Organic Transition States. 6. Thermal Decomposition of 1-Pyrazolines

Philippe C. Hiberty* and Yves Jean*

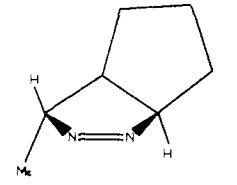
Contribution from the Laboratoire de Chimie Théorique[1] (490), Université de Paris-Sud, 91405 Orsay, France. *Received September 19, 1978*

Abstract: Ab initio SCF calculations have been carried out to study the thermal decomposition of 1-pyrazoline, with a 3 × 3 configuration interaction in minimal (STO-3G) and extended (4-31G) basis sets. Five main mechanisms have been studied. The two first ones (I and II) involve synchronous 2s + 2s cleavage of both C–N bonds, leading respectively to planar and to "face to face" trimethylene diradicals. Pathway IV is characterized by a "nonlinear" extrusion of nitrogen. Pathways III and V are two-step ones, involving nitrogen-containing diradicals, either in trans (III) or in gauche (V) conformation. We found that the nonsynchronous pathway III is the easiest one, with an activation energy of 39.3 kcal/mol, followed by pathway V (42.0 kcal/mol). The synchronous pathways I and II require higher activation energies (44.1 and 47.8 kcal/mol, respectively), while the "nonlinear" pathway IV is much more energetic. On the basis of these results the product distribution of the decomposition of cis and trans alkyl-substituted pyrazolines is discussed.

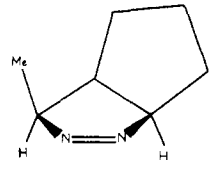
I. Introduction

The thermal decomposition of 1-pyrazolines leads to cyclopropane and olefins. In the case of the pyrazolines labeled at carbons 3 and 5 by alkyl groups, the major product is a cyclopropane with an apparent single inversion of stereochemistry.[2-4] The first mechanism invoked to account for this inversion of stereochemistry involves the simultaneous breaking of both carbon–nitrogen bonds, leading to a planar trimethylene diradical **1**.[2b-e] The extrusion of the nitrogen causes a disrotation of the ring bonds. The diradical can reclose easily by a conrotatory motion of both terminal groups[5] (Scheme I). This mechanism is consistent with the kinetic analysis of the decomposition of *cis*- and *trans*-3,5-dimethylpyrazolines.[2c] It is also supported by the nature of the olefins arising from the starting pyrazolines.[2c] In this scheme, the minor product would arise from the disrotatory closure of the diradical **1** and would lead either to double retention or double inversion of stereochemistry. Since the diradical **1** is planar, one expects to generate racemic products. However, the analysis of the optical purity of the *trans*-1,2-dimethylcyclopropane produced by the thermolysis of the *trans*-3,5-dimethylpyrazoline indicates an excess of double inversion.[2f] This observation is rationalized by assuming that 6% of the product arises from a "pyramidal" diradical.[6]

In order to test this first mechanism, Condit and Bergman studied the decomposition of bicyclic azo compounds **2a** and **2b**.[4a] In these molecules, a three-carbon bridge connects carbons 3 and 4 and should prevent the formation of a planar diradical. One might expect the simple extrusion of nitrogen, leading to the "face to face" diradical **3** by a disrotation of the ring bonds, to be now the easiest pathway for the decomposition (Scheme II). Since the diradical **3** can reclose without activation energy,[8] the major product should exhibit a double retention of configuration. This is not the case, and one still observes a predominant single inversion of configuration. This result led Condit and Bergman to propose a new mechanism, which is an extension of a mechanism suggested earlier by Roth and Martin.[9] In this mechanism, the slow step would be the breaking of only one carbon–nitrogen bond, leading to the diradical **4**. Then the breaking of the second bond in **4** leads to a cyclopropane with an inverted stereochemistry (Scheme III). Later, other experimental data have supported this two-step mechanism.[4b,c,10] It must be noted that, in the case of monocyclic pyrazolines, this mechanism would lead either to single inversion or to double inversion of stereochemistry, if a rotation occurs at the carbon radical center.

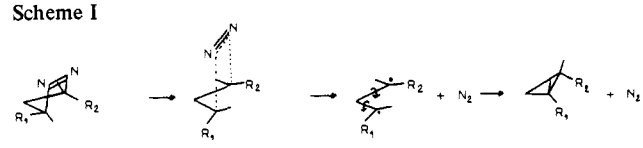


2-a



2-b

Scheme I

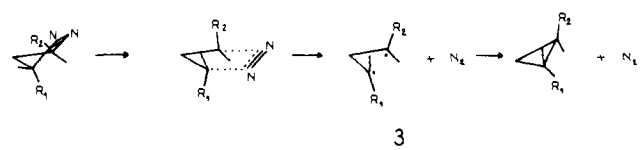


1

Finally, Clarke, Wendling, and Bergman analyzed the yield of each cyclopropane enantiomer formed from *cis*- and *trans*-3-ethyl-5-methyl-1-pyrazolines.[4e,f] The results of this study are summarized in Table I. The trans pyrazoline leads to *trans*-cyclopropane with an excess of double inversion, and to nearly racemic *cis*-cyclopropane (major product). On the contrary, the cis pyrazoline leads to *cis*-cyclopropane with an excess of double retention, and to *trans*-cyclopropane (major product) with a predominant "ethyl rotation". These startling results led the authors to conclude that the product distribution cannot be understood on the basis of only one of the previously mentioned mechanisms. In agreement with a suggestion of Fukui,[11] they propose a new mechanism, in which the initial coordinate "feels like" a $[{}_{\sigma}2_{s} + {}_{\sigma}2_{a}]$ pathway (Scheme IV). The extrusion of nitrogen causes a conrotation of the ring bonds. Then, arguments such as steric effects, mass effects, and least motion principle serve to account for the relative amounts of products.[4f]

