CNDO/2 CALCULATIONS OF ELECTROCYCLIC TRANSFORMATIONS—I

RING OPENING OF AN N-AZIRIDINYL CATION*

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Abstract—CNDO/2 calculations for the thermal electrocyclic transformation of an aziridinyl cation to an 2-azaallyl cation favor a disrotatory mode. The most stable acyclic ion is linear, a 2-azaallenyl cation These semi-empirical conclusions are in accord with experimental results for the solvolyses of N-chloroaziridines.

THE thermal ring openings of N-aziridinyl cations to 2-azaallyl cations (I → II) are particularly interesting since 2, 3 or 4 π-electron electrocyclic transformations (ECTs) can occur. Theory[1] predicts a disrotatory opening if the lone pair of electrons on nitrogen and the developing π-system of II are orthogonal and a conrotatory opening if one or both of the lone pair become a part of the π-system of II. These situations are depicted in Fig. 1 by placing neither, one, or both of the lone pair electrons in the blackened orbital.
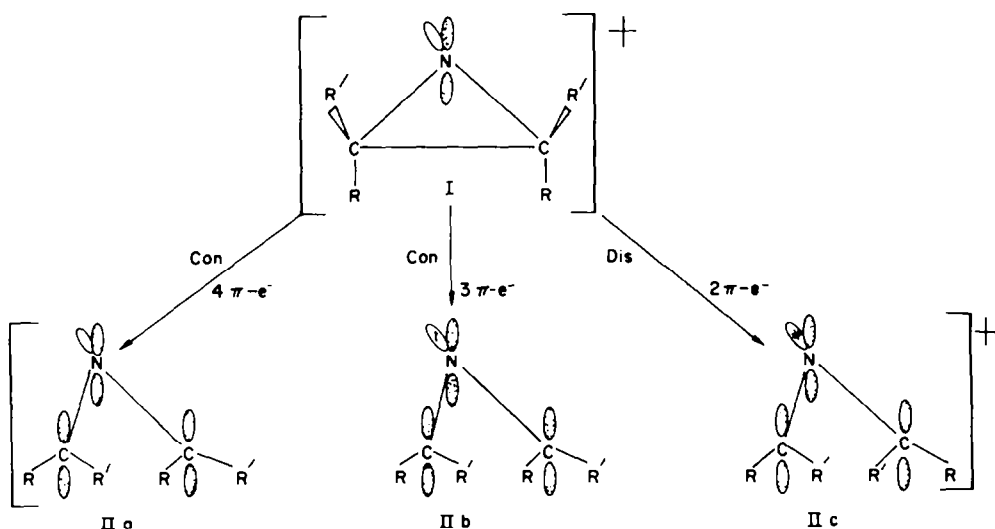

FIG 1. Possible Electrocyclic Ring Opening Paths of an N-Aziridinyl Cation.

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ECTs of related and isoelectronic species show that each of these is plausible. Cyclopropyl cations open to allyl cations by a disrotatory mode (2 π-electrons).[2] Cyclopropilidene yields allene by a conrotatory mode (probably 3 π-electrons).[3] A conrotatory opening (4 π-electrons) of N-carboethoxyaziridines has been elegantly demonstrated by Huisgen et al.[4]

Conclusive evidence that a disrotatory mode is available to N-chloroaziridines has been supplied by Gassman.[5] The relative solvolysis rates for N-chloroaziridine, N-chloro-cis,trans-2,3-dimethylaziridine, and trans-N-chloro-cis,cis-2,3-dimethylaziridine are 1:1490:155,000. This sequence is expected for a disrotatory opening proceeding through a cyclopropyl-like transition state.

In this paper, theoretical reaction coordinates for conrotatory and disrotatory ECTs of I → II are constructed from CNDO (Complete Neglect of Differential Overlap)-SCF-MO generated data. Molecular energy, bond index, and atomic charge data are mapped to find the more favored path.

RESULTS AND DISCUSSION

Method of calculation. A complete description of the CNDO method has been presented elsewhere.[6] The CNDO/2 program of Segal has been found to be quite good in predicting bond angles, charge distributions,[7] bond lengths, and, in some cases, heats of atomization.[8] The method has an unrealistic preference for small cyclic structures: cyclopropyl cation is calculated to be 0·138 a.u. *more* stable than allyl cation.

