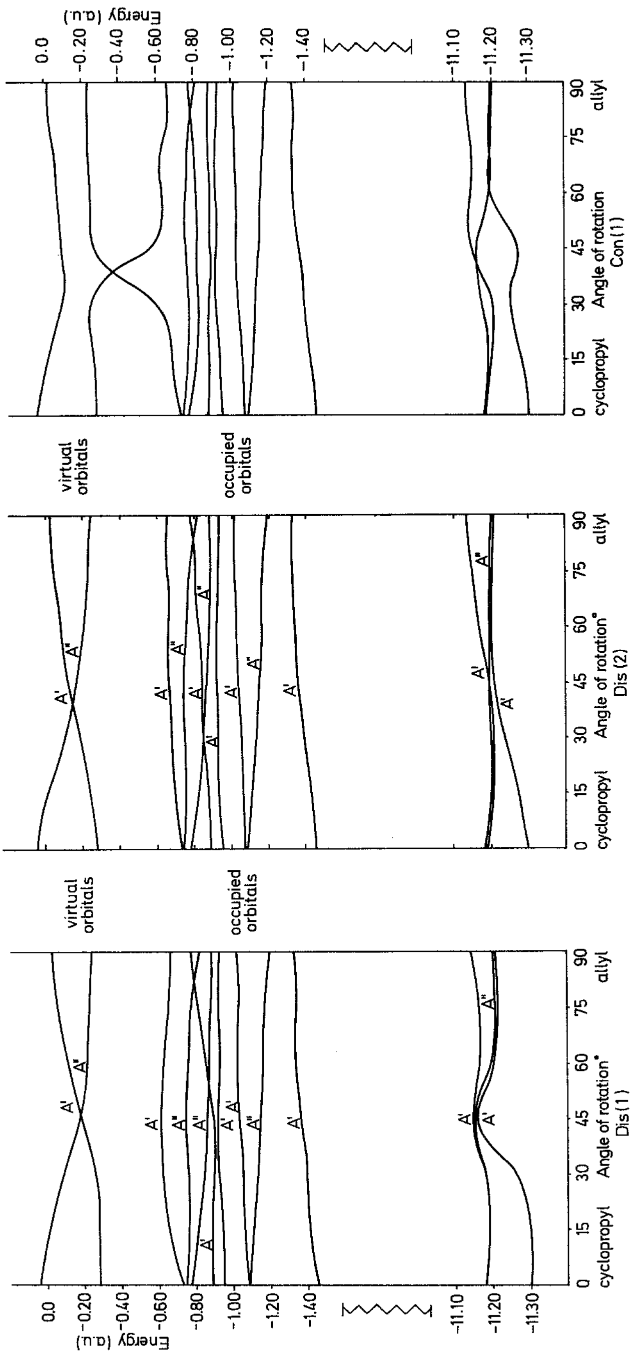

Fig. 7. Orbital correlations for Dis(1), Dis(2) and Con(1) modes of transformation of bent cyclopropyl to allyl cation

determined predominantly by the symmetry of the highest occupied orbital as suggested by Woodward and Hoffmann [12].

It is of considerable interest to investigate the energy differences between the various disrotatory modes; on the one hand between the Dis(0) mode for the planar cyclopropyl cation and the Dis(1) and Dis(2) modes for the "bent" species and also the energy differences between the latter two modes. Table 3 shows an analysis of the various energy terms for the Dis(0), Dis(1) and Dis(2) modes and also the energy differences between the modes. Considering first the two energetically preferred modes of transformation, Dis(0) and Dis(2); for a planar and bent cyclopropyl cation respectively, it can be seen that for small angles of rotation the Dis(0) mode is the lower in energy as a result of the lower nuclear energy. However as H1 moves towards the plane of the ring for the Dis(2) mode, the nuclear energy difference with respect to the Dis(0) mode rapidly drops off so that for a 30° angle of rotation the Dis(2) mode is now the lower in energy. This crossing of the two energy curves was first noted in Kutzelnigg's EHT work [6], however the CNDO-SCF-MO results [1] indicated that the Dis(0) mode was the lower in energy for all angles of rotation, and this almost certainly arises as a result of the overestimate of the nuclear energy previously noted for this method. Thus the transformation of a free cyclopropyl to allyl cation must involve quite a complicated motion with H1 initially in the plane of the ring moving out of the plane and returning as the reaction proceeds towards allyl.