In this article, we report the results of a theoretical study of this decomposition reaction. We performed ab initio Hartree–Fock calculations, using the GAUSSIAN 70 series of programs.[12,13] The geometries of the various conformations have been optimized with a minimal basis set (STO-3G[13a]), and the reaction paths recomputed with an extended basis set (4-31G).[13b] The reliability of this method has been discussed

Scheme II



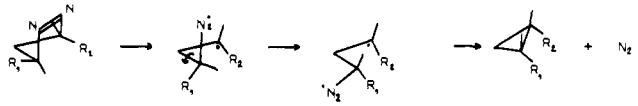
3

0002-7863/79/1501-2538$01.00/0

Table I. Products (%) of the Decomposition of *cis*- and *trans*-3-Ethyl-5-methylpyrazolines (from ref 4f)

starting pyrazoline	"methyl rotation"	"ethyl rotation"	double retention	double inversion
cis	28	38	22	10
trans	36	35	10	17

Scheme III



4

elsewhere (see, for instance, ref 14). Let us simply note that extended basis set calculations are necessary to get reliable relative activation energies for various reaction paths.

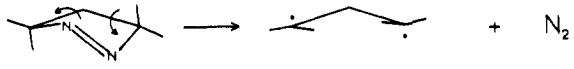
Configuration interaction (CI) is used to describe properly the diradical regions of the potential energy surfaces. It is at least necessary to perform a three-dimensional CI between the three electronic configurations (φ^2, $^1\varphi\varphi'$, and φ'^2) built from the two frontier orbitals φ and φ'.[15] We restrict ourselves to this limited CI for the following reasons: (1) In the diradical regions, the two frontier orbitals are neatly separated from the other orbitals. (2) In their study of the Diels–Alder reaction, Salem et al.[14b] also compared synchronous and two-step pathways. They have shown that the potential energy curves computed with a limited 3 × 3 CI are parallel to that computed with a larger (15 × 15) CI. (3) In a recent work Devaquet et al. studied the synchronous and the two-step decomposition of *cis*-diimide (at the STO-3G level). The energy difference between the two transition states is 78.08 kcal/mol after a 3 × 3 CI,[16a] and 79.95 kcal/mol after a 100 × 100 CI.[16b] Therefore, the large CI modifies the first value by only 1.87 kcal/mol. It is clear that these arguments do not demonstrate that a larger CI would not slightly modify some of our results. However, one can expect that the potential energy surface computed with the limited 3 × 3 CI reproduces the essential features of the true potential energy surface.

Finally, owing to their strong diradical character, some points of the surface are best described by a restricted open-shell[17] calculation, while a closed-shell calculation is more appropriate for other ones. For each point, including the pyrazoline, these two SCF calculations are performed, each being followed by a 3 × 3 configuration interaction, and we accept the lower energy after completion of the CI.

II. Reaction Paths Involving Simultaneous Breaking of Both C–N Bonds

A. $[_\sigma 2_s + {}_\sigma 2_s]$ Pathways. 1. Symmetry Properties. In our study of the simultaneous breaking of the carbon–nitrogen bonds in 1-pyrazoline, we considered the two limiting reaction paths described by Schemes I and II. Considering the symmetry of the highest occupied (HO) and the lowest unoccupied (LU) molecular orbitals (MO) in the diradicals **1** and **3**, one can predict the first reaction path (Scheme I) to be more favorable.[5] Indeed, in **1**, the HOMO is antisymmetrical with respect to the plane perpendicular to the carbon ring, and the LUMO is symmetrical.[5] A favorable interaction between the HOMO (LUMO) of **1** and the π^* (π) orbital of nitrogen in the reverse addition reaction is to be expected. The inverse situation is observed for the diradical **3**, in which the HOMO is symmetrical and the LUMO antisymmetrical. Thus, the formation

Scheme IV



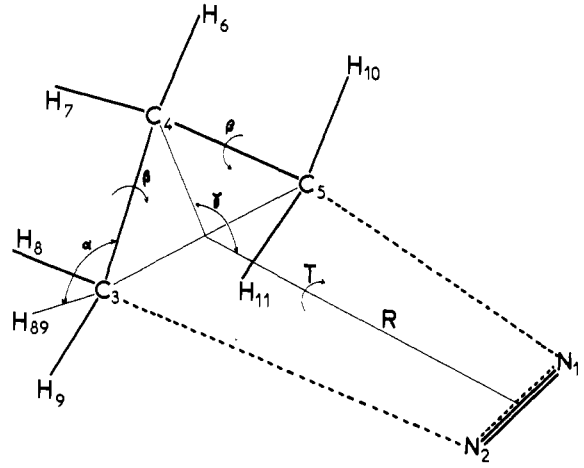


Figure 1. The coordinate system for the decomposition of 1-pyrazoline by simultaneous breaking of both C–N bonds.

of **1** is "allowed", while that of **3** is "forbidden" in a concerted 2s + 2s process. However, since the frontier orbitals in diradicals are nearly degenerate, the energetic difference (after 3 × 3 CI) between the allowed and forbidden reaction paths must be rather small.