C—N *Bond Cleavage in* I. The possibility that C—N bond cleavage can compete with C—C bond cleavage in I is unlikely. The nitrene cations, IIIa and IIIb, are calculated to be 0·108 and 0·100 a.u. more energetic than the highest point along either path from I to II. The charge distributions in III indicate that C—N bond cleavage would be heterolytic, if it occurred. A nitrene carbonium ion which places most of the positive charge on carbon is preferred to a carbon radical and nitrogen cation radical structure, IIIc, obtained from homolytic C—N cleavage of I.
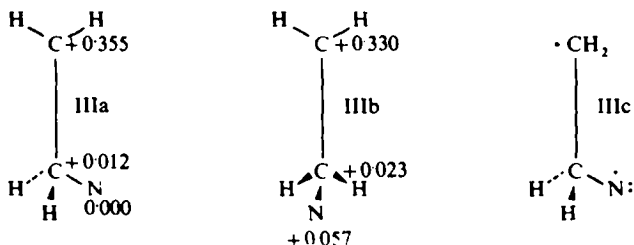

Electrocyclic transformation of I *to* II

Bond index considerations (Graph 1). The bond index, W_{ab}, is defined as the sum of the squares of the individual bond orders, Pa_ib_j, where i and j are occupied atomic orbitals on atoms a and b.[9] The close relationship between bond character and bond index has been discussed at length.[9, 10] In essence, the bond index between a and b increases as the number of covalent bonds between them increases.

$$W_{ab} = \sum_i \sum_j (Pa_ib_j)^2 = \sum_i \sum_j [(\text{occupancy in } i, j) Ca_iCb_j]^2$$

During the reaction, I → II, W(CN) and W(CC) for the disrotatory mode vary smoothly as expected for an allowed process. W(CC) decreases as W(CN) increases. W(CN) and W(CC) for the conrotatory mode are not smoothly varying functions: between structures B and C, $\Delta W(NC) = 0.39$ and $\Delta W(CC) = 0.60$. Large differences in elements of the bond order matrix and in the bond indices between very similar structures like B and C indicate that electronically forbidden processes occur in going from one structure to the other.
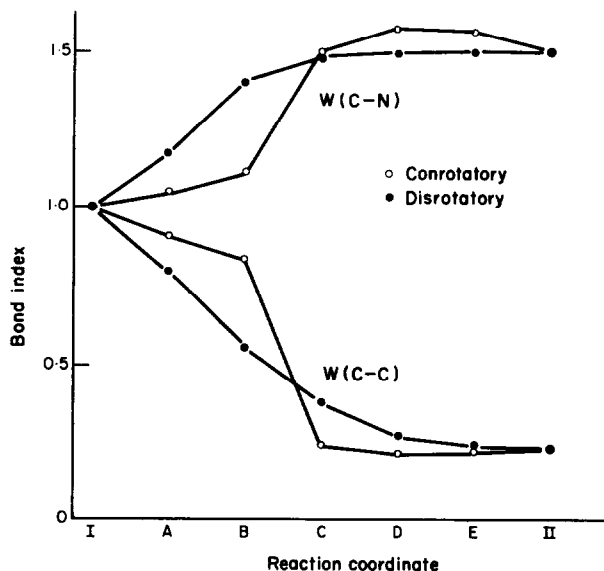
Graph 1. Bond index changes from I to II

Atomic charge considerations (Graph 2). Atomic charge increases on carbon from $+0.04$ to $+0.34$ and decreases on nitrogen from $+0.35$ to -0.09 as I opens disrotatory to II. The remainder of charge is dispersed among the four hydrogens. As expected for a 2 π-electron ECT, the charge on nitrogen is delocalized throughout the developing π-system as I opens:

(1) The lone pair of electrons remain on nitrogen as the ring opens.
(2) The C—C σ-electrons in I become the π-electrons in II.
(3) The unoccupied orbital on nitrogen in I becomes part of the developing π-system and is responsible for the increased electron density on nitrogen in II.

