

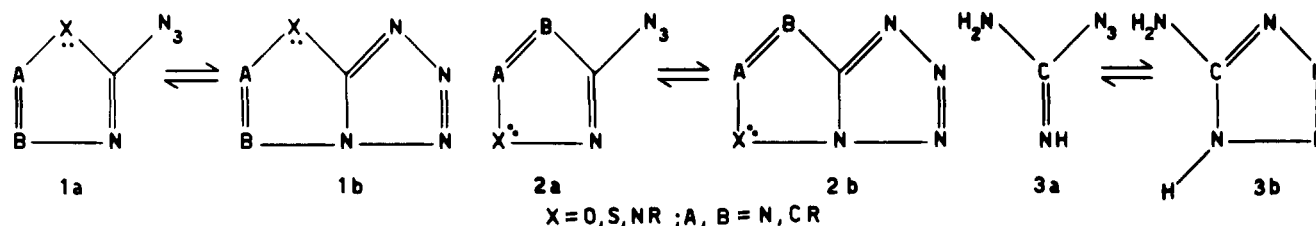
Theoretical Study of the Azido-Tetrazole Isomerization

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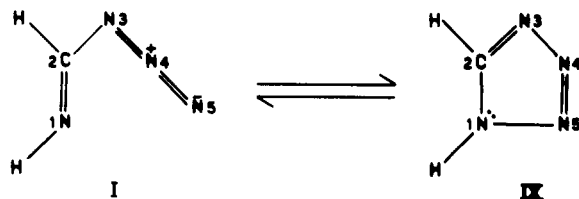
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Abstract: The potential energy hypersurface for the isomerization of azidoazomethine to 1*H*-tetrazole has been studied by ab initio calculations using an STO-3G basis set. The reaction path for this cyclization is such that the heavy atoms remain in the same plane. The formation of the activated complex results from a movement of the lone pair on the NH group toward the terminal nitrogen atom. At the same time, a lone pair is formed on the central nitrogen atom of the azide group at the expense of the π NN bond and the π system is scarcely altered. The transition state was therefore seen to resemble strongly the reactant azide rather than the tetrazole. A keynote in this process is the role of the lone pair on the NH group which permits the formation of the new σ bond. It can be predicted that polar solvents will preferentially stabilize the transition state which is more polarized with respect to the azide form. Thus, the cyclization should be accelerated in polar solvents. Our theoretical results are in reasonable agreement with available experimental ones.

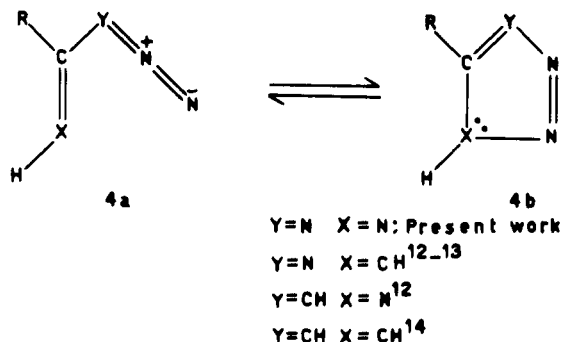
In addition to their interesting aromatic properties,² the aza analogues of pentalene dianion exhibit a ring-chain isomerization between the azide form **a** and the tetrazole form **b**.³ The CNDO/2 and CNDO/S methods, which gave



rather satisfying results for azapentalene aromatics,⁴ proved inadequate when applied to the study of the azido-tetrazole isomerization of the products **1** and **2**.⁵ It was therefore decided to study the problem with a nonempirical method and, in order to simplify the process, the molecules azidoazomethine and 1*H*-tetrazole were chosen.



This isomerization^{6,7} has been described as an electrocyclic reaction⁸ and as a 1,5-dipolar cycloaddition.⁹ However, it can also be thought of in terms of an attack by an azide molecule on azomethine in a 1,3 dipolar cycloaddition, a reaction which is presently being studied by the authors^{1a} in an experimental as well as theoretical point of view. The azidoazomethine-tetrazole isomerization is also of interest in that it is a member of an important family of ring-chain isomers (as given below), the study of which will be given in a future article.