The results in Table 3 indicate that the lower energy of the Dis(2) mode as opposed to the Dis(1) mode arises from the electronic energy terms, the nuclear energy differences being much smaller and favouring the Dis(1) mode. The situation is obviously complex and there is no simple explanation for the energy difference between the modes. For example the main factor contributing to the energy difference for 15°, 30°, 45°, and 60° angles of rotation is the lower orbital energy term for the Dis(2) mode and examination of Fig. 7 suggests that the most likely reason for this is the term arising from the inner shell carbon *s* orbitals. However for a 75° angle of rotation the lower energy of the Dis(2) mode arises largely from the lower electron repulsion term. The conclusions to be drawn from this are that the simple rationalizations previously put forward are not substantiated by detailed calculation, and that the role of "inner shell" electrons previously assumed by chemists to be unimportant, should receive some consideration.

### 3.6. Electronic Distributions

The gross atomic populations and bond overlap populations for the cyclopropyl and allyl cations are presented in Table 4. The chief difference between the electronic populations of the bent and planar cyclopropyl cations occurs in the occupancy of the $p_x$ and $p_z$ orbitals of C1, which of course depends on the conformation of H1. The remaining population terms of the two cations are similar with C1 and the hydrogen atoms having a fractional positive charge while C2 and C3 possess negative charges.

This charge situtation of the carbon atoms is reversed in the allyl cation, where C1 possess a negative charge while C2 and C3 are positively charged. This change is due to the concentration of the $\pi$ electrons at C1, whereas in the cyclopropyl cation the "pseudo-$\pi$" electrons are located at C2 and C3. The main difference

Table 4. *Detailed comparison of energy terms for the* Dis(0), Dis(1) *and* Dis(2) *modes (all energies in a.u.)*