Atomic charges on carbon and nitrogen do not vary smoothly during a conrotatory opening of I. Atomic charges in I to B and in C to II are nearly constant. Alterations in charge between B and C, however, are greater than the total changes between I and II:

$$\Delta N_{B \to C} = 0.48 \qquad \Delta N_{I \to II} = 0.44$$

$$\Delta C_{B \to C} = 0.39 \qquad \Delta C_{I \to II} = 0.31$$

The abrupt change explains the bond index variation between B and C. Electrons in the C—C σ-bond are transferred to the unoccupied orbital on nitrogen while one of the orbitals changes sign.

An extrapolation of the curves for I to B along a conrotatory path to II places a small negative charge on carbon and a large positive charge on nitrogen, just the distribution expected if the orbitals on carbon remain orthogonal to those on nitrogen. Why this path from I to B is not continued to II is discussed later.
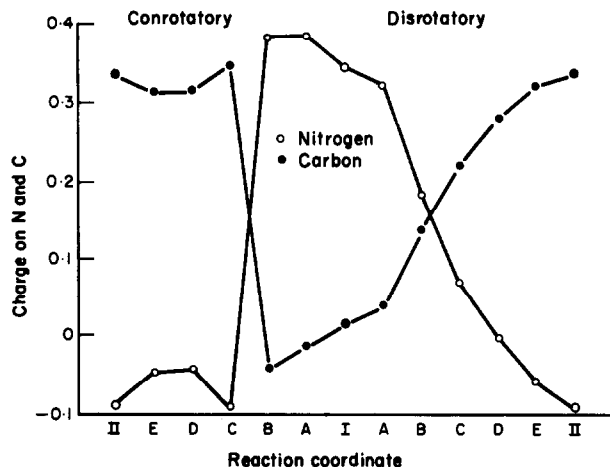
Graph 2. Atomic charge changes from I to II
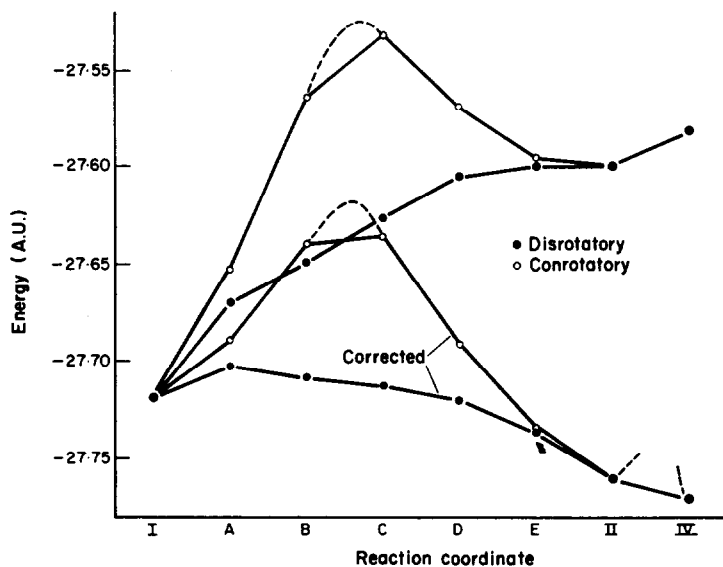
Graph 3. Energy changes from I to IV

Energy considerations (Graph 3). It is known from previous calculations that the CNDO/2 method over-estimates energies by orders of magnitudes.[6] Scaling factors which relate CNDO/2 energies to thermodynamic energies have been proposed by Isaacs[7] and Wiberg.[8] Attempts to apply Wiberg's method to cyclopropyl and allyl cations, to establish if CNDO/2 under-estimates resonance stabilization or under-

estimates strain destabilization, were unsuccessful. The heats of atomization, ΔH(atom), calculated from thermodynamic energies,[11] are

$$\Delta H(\text{atom})_\Delta^+ = 989 \text{ kcal/mole}$$

$$\Delta H(\text{atom})_{A+} = 998 \text{ kcal/mole}.$$

Wiberg's formula for ions calculates

$$\Delta H(\text{atom})_\Delta^+ = 903 \cdot 83 \text{ kcal/mole}$$

$$\Delta H(\text{atom})_{A+} = 873 \cdot 02 \text{ kcal/mole}.$$

Relative energies within a family, as in the conrotatory and disrotatory paths from I to II, however, appear to be reliable for determining relative stabilities. CNDO/2 calculations of ECTs for cyclopropyl to allyl give reasonable answers.[12]