Method

The calculations have been carried out by the LCAO-SCF-MO method where the expansion coefficients are de-

termined by solving Roothaan's equations.¹⁵ The potential hypersurface of the cyclization was constructed using the minimal basis set STO-3G¹⁶ in all calculations. This basis has been proven rather reliable in predicting molecular geometries for a large number of neutral, cyclic, and acyclic molecules.¹⁷ The STO-3G-optimized geometries for the azide, the tetrazole, and the transition state were then used to recalculate the energetics of the azido-tetrazole equilibrium using a medium sized contracted Gaussian basis set (7s-3p).¹⁸

In order to follow the electronic reorganization that takes place during the reaction, centroids of charge for localized molecular orbitals were computed using the Boys method.¹⁹

Calculations

The distance between the terminal nitrogens of the azide structure was chosen as the reaction coordinate for constructing the reaction path. The reason for this particular variable being chosen to represent the reaction coordinate will be given below. All bond lengths between heavy atoms as well as all bond angles were varied to minimize the energy for each value of the independent variable N_1-N_5 . The CH and NH bond lengths were held constant throughout the reaction as 1.07 and 1.00 Å, respectively. Two more geometric parameters were used in order to test the planarity of the cyclization, namely, a rotation about bond C_2-N_1 by which the NH bond is lifted out of the plane of the molecule, and a rotation about bond C_2-N_3 where by bonds N_3-N_4 and N_4-N_5 are lifted out of the plane formed by $N_1-C_2-N_3$. The geometric parameters used in the minimization procedure are defined in Figure 1.

Results

The optimized geometries and bond overlap populations (P_{AB}) for azidoazomethine (**I**) and 1*H*-tetrazole (**IX**) are

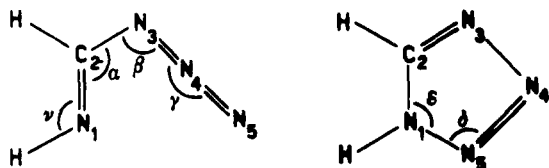


Figure 1. Geometric parameters.

given in Tables Ia and Ib. Both molecules were found to be planar. The numbers in parentheses in Table Ia represent the change in a particular geometric parameter associated with a displacement of 0.5 kcal/mol from the energy of the optimized geometry. The results of the x-ray diffraction studies on 4-phenyl-3(5)-azidopyrazole (**2a**) ($X = \text{NH}$; $B = \text{C}-\text{C}_6\text{H}_5$; $A = \text{CH}$)^{20,21} and tetrazolo[1,5-*b*]benzothiazole (**1b**) ($X = \text{S}$; $AB = \text{C}_6\text{H}_4$)^{22,23} are also given. The optimized geometry for the tetrazole corresponds rather closely to that found by the semiempirical method of Roche and Pujol,²⁴ the results of which are given in Table Ib.

Rotation about bond C_2-N_3 gave a less favorable energy for any given point on the reaction path such that the process of cyclization can be said to be planar. The N_1-H bond, however, was found to rise 10° out of plane for point VI of Table II. Table II gives the optimized geometries of the seven points along the reaction coordinate between the azide and the tetrazole, as well as the energy associated

with each point. Also indicated in Table II are the values for the bond overlap population for each associated bond length.

The cyclization can be divided into two processes. The first consists solely of the bending of the azide angle γ with a concomitant change in lengths N_3-N_4 and N_4-N_5 ; this process lasts up to the transition state IV. From this point until IX there is nonnegligible overlap between N_1 and N_5 and it is this second process that contains the major reorganization of the azide into the tetrazole form. This second process can itself be divided into two parts. The first part, from point IV until point VI, is a process in which angles γ , α , and ν vary simultaneously until α attains the value found in tetrazole. As can be seen in Table II, however, it is only bond N_4-N_5 that changes significantly in length during this process. During the second part of this process angle γ continues to decrease and all bond lengths vary significantly.