| Angle of rotation and mode | | Electronic energy | | | Nuclear energy | Energy differences relative to Dis(0) mode | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $E_1$ | $E_2$ | $E_1+E_2$ | $E_3$ | $\Delta E_1$ | $\Delta E_2$ | $\Delta(E_1+E_2)$ | $\Delta E_3$ | $\Delta E_{\text{Total}}$ |
| 0 | Dis(0) | −82.7310 | −96.9314 | −179.6624 | 68.0297 | 0 | 0 | 0 | 0 | 0 |
| | Dis(1)<br>Dis(2) | −82.8176 | −97.1727 | −179.9903 | 68.4208 | 0.0866 | 0.2413 | 0.3279 | −0.3911 | −0.06317 |
| 15 | Dis(0) | −82.5938 | −95.5008 | −178.0946 | 66.4590 | 0 | 0 | 0 | 0 | 0 |
| | Dis(1) | −82.5742 | −95.7008 | −178.2750 | 66.7125 | −0.0196 | 0.2000 | 0.1804 | −0.2535 | −0.07310 |
| | Dis(2) | −82.7316 | −95.6170 | −178.3486 | 66.7269 | 0.1378 | 0.1162 | 0.2540 | −0.2679 | −0.01394 |
| 30 | Dis(0) | −82.5274 | −94.5473 | −177.0747 | 65.4341 | 0 | 0 | 0 | 0 | 0 |
| | Dis(1) | −82.4782 | −94.6675 | −177.1457 | 65.5835 | −0.0492 | 0.1202 | 0.0710 | −0.1494 | −0.07842 |
| | Dis(2) | −82.6098 | −94.6426 | −177.2524 | 65.6030 | 0.0824 | 0.0953 | 0.1777 | −0.1689 | 0.00871 |
| 45 | Dis(0) | −82.4020 | −94.0358 | −176.4378 | 64.7764 | 0 | 0 | 0 | 0 | 0 |
| | Dis(1) | −82.3750 | −94.0935 | −176.4685 | 64.8563 | −0.0270 | 0.0577 | 0.0307 | −0.0799 | −0.04924 |
| | Dis(2) | −82.4566 | −94.0881 | −176.5447 | 64.8732 | 0.0546 | 0.0523 | 0.1069 | −0.0968 | 0.01096 |
| 60 | Dis(0) | −82.2958 | −93.6248 | −175.9206 | 64.2293 | 0 | 0 | 0 | 0 | 0 |
| | Dis(1) | −82.2822 | −93.6456 | −175.9278 | 64.2598 | −0.0136 | 0.0208 | 0.0072 | −0.0305 | −0.02333 |
| | Dis(2) | −82.3340 | −93.6325 | −175.9665 | 64.2697 | 0.0382 | 0.0077 | 0.0459 | −0.0404 | 0.00553 |
| 75 | Dis(0) | −82.2718 | −93.6463 | −175.9181 | 64.1981 | 0 | 0 | 0 | 0 | 0 |
| | Dis(1) | −82.2818 | −93.6367 | −175.9185 | 64.2049 | 0.0100 | −0.0096 | 0.0004 | −0.0068 | −0.00637 |
| | Dis(2) | −82.2818 | −93.6475 | −175.9293 | 64.2078 | 0.0100 | 0.0012 | 0.0112 | −0.0097 | 0.00159 |
| 90 | Dis(0)<br>Dis(1)<br>Dis(2) | −82.2822 | −93.6948 | −175.9770 | 64.2426 | 0 | 0 | 0 | 0 | 0 |

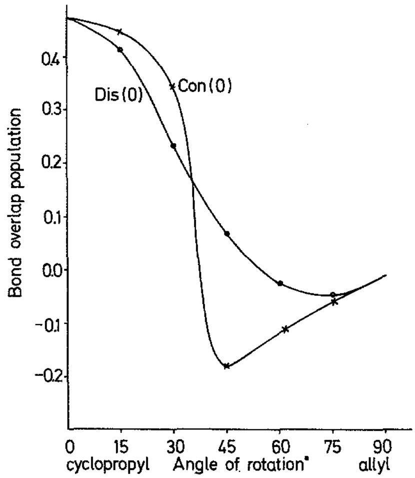

Fig. 8. Bond overlap populations of $C_2$–$C_3$ for Dis(0) and Con(0) modes of transformation of planar cyclopropyl to allyl cation

however, between the cyclopropyl and allyl cations is the C2–C3 bond order which is strongly bonding for the cyclopropyl cation but slightly anti bonding for the allyl cation.

Fig. 8 and 9 illustrate the change in the C2–C3 bond orders for the Dis(0), Con(0) and Dis(1), Dis(2), Con(1) modes respectively. For angles of rotation < ~40° the striking feature is the close similarity in bond orders for the disrotatory and conrotatory modes. Reference to Figs. 4 and 6 indicate clearly that the largest energy differences, between the modes also occur in the same range. For larger angles of rotation, the bond orders for the conrotatory modes rapidly become antibonding and go through minima and finally for allyl the bond order is virtually zero. The disrotatory modes exhibit a slower fall off in bond order to allyl. As a

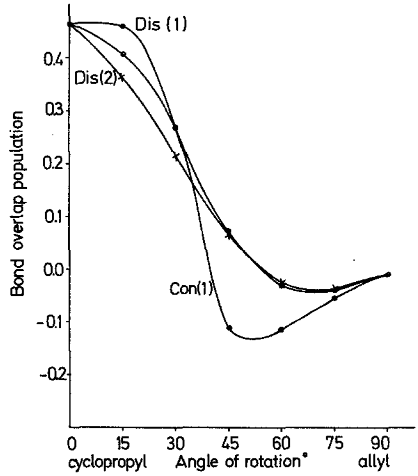

Fig. 9. Bond overlap populations of $C_2$–$C_3$ for Dis(1), Dis(2) and Con(1) modes of transformation of bent cyclopropyl to allyl cation