2. Geometrical Model. In our calculations, the pyrazoline and nitrogen have been given standard parameters. The geometries of the various trimethylene diradicals have been previously optimized.[8] The pyrazoline has C_s symmetry (see the coordinate system in Figure 1), with C_3C_4 = 1.54 Å, N_1N_2 = 1.25 Å, C_3N_2 = 1.47 Å, all C–H = 1.09 Å, $\angle C_3C_4C_5$ = 105°, $\angle H_6C_4C_3 = \angle H_7C_4C_3$ = 110°, $\angle H_8C_3C_4 = \angle H_8C_3N_2 = \angle H_9C_3C_4 = \angle H_9C_3N_2$ = 110.5°, puckering angle γ = 155°.[18] The trimethylene diradicals have C_{2v} symmetry, with C_3C_4 = 1.523 Å, all C–H = 1.09 Å, $\angle C_3C_4C_5$ = 113.5°, $\angle H_6C_4H_7$ = 107.6°, $\angle H_8C_3H_9$ = 117.6°, the atoms C_4, C_3, H_8, and H_9 being coplanar. The segment H_8–H_9 is in the plane of the carbons for the planar conformation **1**, and perpendicular to this plane for the "face to face" conformation **3**. The N_1–N_2 bond length is 1.10 Å in the nitrogen molecule.

In a first step, we considered a simplified mechanism, intermediate between Schemes I and II, a simple extrusion of N=N leading to a pyramidal trimethylene diradical. In this process, the puckering angle is kept constant along the reaction and the terminal methylene groups do not rotate to form either diradical **1** or **3**. The reaction coordinate is R, the distance between the C_3C_5 axis and the N_1–N_2 axis. The N_1–N_2 bond length was optimized at each calculated point. Then we studied in detail pathways I and II (Schemes I and II), using the N_1–N_2 values optimized during the first approach. For both pathways, the energy curve was first calculated roughly by varying each parameter smoothly along with the reaction coordinate R. Then the main parameters of the transition state were optimized, and the definitive curve was obtained by correcting the parameters of the remaining points to interpolated values between reactant and transition state and between transition state and products. These main parameters are N–N, ∠CCC, α and β for both pathways, plus γ for pathway I[19] (see Table II).

3. Results. Our minimal basis set calculations predict pathway I to be the easiest one, in agreement with our analysis in section 1. The activation energy is calculated to be 73.1 kcal/mol. The corresponding transition state is reached with C–N = 2.15 Å. The less favorable pathway II requires a larger activation energy, 76.0 kcal/mol. The transition state is reached with C–N = 2.20 Å and a relatively large $\angle C_3C_4C_5$ angle (118.3°). This large increase of the $\angle C_3C_4C_5$ angle can be easily understood: it tends to produce a crossing between

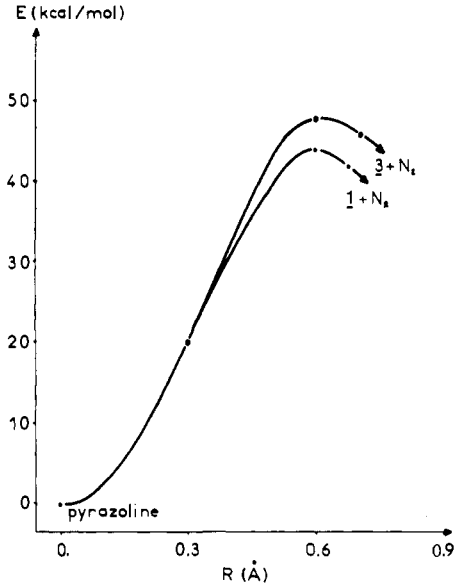


Figure 2. Energy profiles of pathways I (leading to **1** + N_2) and II (leading to **3** + N_2) calculated in 4-31G basis set followed by 3 × 3 CI.

Table II. Parameters of the Transition States Corresponding to Pathways I and II

parameters	pathway I	pathway II
C_3C_4	1.531 Å	1.531 Å
C_3N_2	2.151 Å	2.200 Å
N_1-N_2	1.151 Å[a]	1.143 Å[a]
all C-H	1.09 Å	1.09 Å
$\angle C_3C_4C_5$	113.1° [a]	118.3° [a]
$\angle H_6C_4C_3$	109.5°	109.5°
$\angle H_7C_4C_3$	109.5°	109.5°
$\angle H_8C_3C_4$	116.0°	115.1°
$\angle H_9C_3C_4$	116.0°	115.1°
α[b]	145.1° [a]	142.7° [a]
β[c]	129.6° [a]	159.7° [a]
γ	130.6° [a]	167.5°

[a] Optimized parameters at the transition state, in STO-3G basis set with 3 × 3 CI. [b] If H_{89} is the middle of the H_8-H_9 segment, α is the $\angle H_{89}$-C_3-C_4 angle. [c] β is the dihedral angle between the H_{89}-C_3-C_4 plane and the $C_3C_4C_5$ plane; positive values indicate that H_{89} and H_6 are on both sides of the $C_3C_4C_5$ plane. β = 180° when H_{89}, C_3, C_4, C_5 are coplanar with H_{89} and C_5 on both sides of the C_3-C_4 axis.

the frontier orbitals of the "face to face" structure (**3**), and consequently to make the reaction less forbidden. The detailed geometries of both transition states are displayed in Table II. Of course, owing to the minimal character of the basis set, the calculated energies widely overestimate the experimental activation energy (42.4 kcal/mol[2a]). In order to get more reliable values, we recalculated both energy curves in 4-31G basis set, with a 3 × 3 CI (Figure 2). The transition states are slightly displaced with respect to the minimal basis set calculations (C-N = 2.06 Å for pathway I and 2.07 Å for pathway II), and the activation energies are respectively 44.1 and 47.8 kcal/mol.