Figure 2 gives the centroids of charge calculated by the Boys procedure for several points along the reaction coordinate. FF gives the position of the centroid; +, -, or * indicate whether an atom or centroid is above, below, or in the plane of the page. The solid lines connect a centroid with the nearest atom or pair of atoms (they must not be considered in the classical sense of a line representing an electron pair). The broken lines in IV, VI, and VII show the migration of a particular centroid from its previously shown position; in VIII the broken line indicates the proximity of the

Table I

(a) Azidoazomethine Geometries and Bond Overlap Populations										
	N_1-C_2^a	C_2-N_3^a	N_3-N_4^a	N_4-N_5^a	α , deg	β , deg	γ , deg			
STO-3G	1.29 (± 0.01)	1.44 (± 0.04)	1.28 (± 0.02)	1.16 (± 0.02)	122 (± 1)	110 (± 2)	182 (± 5)			
P_{AB}	0.504	0.336	0.330	0.554						
X-ray 2a ²⁰	1.351	1.407	1.244	1.140	121.5	114.2	171.9 ^b			
X-ray 3a ²¹	1.302	1.393	1.365	1.110	123.0	114.2	188.1			
(b) 1H-Tetrazole Geometries										
	N_1-C_2^a	C_2-N_3^a	N_3-N_4^a	N_4-N_5^a	N_5-N_1^a	α , deg	β , deg	γ , deg	δ , deg	ϵ , deg
STO-3G	1.37	1.31	1.37	1.31	1.36	110.0	107.0	110.0	108.0	106.0
P_{AB}	0.401	0.469	0.305	0.376	0.314					
X-ray 1b ²²	1.344	1.322	1.372	1.309	1.352	109.3	104.2	112.6	104.5	109.4
X-ray 3b ²³	1.329	1.321	1.373	1.255	1.381	109.8	105.0	111.1	107.6	106.4
Roche ²⁴	1.375	1.305	1.375	1.310	1.375	109.5	106.5	110.0	107.5	106.5

^a Lengths in ångströms. ^b Out of plane.

Table II. Geometric Parameters Along the Reaction Path (Bond Lengths and Angles with Associated Energies and Bond Overlap Populations)

Form	N_1-N_5^a	N_1-C_2^a	C_2-N_3^a	N_3-N_4^a	N_4-N_5^a	α , deg	β , deg	γ , deg	$-E(-253)$, au
I	3.21	1.29	1.44	1.28	1.16	122	110	182	0.362 209 475 ^b
	0.000	0.504	0.336	0.330	0.554				2.620 738 049 ^c
II	2.77	1.29	1.44	1.30	1.19	122	110	156	0.350 525 563
	0.003	0.504	0.332	0.334	0.507				
III	2.55	1.29	1.44	1.32	1.21	122	110	144	0.344 459 002
	0.008	0.504	0.331	0.327	0.479				
IV [≠]	2.40	1.29	1.44	1.32	1.22	122	110	136	0.342 530 691 ^b
	0.017	0.503	0.331	0.332	0.457				2.612 703 043 ^c
V	2.18	1.29	1.44	1.33	1.25	114	110	132	0.347 187 229
	0.037	0.500	0.333	0.338	0.416				
VI	1.95	1.30	1.43	1.33	1.27	110	108	126	0.364 454 11
	0.086	0.485	0.348	0.341	0.388				
VII	1.81	1.31	1.41	1.35	1.27	110	106	120	0.382 311 299
	0.134	0.462	0.374	0.323	0.385				
VIII	1.55	1.34	1.35	1.36	1.29	110	106	116.2	0.447 929 526
	0.239	0.431	0.428	0.312	0.379				
IX	1.36	1.37	1.31	1.37	1.31	110	106	110	0.467 741 570 ^b
	0.314	0.401	0.469	0.305	0.376				2.696 708 149 ^c

^a Lengths in ångströms. ^b STO-3G. ^c 7s-3p.