Although I is calculated to be more stable than II, the CNDO/2 energies show a clear preference for a disrotatory opening. Points on Graph 3 can be ordered correctly with respect to one another by rotating their curves about I until II is *ca* 9 kcal/mole lower in energy than I.* After this correction, disrotatory opening of I is still favoured. The corrected curves possess energy maxima and resemble "normal" Morse curves. The maximum along the conrotatory path occurs between B and C, the segment of greatest bond and charge alteration. The disrotatory curve rises slightly from I to A and plateaus to D. Its low energy of activation is consistent with experiments conducted thus far.[5]
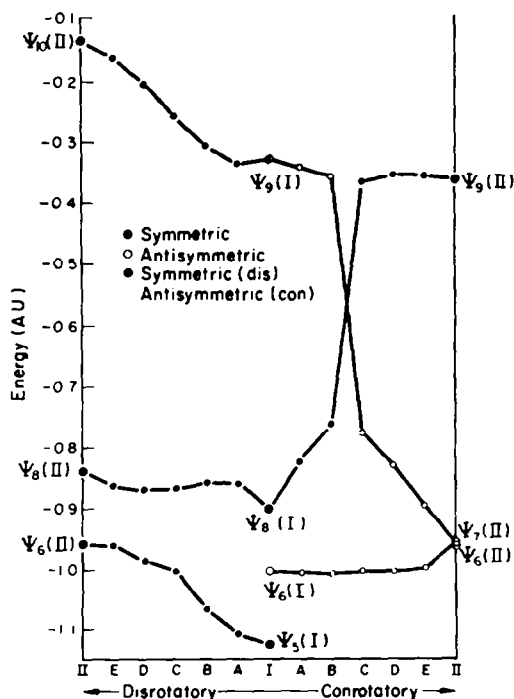
Graph 4. CNDO/2 M.O. changes during ring opening.

* The energy difference between I and II should be close to that between cyclopropyl cation and allyl cation, i.e., *ca* 9 kcal/mole. 1 a.u. $\simeq$ 220 kcal/mole according to Wiberg's scaling factor.[8]

Significantly, the corrected curve places the 2-azaallenyl cation, IV, lower in energy than II. Since the energy of II was minimized, an energy barrier must exist between II and IV. The magnitude of the second barrier, from II to IV, was not calculated.

The non-planar 2-azaallyl cations, V and VI, being much more energetic than planar II, are discarded from consideration. The planar and linear ion, VII, being more energetic than IV, is discarded, also. Energies in Fig. 2 are corrected as described above.
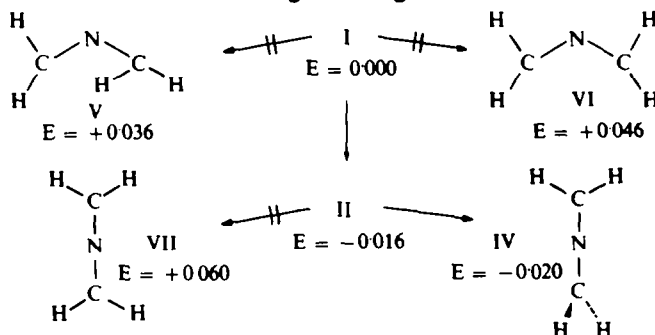

FIG 2. 2 Structures considered and their energies (a.u.).

*Correlation diagrams.** Assuming sp^5 for the two nitrogen orbitals bonding to carbons in I,† 2/3 s and 4/3 p remain to form the other two nitrogen orbitals. 2s electrons being more stable than 2p, the occupied orbital will be enriched in s character. In the following argument, p and sp^2 hybridizations are assumed for the unfilled and filled orbitals on nitrogen in I. The conclusions are independent of the initially chosen hybridization.