B. $[\sigma 2_s + \sigma 2_a]$ Pathway. In this mechanism (Scheme IV), the molecule is distorted with a pseudoconrotation of the ring bonds, while both CN bonds are stretched simultaneously.[20]

1. Geometrical Model. For the sake of simplification, the initial 1-pyrazoline is planar ($\gamma = \beta = 180°$) and all parameters are standard (see section IIA2). All along the reaction process, a C_2 axis is kept, going through C_4 and the middle of the N_1-N_2 bond. The reaction coordinates are R, the distance between the C_3-C_5 axis and the N_1-N_2 axis, T, twisting of the

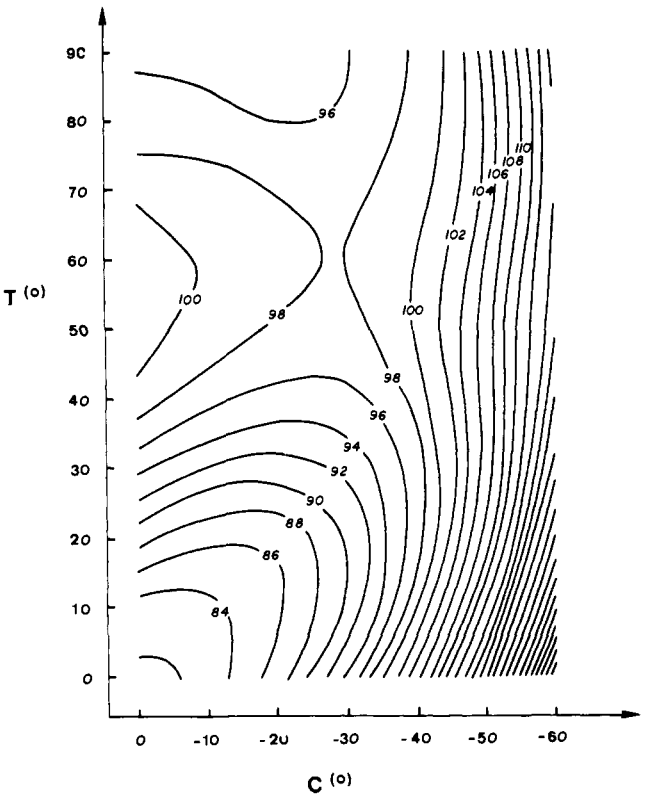


Figure 3. Potential energy surface for the 2s + 2a extrusion, corresponding to ΔR = 0.6 Å. STO-3G energies are in kcal/mol. $T = C = 0°$ in the planar 1-pyrazoline.

N_1-N_2 segment around the C_2 axis, and C, conrotation of both methylene groups around the C_3C_4 and C_4C_5 segments, respectively (Figure 1). The value of the N_1-N_2 bond length is optimized at some points of the potential surface and interpolated at the remaining points. All other parameters, such as the pyramidalization of the methylene groups, the ∠CCC angle, and the CC bond lengths, are constant throughout the potential surface.

2. Results. The three-dimensional $E(R,T,C)$ potential surface is composed of a set of three two-dimensional potential surfaces, corresponding respectively to ΔR = 0.2, 0.4, and 0.6 Å, and calculated in STO-3G basis set with 3 × 3 CI. This corresponding to ΔR = 0.6 Å is displayed in Figure 3. The two other ones exhibit a similar aspect. These surfaces clearly show that, for each value of R, the minimum energy point corresponds to the initial values of C and T, namely, 0°. A secondary minimum exists, for T = 90°, but its energy, calculated in the 4-31G basis set, is 10.8 kcal/mol above that of the primary one. Thus, the nonlinear $[\sigma 2_s + \sigma 2_a]$ extrusion of N_2 coupled with the conrotation of the methylene groups is an unfavorable process, which evolves to pathway II when C and T are optimized. One can explain this in the following way: in the "face to face" diradical **3** the symmetrical HOMO is very close to the antisymmetrical LUMO. Hence, all other things being equal, $[\sigma 2_s + \sigma 2_a]$ and $[\sigma 2_s + \sigma 2_s]$ processes are expected to be grossly isoenergetic. The $[\sigma 2_s + \sigma 2_a]$ nonlinear extrusion, being much more strained than the $[\sigma 2_s + \sigma 2_s]$ pathway II, is therefore strongly unfavorable.

III. Two-Step Reaction Path Involving a Nitrogen-Containing Diradical

A. (θ, ϕ) Potential Surface. Let us consider the cleavage of the C_3-N_2 bond (Figure 4). Two main geometrical parameters are used to describe this rupture: θ, rotational angle of N_1-N_2 around the C_5-N_1 bond, and φ, dihedral angle between the

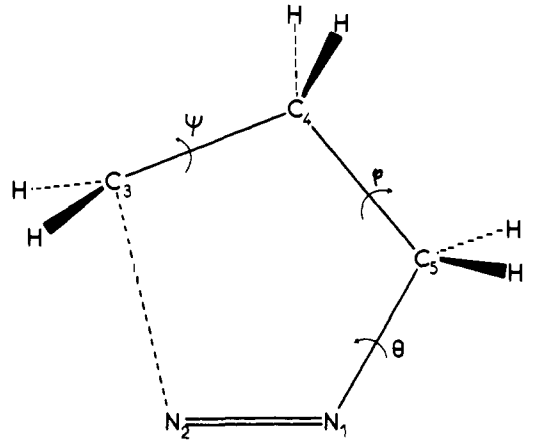


Figure 4. The coordinate system for the breaking of a single C-N bond in 1-pyrazoline.