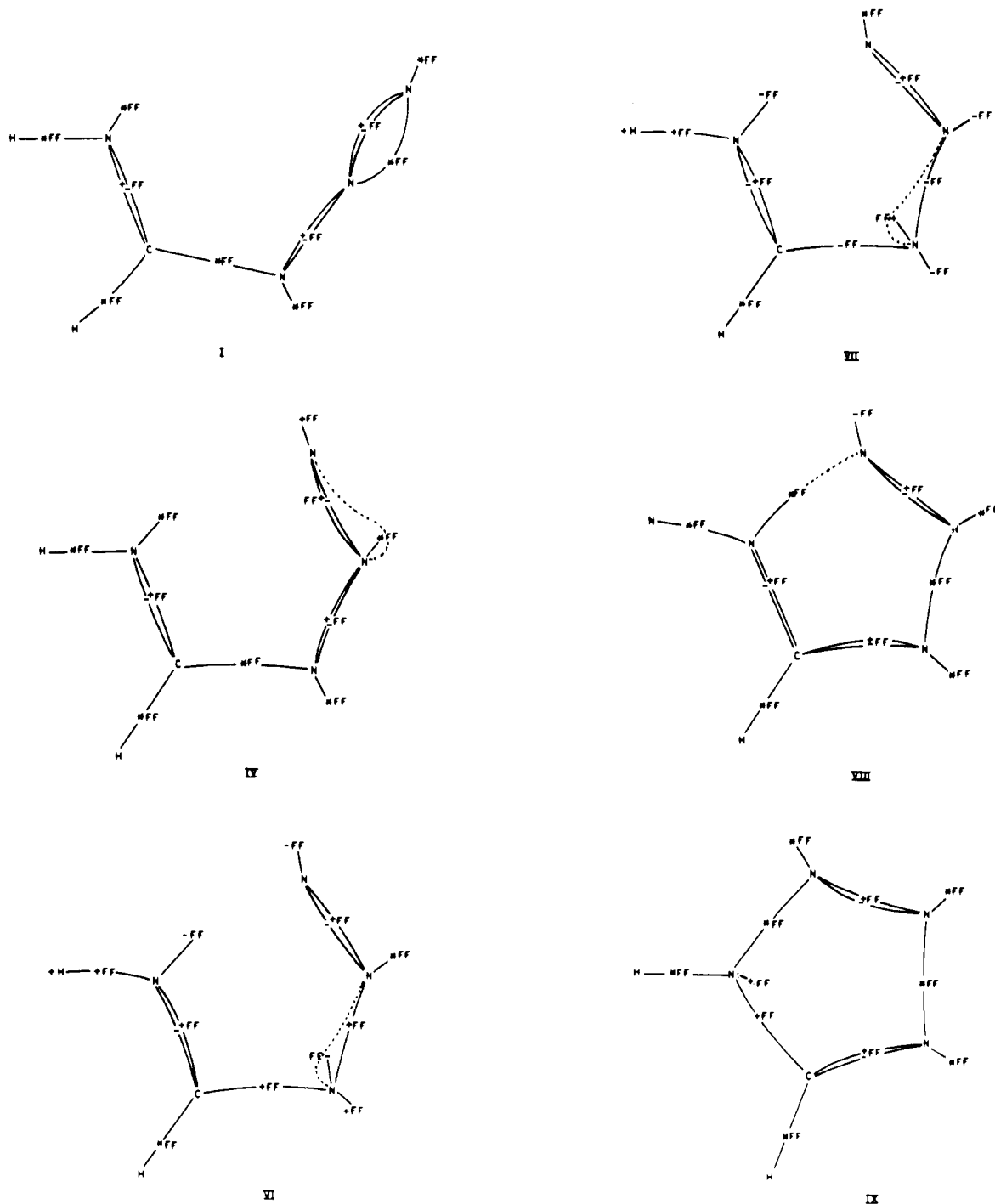


Figure 2. Centroids of charge along the reaction path.

centroid to N_5 as well as N_1 . The two processes explained above can be differentiated in this figure. From I until IV there has been the formation of a lone pair on N_4 and the elongation of the distance between N_1 and the centroid of its lone pair. The first part of the second process is seen to terminate in VI. There has been little change in the bonding centroids but the centroid for the lone pair on N_1 continues to move toward N_5 . The second part contains the reorganization of the bonding centroids. First the centroid of bond N_3-N_4 moves to C_2-N_3 (point VII), and then the lone pair centroid 1 is formed on N_1 in point IX.