State correlations select among thermal 2, 3 and 4 electron ECTs.* Conrotatory 3 π-electron and disrotatory 3 and 4 π-electron ECTs require excited states of I and II to correlate. A conrotatory 4 π-electron ECT correlates an excited state of I with the ground state of II. Although a conrotatory 2 π-electron ECT correlates the ground state of I with an excited state of II, electron interaction allows a ground state to ground state reaction with a substantial energy barrier. Only a disrotatory 2π-electron ECT is predicted to proceed from the ground state of I to the ground state of II with a low energy barrier (Fig. 3).
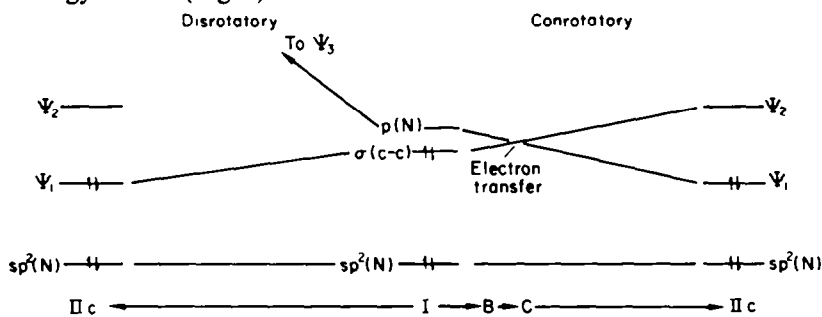

FIG. 3. Hückel M.O. correction diagram for ground state ECT.

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* State correlation diagrams of cyclopropyl-allyl cation, radical, and anion ECTs may be used for 2, 3, and 4 π-electron ECTs, respectively, of I → II.

† From ^{13}C-^{13}C coupling constants, Weigert and Roberts[13] calculate the hybridization of the internal bonds in cyclopropane to be sp^5.

The CNDO calculations show that these qualitative arguments are quantitatively correct. The disrotatory opening of I has a very low calculated energy of activation. The charge slowly decreases on nitrogen and increases on carbon as the ring opens. From the eigenvector matrices and eigenvalues of the CNDO/2 program, Ψ_8 (I) becomes Ψ_8 (II) although Fig. 3 predicts a correlation with Ψ_6 (II) (see Table 3 and Graph 4). An explanation is found upon examination of the symmetries and eigenvalues of the pertinent wave functions. Ψ_5 (I), Ψ_6 (II), and Ψ_8 (I → II) are symmetric with respect to a σ-plane perpendicular to and bisecting the ring. From Graph 4, Ψ_5 (B) becomes Ψ_6 (C). The eigenvalues for Ψ_6 (D → II) and Ψ_8 (D → II) dip toward one another but do not cross.* Thus, in the CNDO treatment which includes all eigenvectors, the lower of the two $\sigma(C-C)$-like MOs, Ψ_5 (I), correlates with the lowest energy π-M.O., Ψ_6 (II).

TABLE 3. MOLECULAR ORBITALS FROM CNDO/2 CALCULATIONS

CNDO/2 M.O.	Hückel M.O.[a, b]
Ψ_5 (I) $\simeq -0.2428s(N) -0.1156s(C) -0.1156s(C') -0.5917p_x(N) +0.204p_x(C)$ $+0.2041p_x(C') -0.3867p_y(C) +0.3867p_y(C')$	$\sigma(C-C)$
Ψ_6 (I) $\simeq 0.1172s(C) -0.1172s(C') -0.3647p_x(C) +0.3647p_x(C') -0.7229p_y(N)$ $+0.1480p_y(C) +0.1480p_y(C')$	$\sim \sigma(N-C)$
Ψ_8 (I) $\simeq 0.1273s(N) +0.3771p_x(N) -0.4387p_x(C) -0.4387p_x(C') -0.4615p_y(C)$ $+0.4615p_y(C')$	$\sigma(C-C)$
Ψ_9 (I) $\simeq 0.9097p_z(N)$	$p(N)$
Ψ_6 (II) $= 0.7355p_z(N) +0.4791p_z(C) +0.4791p_z(C')$	Ψ_1
Ψ_7 (II) $\simeq -0.2066p_x(C) +0.2066p_x(C') -0.3666p_y(N) +0.4593p_y(C) +0.4593p_y(C')$	σ^*
Ψ_8 (II) $\simeq 0.2975s(N) -0.1036s(C) -0.1036s(C') -0.7097p_x(N) +0.2972p_x(C)$ $+0.2972p_x(C')$	$\sigma(N-C)$
Ψ_9 (II) $= 0.7071p_z(C) -0.7071p_z(C')$	Ψ_2
Ψ_{10} (II) $= -0.6775p_z(N) +0.5201p_z(C) +0.5201p_z(C')$	Ψ_3