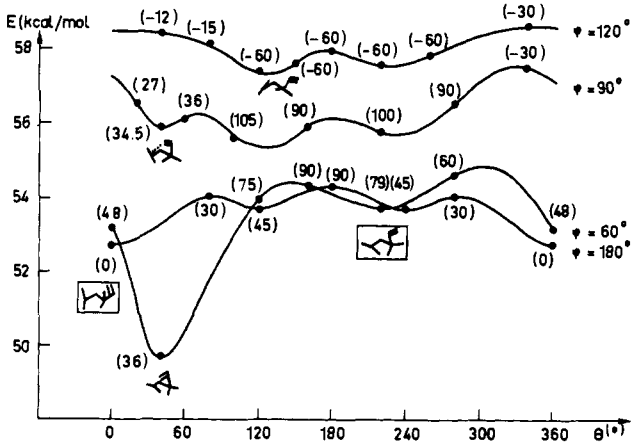
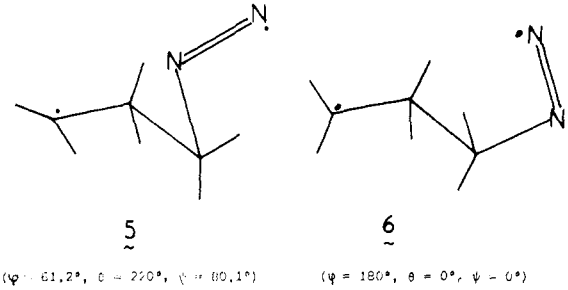


Figure 5. Conformational energy of the nitrogen-containing diradical as a function of the rotational angles θ and φ. The energies are calculated at the STO-3G level (plus 3 × 3 CI). The zero of energy corresponds to the starting pyrazoline. Optimized values of ψ are indicated in parentheses. The gauche and trans secondary minima are bordered.

$C_3C_4C_5$ and the $C_4C_5N_1$ planes. Note that the diradical **4**, involved in Scheme III, corresponds to $\varphi = 180°$ and to an undefined value of θ. We calculated the two-dimensional (θ, φ) potential surface, optimizing at each point the angle ψ, rotational angle of the methylene group C_3HH around the C_3-C_4 bond. We optimized also the angle $\angle C_5N_1N_2$ for some points of the surface and chose intermediate values for the other points; the result is that this angle goes from 108° in the starting pyrazoline to 120° in the diradical structures. Lastly, all the diradical structures have in common the values 1.507 and 1.218 Å for the parameters C_5N_1 and N_1-N_2, respectively, optimized for a particular point. We have verified that these values are roughly independent of the diradical conformation. Standard values have been assumed for the other parameters $\angle C_3C_4C_5 = 109.5°$, C_3-C_4 = 1.54 Å, and tetrahedral bond angles for tetracoordinated carbons. Unless otherwise specified, the radical center C_3 is trigonal.

The (θ, ϕ) potential energy surface is displayed in Figure 5. For each point, the optimum value of ψ is indicated in parentheses. Each curve exhibits several minima. Among these, only two are absolute secondary minima on the (θ, ϕ) surface: the first one is a gauche diradical (**5**) corresponding to $\phi = 61.2°$ and $\theta = 220°$; its optimized values of ψ and of the pyramidalization[21] at C_3 are 80.1 and 24°, respectively. The second one is a trans diradical (**6**) with the values $\phi = 180°$, $\theta = 0°$,[22] and $\psi = 0$. In this conformation, the bonds N_1-N_2 and C_4-C_5 are eclipsed. This result, in contradiction with simple steric arguments, can be rationalized by the analysis of the interactions between the π and π^* orbitals of the unsaturated linkage N=N and the π_{CH_2} and $\pi^*_{CH_2}$ orbitals of the neighboring CH_2 group. Hyperconjugation favors the eclipsed structure, as has been shown by Hehre and Salem in the case of vinylic methyl groups.[23]



5 (φ = 61.2°, θ = 220°, ψ = 80.1°)

6 (ψ = 180°, θ = 0°, ψ = 0°)

In summary, *two* structures of the nitrogen-containing diradical, respectively gauche ($\phi = 61.2°$) and trans ($\phi = 180°$), are likely to play a role in the thermal decomposition of pyrazolines. Their energies are 52.6 (trans **6**) and 53.8 kcal/mol (gauche **5**) above that of pyrazoline. The barrier between them is 3.4 kcal/mol. The barriers for the reclosures of diradicals **5** and **6** are 0.7 and 4.5 kcal/mol, respectively. This is in strong analogy with the results of the theoretical study, by Segal,[24] of the thermal decomposition of cyclobutane, which also involves two structures of the tetramethylene diradical, separated by an energy barrier of 3.55 kcal/mol.

B. Reaction Path III, Going through the Trans Diradical. 1. Geometrical Model. For the first step, the breaking of the C_3-N_2 bond, the reaction coordinate is φ, the value of θ being chosen so as to minimize the energy along the reaction path from the starting pyrazoline to the diradical **6.** The second step consists in breaking the C_5-N_1 bond in **6.** In order to get a correct description of the products (nitrogen + cyclopropane), the lengthening of this bond is accompanied, in our calculations, by the optimization of (1) the $\angle C_3C_4C_5$ angle, (2) the pyramidalization of the terminal CH_2 groups, (3) the N_1-N_2 bond length, and (4) the θ angle.[25]

2. Results. At the STO-3G level, the energy required to perform the first step is 57.1 kcal/mol. The maximum of the energy curve occurs approximately at $\theta = 117°$ and $\varphi = 120°$. The optimized parameters of this transition state are C_5N_1 = 1.507 Å, $\angle C_5C_4C_3 = 111.3°$, N_1N_2 = 1.213 Å, and $\psi = -60°$. The second step requires a supplementary activation energy of 13.0 kcal/mol. The transition state calculated at the STO-3G level looks like structure **6,** but with a stretched C_5-N_1 bond (1.93 Å). Its energy lies 70.1 kcal/mol above that of pyrazoline.