The total charge on each atom as well as the charges for the π system for several points on the reaction coordinate are given in Table III. The total charge on N_1 remains negative from the azide to tetrazole although N_1 for the π sys-

Table III. Total and π Atomic Populations for Different Points on the Reaction Path

Point	I	III	IV ^a	VII	IX
N_1	7.337 1.125	7.342 1.142	7.343 1.160	7.279 1.592	7.243 1.612
C_2	5.866 0.963	5.876 0.950	5.874 0.938	5.855 0.925	5.873 1.015
N_3	7.199 1.467	7.184 1.399	7.183 1.378	7.192 1.234	7.181 1.136
N_4	6.890 1.149	6.952 1.077	6.970 1.052	7.047 1.024	7.063 1.121
N_5	6.963 1.295	6.911 1.431	6.903 1.471	7.000 1.224	7.029 1.116

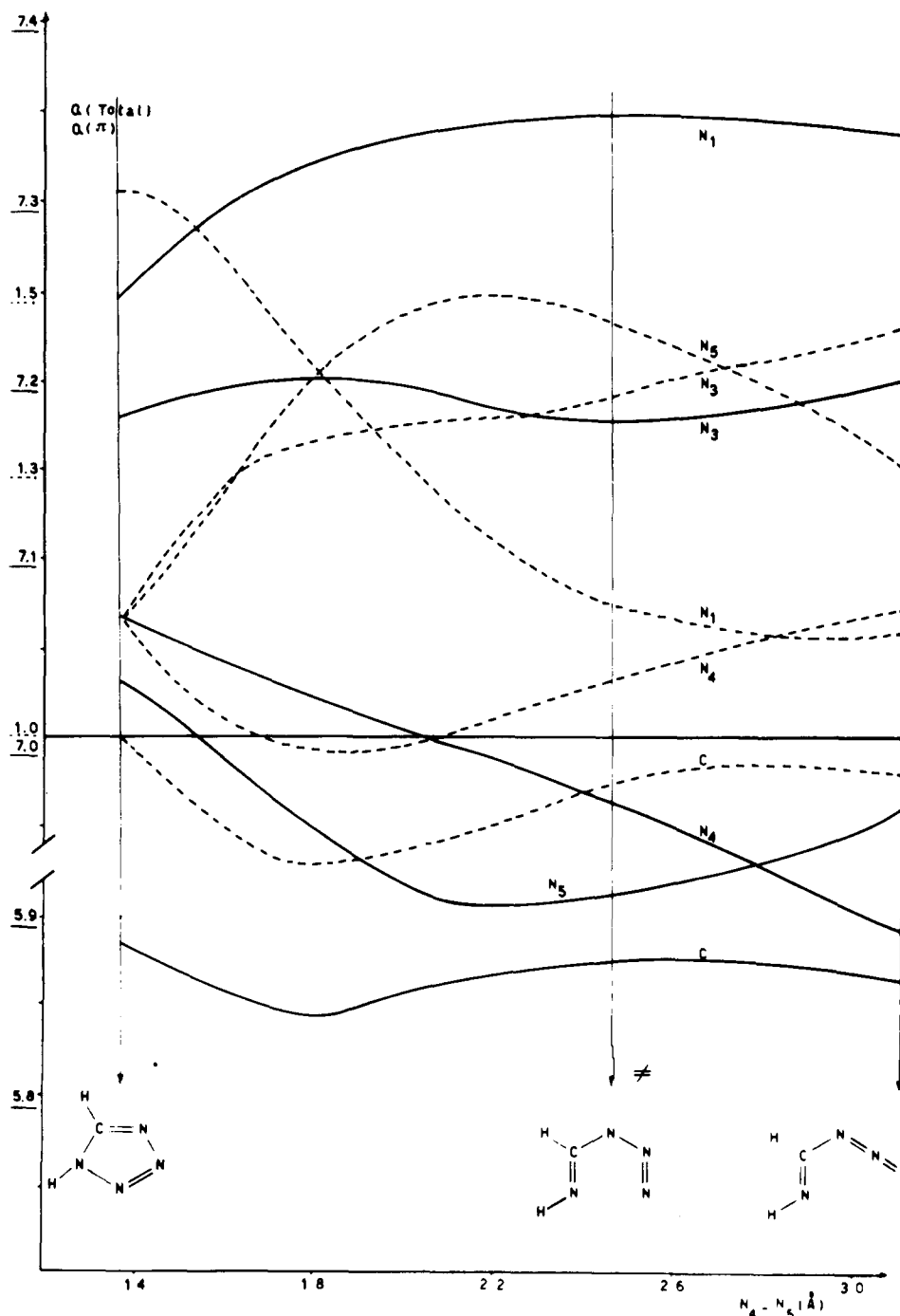


Figure 3. Evolution of the total and π atomic populations.

tem in tetrazole contains less than two electrons. As for the azide constituent of azidoazomethine, it is seen to become more and more a dipole as the transition state is reached. N_3 remains negative while N_5 becomes more positive; N_4 becomes almost neutral during the formation of its lone pair. Figure 3 shows the evolution of the total and π atomic populations along the reaction coordinate.