[a] Corresponding orbitals in Hückel treatment.
[b] See Fig 3.

The conrotatory opening of I has a high calculated energy of activation. Graphs 1, 2, 3 and 4 indicate that the predicted electron transfer between the highest occupied M.O. and lowest unoccupied M.O. occurs between B and C. The small energy change between B and C is necessary for electron transfer since the electronic states must be isoenergetic at the time of transfer.

The conrotatory eigenvector matrices again afford an insight into the changes which are occurring. Ψ_8 (B), the highest occupied M.O., becomes the lowest unoccupied M.O., Ψ_9 (C).† Ψ_9 (B) becomes Ψ_8 (C) and decreases in energy to Ψ_6 or Ψ_7 in II. The ambiguity arises because Ψ_6 (E) and Ψ_7 (E) which are mutually antisymmetric with

* CNDO does not include configuration interaction. If it did, Ψ_6(D) and Ψ_8(D) would probably mix strongly.

† It is interesting to note that correlation diagrams which use only orbitals of bonds being broken and formed predict that the highest occupied M.O. of I will correlate with both the non-bonding π-M.O. (conrotatory) and the lowest bonding π-M.O. (disrotatory) of II. Here, this is not true (*vide ante*).

respect to a C_2 axis which bisects the CNC angle converge to nearly isoenergetic M.O.'s in II. Fig. 3 predicts Ψ_9 (I) and Ψ_6 (II) should correlate.

The success of this treatment suggests that other ambiguous symmetry controlled reactions, *e.g.*, chelotropic and radical, may be clarified by CNDO synthesis of their reaction coordinates.

EXPERIMENTAL

Calculations were performed on an IBM 360/50 computer at the University of Connecticut Computing Center. The CNDO/2 program written by G. A. Segal was obtained from Quantum Chemistry Program Exchange, Bloomington, Indiana. It was modified by substituting Wiberg's[8] parameters (ionization potentials, core charges, Slater exponents, and β-proportionality constants) for those in the program. The matrix diagonalization subroutine in the program was unsatisfactory for very symmetric molecules. The problem was circumvented by adding 0·001 A° to one coordinate of one of the atoms, thereby destroying some of the symmetry. Bond indices[9] were calculated on a Friden 1151 Programmable Calculator from bond order matrices of the CNDO/2 program's print-outs.

Unless stated otherwise, assumed bond lengths and angles are those of Table 1. Geometries along the reaction coordinate of I → II are listed in Table 2. Bond lengths and angles from I → II were varied linearly and point values were calculated at $\Delta\theta = 10°$. The energy of II was minimized with respect to its CNC angle ($\pm 2°$) and its N—C bond length ($\pm 0·02$ A°). All structures were electronic singlets.

TABLE 1

Bond	Length (A°)	Angle	
C—H	1·10	C⋯N—C	120°
≡C—C≡	1·54	H—C—H	120°
≡C—C=	1·54		
≡C—N—	1·47	H—C—C	120°
≡C—N	1·37		
		H—C—H	109·5°
		C—C—N	109·5°
		H—C—H (C—C)	120°

TABLE 2

	L (A°)	θ	ϕ	C—H (A°)
I	1·470	58·4°	90°	1·10
A	1·454	70	75	1·10
B	1·436	80	60	1·10
C	1·420	90	45	1·10
D	1·403	100	30	1·10
E	1·386	110	15	1·10
II	1·370	120	0	1·10
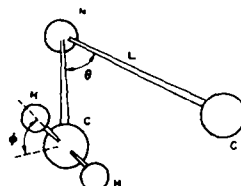
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