The extended basis set calculation with 3 × 3 CI does not qualitatively modify the energy profile for the first step (see Figure 6). The maximum is still calculated for $\varphi = 120°$ and $\theta = 117°$. However, the energy of this point is considerably lowered: it lies now 39.3 kcal/mol above that of pyrazoline. On the contrary, a drastic change occurs in the second step, which now can be performed without any supplementary activation energy (Figure 6). At the 4-31G level, the transition state for this mechanism is therefore a structure in which only one carbon-nitrogen bond is broken (a "pure" diradical). Furthermore, the energy of this transition state (39.3 kcal/mol) is lower than that calculated for the synchronous mechanism (44.1 kcal/mol).[26]

3. Analysis of the Product Distribution. In the case of bicyclic pyrazolines (**2a** and **2b**), the rotation at the radical center C_3 is prevented by the carbon bridge connecting carbons 3 and 4. Therefore, this mechanism can only lead to single inversion of stereochemistry.

The situation is a little more complex in monocyclic pyra-

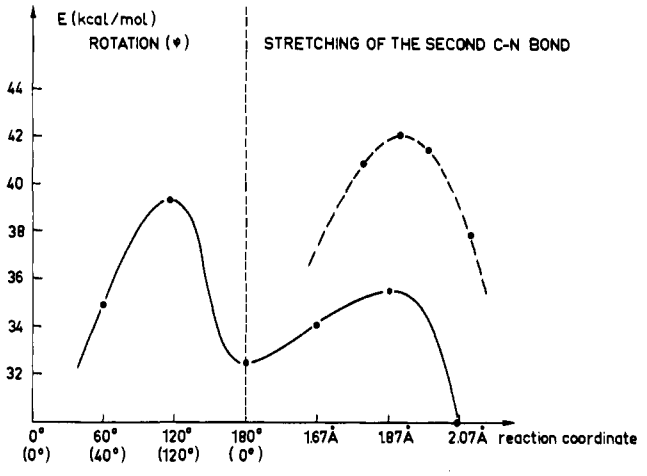


Figure 6. Energy profile for both steps of pathway III (full lines) and for the second step of pathway V (dotted lines), calculated in 4-31G basis set followed by 3 × 3 CI. The reaction coordinate is φ for the first step (values of θ are indicated in parentheses) and the C-N bond length for the second step. The stretching of the C-N bond occurs when $\varphi = 180°$ for pathway III and $\varphi = 60°$ for pathway V.

zolines; indeed, rotation at C_3 could occur at some points of the reaction path, leading to double inversion of stereochemistry. The STO-3G potential surface seems to indicate that such a rotation occurs, since, at the minimum for $\phi = 90°$, the methylene group at carbon C_3 is approximately in the plane of the carbon ring ($\psi \sim 90°$). One can note, however, that the rotational barriers for ψ are very small (~0.5 kcal/mol). Since this point is crucial for the analysis of the stereochemical course of this mechanism, we recomputed the curve $\phi = 90°$ at the 4-31G level. The minimum is found for $\theta = 60°$ (instead of 120° at the STO-3G level). It is noteworthy that this value of θ makes the C_3N_2 distance as short as possible.[27] The optimum value of ψ is now only 20°, instead of 90° in STO-3G calculations. These results strongly suggest that the reaction path between the pyrazoline and the trans diradical **6** is such that a residual bond between C_3 and N_2 is kept as long as possible and that the transition state is reached *without inversion at* C_3. The best value for ψ in the transition state is −30° (instead of −60° at the STO-3G level). Therefore ψ is expected to vary straightforwardly from +20° to −30° when ϕ goes from 90° to 120° (ψ being equal to 0° when $\varphi = 180°$, both in STO-3G and 4-31G calculations).

In summary, this mechanism leads to single inversion of stereochemistry as the major product, and to double inversion of configuration as the minor product. The minor product is formed if a rotation occurs at the carbon C_3. At the 4-31G level, the energy barrier for this rotation is 1 kcal/mol in the transition state, and 5.4 kcal/mol in the trans diradical **6.** No double retention of configuration is expected from this mechanism.

C. Reaction Path V, Going through the Gauche Diradical. Two reaction paths starting from the gauche diradical can be envisaged: in the first one, the rotation of φ is the main reaction coordinate. Then the trans diradical **6** is formed, after passing through an energy barrier of 3.4 kcal/mol. In other words, this reaction path would evolve to reaction path III. In the second one (pathway V) the main reaction coordinate is the extrusion of N_2, the φ angle being roughly constant.

1. Geometrical Model. In this section we studied in detail the second step of this pathway. The reaction coordinate is obviously the C_5–N_1 bond length, and for each calculated point we optimized the parameters ∠NNC, ψ, and φ. The angle θ was also considered, and the values of the N_1N_2 bond lengths were evaluated as a function of C_5N_1, according to the N_1N_2 optimization results of the pathway going through the trans diradical.

2. Results. As C_5N_1 increases, the barrier to rotation of θ is weaker and weaker, so that, before the transition state is reached, θ may easily collapse to the value 30°, in order to stabilize the molecule by a residual bond between C_3 and N_2. The angle φ remains constant, along the reaction path, while the angle ψ decreases to about 60° near the transition state. The ∠NNC angle decreases too, as expected. The transition state corresponds to a C_5–N_1 value of 1.98 Å, at the STO-3G level. Its optimized parameters are $\angle N_2N_1C_5 = 111.9°$, $\psi = 59.7°$, $\varphi = 62.7°$, $\angle C_3C_4C_5 = 111.6°$, $\theta = 30.9°$, pyramidalization at $C_3 = 32.0°$, pyramidalization at $C_5 = 39.5°$, and $N_1N_2 = 1.153$ Å. Its energy, at the STO-3G level, is 72.5 kcal/mol above that of pyrazoline. We recalculated the energy curve in the 4-31G basis set, and found the transition state slightly displaced with a C_5–N_1 value of 1.90 Å (Figure 6), its energy being 42.0 kcal/mol above that of pyrazoline. This transition state is that of the overall pathway V since the gauche diradical collapses to the starting pyrazoline with a very weak barrier. Thus, contrary to what is observed for pathway III, the transition state is located in the second step of the mechanism, i.e., during the breaking of the second C–N bond. This, again, is in analogy with the results obtained by Segal in his study of the thermal decomposition of the cyclobutane.[24]

3. Analysis of the Product Distribution. After passing through the transition state, a "pyramidal" trimethylene diradical is formed, in which the rotational angles (φ, ψ) of the terminal methylene groups are approximately 60°. This diradical can evolve to the planar diradical **1,** and reclose in a conrotatory manner, thus leading predominantly to single inversion of stereochemistry (see section IIA4). Another possibility is a disrotatory reclosure; in that case one can predict *more double retention than double inversion,* owing to the values of nearly 60° of φ and ψ in the transition state.

IV. Discussion

A. Unsubstituted Pyrazoline. At the 4-31G level, the calculated activation energies for the pathways I, II, III, and V are 44.1, 47.8, 39.3, and 42.0 kcal/mol, respectively. The nonlinear extrusion (pathway IV) has an activation energy higher than that of pathway II. The lowest pathway is the two-step pathway going through the trans diradical. It leads to single inversion as the major product and to double inversion as the minor product. Another low-energy pathway is again a two-step one, going through the gauche diradical. It leads to single inversion and to an excess of double retention over double inversion. The two pathways in which both C–N bonds are broken simultaneously (I and II) appear to be less favorable.

It must be noted that, if the trans diradical **6** is a deep minimum on the potential energy surface, the same does not hold true for the gauche diradical **5** since its barrier to reclosure to the pyrazoline is very small. However, our mechanistic scheme does not depend on the existence of a true minimum with a gauche conformation. Indeed, the lengthening of the C_5N_1 bond in the gauche diradical is accompanied by a rotation of N_2N_1 in a way to restore a residual bond between C_3 and N_2. It is clear that the transition state thus reached could be attained directly without breaking the residual bond, thus avoiding the gauche secondary minimum. What is crucial in our mechanistic scheme is the value of φ for which the second C–N bond is broken, since it governs the retention or the inversion at carbon C_5.

B. Substituent Effects. Prior to any calculation, one can try to evaluate qualitatively the influence of alkyl substituents, in cis or trans position, on the relative energies of the transition states of pathways III and V. Let us first consider the most

Table III. Evaluated Activation Energies (kcal/mol) for the Decomposition of Substituted Pyrazolines via Pathways I, III, and V

	cis-dimethylpyrazoline	*trans*-dimethylpyrazoline
pathway I	42.3	43.1
pathway III	39.5	39.3
pathway V	40.6	42.1

favorable pathway III. Starting from a trans (cis) pyrazoline, one reaches a trans diradical **6** in which the two alkyl groups are cis (trans) relative to the CCC plane. Owing to steric hindrance, the amount of minor product (double inversion) arising from this pathway should be more important for a trans than for a cis pyrazoline. This is in agreement with the experimental data displayed in Table I. In the transition state of pathway V, the substituents are in sterically favorable pseudoequatorial position when one starts from a cis pyrazoline, whereas one of the substituents is in pseudoaxial position in the case of trans pyrazoline. Thus one can expect this reaction path to be more favorable for a cis pyrazoline than for a trans. Consequently, the amount of double retention should be larger in the case of cis pyrazoline. This, again, is in agreement with the experimental data (Table I).

It remains to explain the relative amounts of ethyl and methyl rotations in the major product arising from *cis*- or *trans*-3-ethyl-5-methylpyrazoline (Table I). A possible explanation could be based upon the interaction between the azo group and an alkyl substituent during the first step of both pathways III and V. For the cis pyrazoline, the outward rotation is the easiest one, since it prevents any steric repulsion between the substituents. In this motion the nitrogen atom N_2 encounters the substituent borne by C_3, and the reaction should be easier if this substituent is a methyl rather than an ethyl. So the ethyl rotation at carbon C_5 is expected to be the easiest one. For the trans pyrazoline, both methyl end ethyl rotation can be achieved so that the N_2 atom avoids any interaction with the alkyl group beared by carbon C_3. So ethyl and methyl rotation are expected to be equally favorable.

We tried to verify some points of this qualitative analysis by evaluating the energies of the various transition states substituted by two methyl groups. Using the geometries optimized in the unsubstituted cases, we calculated the energies of the substituted transition states at the STO-3G level. Then we deduced the alterations of the activation energies due to the methyl groups at the STO-3G level. Assuming that these alterations are not too dependent on the basis set, we estimated the 4-31G energies of the transition states. The corresponding activation energies are displayed in Table III. As expected, reaction path V is more favorable for the cis pyrazoline than for the trans one. Therefore, both trans and cis pyrazolines are likely to decompose mainly by pathway III, the contribution of pathway V being larger in the case of cis pyrazoline.

C. Summary. Our calculations indicate that the two most favorable pathways for the thermal decomposition of 1-pyrazolines involve nonsynchronous cleavage of the two C–N bonds. In the first one (pathway III), the transition state is a nitrogen-containing diradical. In the second one, the transition state looks like a pyramidal trimethylene diradical still interacting with nitrogen, the two C–N bonds being unequal. The reaction paths involving simultaneous breaking of both C–N bonds require higher activation energies. It is clear that the reliability of the computed activation energies suffers from the nature of the limited configuration interaction and from the only partial optimization of each structure. Also, the relative energies of various structures of the nitrogen-containing diradical are found to depend on the choice of basis set. With these restrictions in mind, it appears that our calculations suggest a rather simple reactive scheme which accounts for most of the experimental observations described in the Introduction. It is our hope that this result will stimulate further experimental investigations.

Acknowledgments. The authors thank Professor L. Salem for stimulating discussions and for critical readings of the manuscript.

References and Notes

(1) The Laboratoire de Chimie Théorique is associated with the CNRS (ERA no. 549).
(2) (a) R. J. Crawford, R. J. Dummel, and A. Mishra, *J. Am. Chem. Soc.*, **87**, 3023 (1965); (b) R. J. Crawford and A. Mishra, *ibid.*, **87**, 3768 (1965); (c) *ibid.*, **88**, 3963 (1966); (d) R. J. Crawford and G. L. Erickson, *ibid.*, **89**, 3907 (1967); (e) R. J. Crawford and L. H. Ali, *ibid.*, **89**, 3908 (1967); (f) A. Mishra and R. J. Crawford, *Can. J. Chem.*, **47**, 1515 (1969); (g) M. P. Schneider and R. J. Crawford, *ibid.*, **48**, 628 (1970); (h) R. J. Crawford and M. Ohno, *ibid.*, **52**, 3134 (1974); (i) R. J. Crawford and H. Tokunaga, *ibid.*, **52**, 4033 (1974).
(3) D. E. McGreer, N. W. K. Chiu, M. G. Vinje, and K. C. K. Wong, *Can. J. Chem.*, **43**, 1407 (1965).
(4) (a) P. B. Condit and R. G. Bergman, *Chem. Commun.*, 4 (1971); (b) D. H. White, P. B. Condit, and R. G. Bergman, *J. Am. Chem. Soc.*, **94**, 7931 (1972); (c) R. A. Keppel and R. G. Bergman, *ibid.*, **94**, 1350 (1972); (d) R. G. Bergman in "Free Radicals", Vol. 1, J. Kochi, Ed., Wiley, New York, 1973, Chapter 5; (e) T. C. Clarke, L. A. Wendling, and R. G. Bergman, *J. Am. Chem. Soc.*, **97**, 5638 (1975); (f) *ibid.*, **99**, 2740 (1977).
(5) R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 1475 (1968).
(6) Such a pyramidal diradical was already suggested by Allred and Smith to explain the double inversion observed during the decomposition of bicyclic azo compounds.[7]
(7) A. L. Allred and R. L. Smith, *J. Am. Chem. Soc.*, **89**, 7133 (1967).
(8) (a) Y. Jean, L. Salem, J. S. Wright, J. A. Horsley, C. Moser, and R. M. Stevens, *Pure Appl. Chem. Suppl.*, **1**, 197 (1971); (b) Y. Jean, Thèse d'Etat, Orsay, 1973.
(9) (a) W. R. Roth and M. Martin, *Tetrahedron Lett.*, 4695 (1967); (b) *Justus Liebigs Ann. Chem.*, **1**, 702 (1967).
(10) T. Sasaki, S. Eguchi, and F. Hibi, *J. Chem. Soc., Chem. Commun.*, 227 (1974).
(11) S. Iganaki and K. Fukui, *Bull. Chem. Soc. Jpn.*, **45**, 824 (1972).
(12) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, QCPE No. 236, Indiana University, Bloomington, Ind.
(13) (a) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1970); (b) R. Ditchfield, W. J. Hehre, and J. A. Pople, *ibid.*, **54**, 724 (1971).
(14) (a) G. A. Segal, *J. Am. Chem. Soc.*, **96**, 7892 (1974); (b) R. E. Townshend, G. Ramunni, G. A. Segal, W. J. Hehre, and L. Salem, *ibid.*, **98**, 2190 (1976).
(15) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).
(16) (a) B. Bigot, private communication; (b) B. Bigot, A. Sevin, and A. Devaquet, *J. Am. Chem. Soc.*, **100**, 2639 (1978).
(17) R. K. Nesbet, *Rev. Mod. Phys.*, **35**, 552 (1963).
(18) The puckering angle is the dihedral angle between the C_3–C_4–C_5 plane and the C_3–N_1–N_2–C_5 plane.
(19) Optimization of γ in pathway II would lead to values corresponding to the lower pathway I.
(20) The rotational angles of the terminal groups in the case of substituted pyrazolines depend on the size of the substituents in the mechanism outlined in ref 4f.
(21) The pyramidalization angle is defined as the complement of the angle between the CC bond and the bisector of the ∠HCH angle ($180° - \alpha$ in Figure 1).
(22) There is a second minimum on the curve $\phi = 180°$, corresponding to $\theta = 120°$ (or 240°). However, the barrier between this minimum and the more stable secondary minimum found for $\theta = 0$ is less than 0.3 kcal/mol.
(23) W. J. Hehre and L. Salem, *J. Chem. Soc., Chem. Commun.*, 754 (1973).
(24) G. A. Segal, *J. Am. Chem. Soc.*, **96**, 7892 (1974).
(25) The optimum value of θ is always 0° along this path.
(26) In an earlier report of preliminary calculations (P. C. Hiberty and Y. Jean, *Bull. Soc. Chim. Belg.*, **85**, 1005 (1976)), we indicated that pathways I and III were nearly isoenergetic. We had assumed the N=N bond length to be constant (1.25 Å) during the first step of pathway III. Surprisingly, a further optimization of this bond length in the diradical structures gave a significantly smaller value (~1.215 Å). The resulting stabilization energy at the STO-3G level is rather small (~1.7 kcal/mol). At the 4-31G level, this stabilization increases to 5.1 kcal/mol.
(27) This tendency of 4-31G calculations to decrease the optimum value of θ could well be observed for $\phi = 120°$. Therefore, the true transition state, at the 4-31G level, could have a θ value smaller than that found on STO-3G calculations ($\theta = 117°$).