The activation energy for the cyclization reaction is found to be 12.3 and 5.0 kcal/mol with STO-3G and 7s-3p basis sets, respectively, and the reaction energy is found to be -66.1 and -47.7 kcal/mol with STO-3G and 7s-3p basis sets, respectively. The reaction path for the cyclization of azidoazomethine to 1H-tetrazole is shown in Figure 4.

Discussion

Since activation energies are generally exaggerated in the

SCF framework for reactions involving the making or breaking of a bond, one might question the appropriateness of the SCF for this cyclization reaction. However, it is seen that the transition state IV contains the same number of electron pairs in almost the same location as found in the reactant azide I. One might therefore expect the SCF to give a reasonably accurate energy of activation for the cyclization reaction whereas the energy of activation for the opening of tetrazole and, of course, the reaction energy $I \rightleftharpoons IX$ remains suspect within the SCF framework. Another factor which affects theoretical activation energies is the choice of the reaction coordinate. In the present case the distance N_5-N_1 was chosen because it is between these atoms that a bond is formed or broken. Furthermore, it was found between the transition state IV and point VI that if another variable, such as the bending of the azide angle γ ,

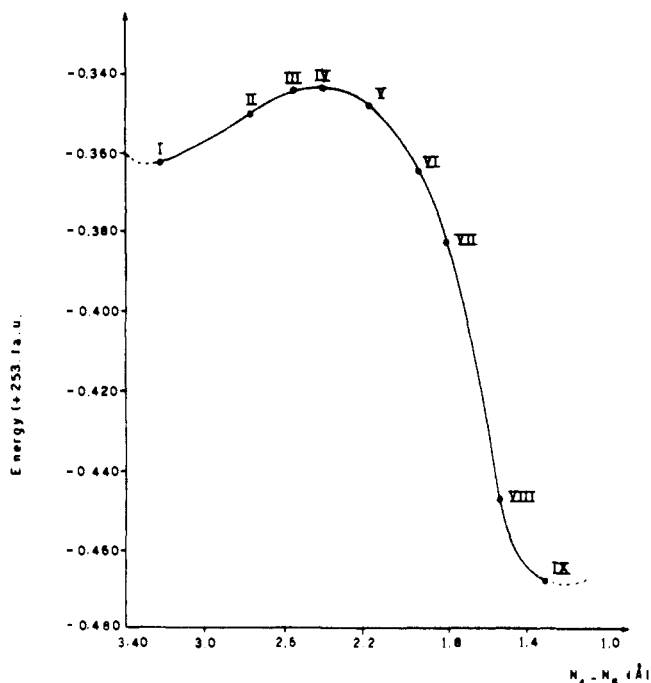
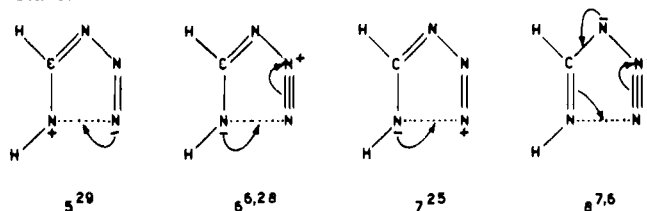


Figure 4. Reaction pathway.

is taken as the independent variable, a change in any other variable would give a lower energy only if the distance N_1-N_5 was shortened.

No precise experimental data have ever been given for the transformation $I \rightleftharpoons IX$; indeed, the tetrazole IX is the sole form observed, even in the vapor phase at 93 °C.²⁵ As for the energy of activation, an experimental value of 17.8 kcal/mol was found for the cyclization of guanylazide **4a** into aminotetrazole **4b** ($X = Y = N$, $R = NH_2$).²⁶ Accounting for the effects of substituents and solvents, temperature, and ZPE corrections, the theoretical calculated values for the energetics, as given in Figure 4, can hardly be compared with available experimental results. We propose to examine in a future work the thermodynamic and kinetic aspects of the azido-tetrazole equilibrium using a range of substituents on C_2 and N_1 . As for the effect of solvents, it can be predicted that polar solvents will preferentially stabilize the transition state IV which is more polarized with respect to product I (Table III). Thus, the cyclization should be accelerated in polar solvents.