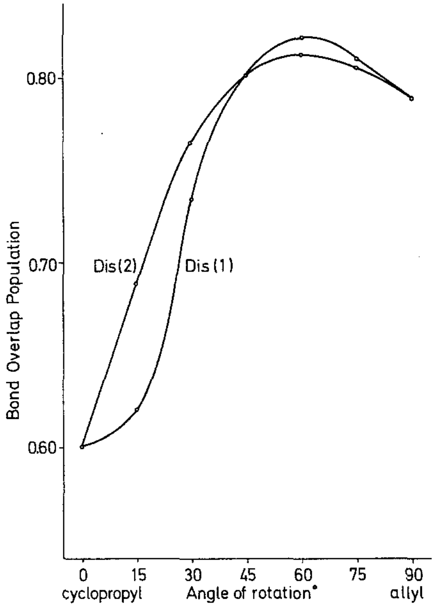

Fig. 10. Overlap bond populations between atoms $C_1$–$C_2(C_3)$ for Dis(1) and Dis(2) modes

corollary to the Woodward-Hoffmann analysis of the ring opening modes of cyclopropyl cation, it has been suggested [12, 7], that the energy difference between the conrotatory and disrotatory modes may be visualized as arising from a C2–C3 antibonding situation in the former during the transformation. However the

Table 5. *Electron densities and bond overlap population for bent and planar cyclopropyl and allyl cations*

| | | Bent cyclopropyl cation | Planar cyclopropyl cation | Allyl cation |
|---|---|---|---|---|
| C1 | $s$ | 2.746 | 2.770 | 2.643 |
| | $p_z$ | 0.881 | 1.459 | 1.343 |
| | $p_y$ | 1.313 | 1.328 | 1.163 |
| | $p_x$ | 0.570 | 0.112 | 1.094 |
| | Total | 5.510 | 5.669 | 6.243 |
| C2(C3) | $s$ | 2.675 | 2.651 | 2.717 |
| | $p_z$ | 1.019 | 1.024 | 1.336 |
| | $p_y$ | 1.102 | 1.113 | 1.286 |
| | $p_x$ | 1.408 | 1.406 | 0.453 |
| | Total | 6.204 | 6.194 | 5.792 |
| H1 | | 0.862 | 0.750 | 0.833 |
| H2, H4 | | 0.804 | 0.798 | 0.823 |
| H3, H5 | | 0.806 | 0.798 | 0.846 |
| C1–C2 | | 0.601 | 0.603 | 0.788 |
| C2–C3 | | 0.461 | 0.473 | −0.009 |
| C1–H1 | | 0.684 | 0.636 | 0.694 |
| C2–H2 | | 0.671 | 0.669 | 0.693 |
| C2–H3 | | 0.683 | 0.669 | 0.699 |

analysis presented here shows that although it is true that an antibonding situation does develop during the conrotatory transformation, the major energy difference between the modes is reached *before* this occurs.

For the concerted ring opening reaction a pictorial interpretation of the difference in disrotatory modes has been presented [13]. With the assumption that the orbitals concerned are *p* orbitals located on each carbon atom, models show [13] quite clearly that the interaction between C2 and C3 and the developing cationic centre at C1 is more favourable for the Dis(2) mode. If this has any theoretical foundation it should obviously show up as a large difference in the C1–C2(C3) bond overlap populations for the Dis(2) and Dis(1) modes. Furthermore the major differences should correspond to angles of rotation where the *energy* differences between the modes is large i.e. $<45°$ angle of rotation. Fig. 10 shows a plot of the C1–C2(C3) bond overlap populations for the Dis(1) and Dis(2) modes. It is evident that in this case the detailed calculations provide a reasonable justification for the simple pictorial model.

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