In studying the isomers I and IX, the experimentalists have proposed different representations for the transition state.



The present study of the isomerization of the azide I into 1*H*-tetrazole IX in "the gas phase at 0 K and 0 mode of vibration" allows an analysis of the mechanism of this reaction by giving the characteristics of the transition state and of the electronic reorganization along the reaction pathway. These results are described in Figure 5. It was found that the formation of the activated complex entails a movement of the lone pair on N_1 toward atom N_5 at the same time as a lone pair is being formed on N_4 at the expense of the bond π_{45} . The π system involving the five heavy atoms, however, is scarcely altered. The only geometric parameters which vary appreciably in the first part of the reaction are the angle γ and the distances N_3-N_4 and N_4-N_5 , which thus give a transition state resembling the reactant azide. This is in accord with experimental results⁴ and the Hammond postulate. In light of this postulate, it is not surprising that the transition state has an energy content and electronic structure very similar to the reactant azide since the substituted azide is itself often an unstable intermediate in the formation of tetrazoles.

After the transition state IV all the geometric parameters evolve toward the values observed in the tetrazole IX. The reorganization of the π system, however, only starts with point VI on the reaction path. One then observes successively the formation of the double bond C_2-N_3 and the lone pair on N_1 of tetrazole.

A keynote in this process is the role of the lone pair N_1 which permits the formation of the bond σ_{15} without having to turn the π_{12} system. Most likely, the mechanism will be different for the cyclization $4a \rightarrow 4b$ in the case where $X = CH$. This is similar to the case of 1,3-dipolar cycloadditions wherein the reactants approach each other in two parallel or perpendicular planes according to the nature of the dipole and the dipolarophile.^{11,27} The activation energy for $X = N$ ($Y = N$ or CH) is around 5 kcal/mol less than for $X = CH$ ($Y = N$ or CH).^{12,14} Also, it is known that the forma-

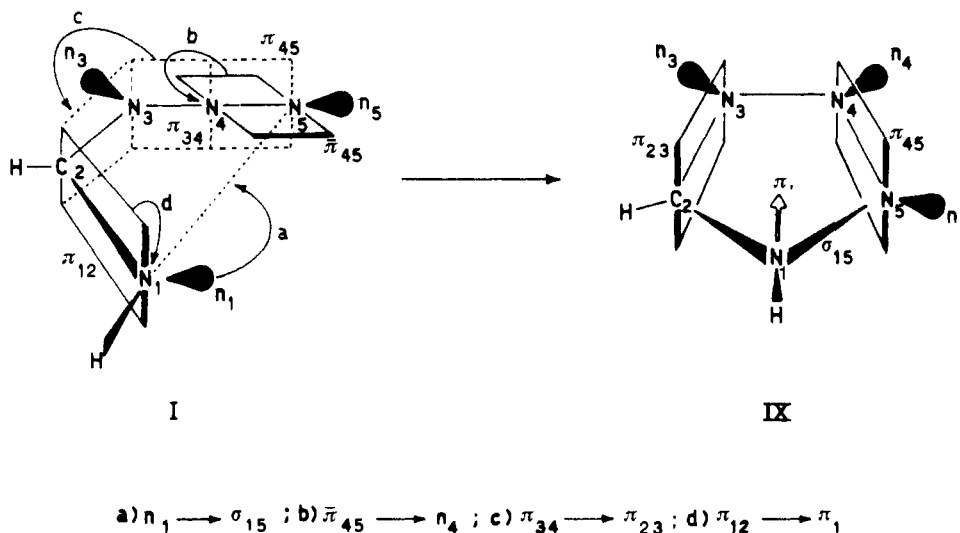


Figure 5. Electronic reorganization along the reaction pathway.

tion of the carbanion ($X = C^-$; $Y = N$) facilitates the closing of vinylazides to the anions of *V*-triazole, while guanlyazide hydrochloride (**4a**) ($X = N^+H_2$; $Y = N$; $R = NH_2$) is stable contrary to the case for guanlyazide itself.

Finally, one can say qualitatively that the activation energy for the process $I \rightarrow IV$ is due essentially to the bending of angle γ ($N_3-N_4-N_5$) while that for the process $IX \rightarrow IV$ is due to the rupture of the bond σ_{15} and to the loss of the delocalization energy in tetrazole.

References and Notes

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The Mercury $6(^3P_1)$, Cadmium $5(^3P_1)$, and Benzene ($^3B_{1u}$) Photosensitization of Vinyl Fluoride

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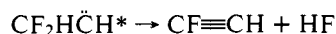
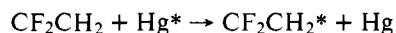
Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2. Received July 11, 1975

Abstract: Triplet state vinyl fluoride molecules containing different amounts of excess vibrational energies were produced by energy transfer from Hg (3P_1) atoms at 27 °C, Cd (3P_1) atoms at 275 °C, and benzene ($^3B_{1u}$) molecules at 27 °C. In all three systems vinyl fluoride was found to undergo unimolecular decomposition to yield acetylene and hydrogen fluoride with a zero pressure extrapolated quantum yield of approximately unity in the metal atom sensitized systems, and 0.31 in the benzene-sensitized system. The decomposition sequence involves at least two different excited intermediates, the (π, π^*) triplet ethylene and probably its isomeric triplet 2-fluoroethylidene. From the rate constant values determined ($k(\text{Hg}) = 3.8 \times 10^{10} \text{ s}^{-1}$ (27 °C), $k(\text{Cd}) = 8.3 \times 10^8 \text{ s}^{-1}$ (275 °C), and $k(\text{C}_6\text{H}_6) = 4.6 \times 10^8 \text{ s}^{-1}$ (27 °C)) the following values were derived for the Arrhenius parameters of the decomposition reaction, $^3(\text{CH}-\text{CH}_2\text{F}) \rightarrow \text{C}_2\text{H}_2 + \text{HF}$, $A = (2.1 \pm 1.0) \times 10^{12} \text{ s}^{-1}$ and $E_a = 22.4 \pm 1.7 \text{ kcal/mol}$. The Arrhenius parameters for the $^3(\text{CH}_2\text{CHF}) \rightarrow ^3(\text{CH}-\text{CH}_2\text{F})$ rearrangement were estimated to have the values: $A = 9 \times 10^{10} \text{ s}^{-1}$ and $E_a = 6.0 \text{ kcal/mol}$.

Earlier studies^{1,2} of the mercury $6(^3P_1)$ photosensitized decomposition of vinyl fluoride at room temperature have shown that triplet excited vinyl fluoride molecules decompose exclusively to acetylene and hydrogen fluoride and that hydrogen elimination does not occur. The reaction follows an excited state mechanism involving one or more reactive intermediates. Because of the lack of sufficient accuracy in the kinetic data due to the small effect of pressure on the decomposition, it was not possible to establish the number of intermediates involved. The observed linear pressure dependence for the quantum yield of acetylene formation, $\phi(\text{C}_2\text{H}_2) = A - B[\text{C}_2\text{H}_3\text{F}]$, is inconsistent with any plausible mechanism. The decomposition rate constant for vinyl fluoride and vinyl chloride³ was an order of magnitude higher than that for ethylene.⁴⁻⁶ The shorter lifetime of the reaction intermediates and higher rate constant for the decomposition reaction was attributed to the lower energy of the triplet ethylidene state and the more favorable energetics of the hydrogen halide elimination step: $\text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_2$

+ H_2 , $\Delta H = 41.7 \text{ kcal/mol}$; $\text{C}_2\text{H}_3\text{F} \rightarrow \text{C}_2\text{H}_2 + \text{HF}$, $\Delta H = 18 \text{ kcal/mol}$.

The mercury (3P_1) photosensitized decomposition of the three isomeric difluoroethylenes, *cis*-CHFCHF, *trans*-CHFCHF, and CH_2CF_2 , has also been investigated.² These reactions are somewhat slower and even though it was possible to obtain reproducible and reasonably accurate kinetic data, they appeared to satisfy equally well a one excited state and a two excited state mechanism. Furthermore, while the experimental decomposition kinetics of the three isomeric molecules were identical, the 1,1 and 1,2 isomers were postulated to follow different decomposition paths, the former involving a triplet ethylidene intermediate:



and the latter not involving such species: