group in whose vertical column it lies has the operation given horizontally at the left-hand side of the table, with the relevant transformation properties. The totality of entries in a vertical column thus corresponds to the total set of symmetry operations of that particular point group.

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Theoretical Study of the Vinyl Azide–v-Triazole Isomerization

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Abstract: The properties of the cyclization of vinyl azide to v-triazole are studied using the STO-3G minimal basis set to construct an energy hypersurface. Then, a split valence 4-31G basis set is used for the geometries found for the transition state, vinyl azide, and v-triazole. The activation energy, E_a, is 32.9 kcal/mol in STO-3G and 41.4 kcal/mol in 4-31G; the heat of reaction is −10.8 kcal/mol in 4-31G. Various limited configuration interactions (CI) were employed for points around the SCF transition state but the new transition state differed only slightly. The various properties calculated, along with localized molecular orbitals, permit the reaction to be classed as a 1,5-dipolar electrocyclic reaction. In addition, using the geometry of the vinyl azide transition state as a start, a similar transition state was found for the isoelectronic species, protonated azidoazomethine. The activation energy in STO-3G is 42.9 kcal/mol, and is to be compared with 12.3 kcal/mol previously found for the cyclization of neutral azidoazomethine.

The thermolysis or photolysis of vinyl azides **1** give azirines **3** as products or as intermediates for final products.[1] Three mechanisms for the formation of azirines have been proposed,[2] the first of which, formation of a vinyl nitrene **2a**, has been
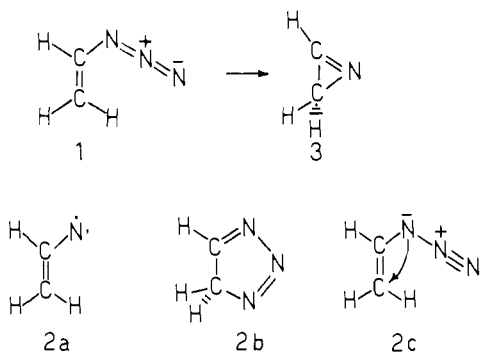

excluded on the basis of kinetic results which show that vinyl azides give moderate activation energies (26–30 kcal/mol) and low entropies of activation (−3 to +5 eu).[3] This is in contrast with the decomposition of aryl azides to nitrenes (ΔE_a = 39 kcal/mol, $\Delta S^{\ddagger}$ = 19 eu for phenyl azide).[4] Kinetic evidence has not been conclusive, however, in choosing between the two remaining proposed mechanisms. One would have the formation of v-triazole **2b** which would further lose N_2 to give azirine **3**. The other one would have a concerted process **2c** wherein the loss of N_2 is simultaneous with ring closure.

The present work is an ab initio theoretical study of the first part of the second proposed mechanism, closure of vinyl azide to v-triazole. Evidence for the involvement of this intermediate comes from the cyclization of diazopropene **4**, which is isoelectronic with vinyl azide **1**. An intermediate has been detected[4] in the formation of product 1*H*-pyrazole **5** and has been attributed[4] to 3*H*-pyrazole **6**. The kinetics of this reaction have
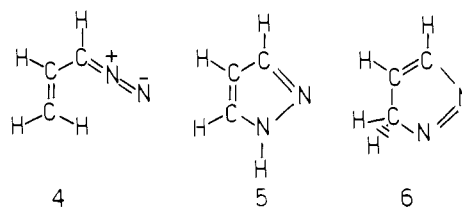

been studied[3] and found to be similar to those for vinyl azides (E_a = 32.0 kcal/mol, $\Delta S^{\ddagger}$ = −3.6 eu).

Additional interest as to the involvement of v-triazole comes from the findings that vinyl azides possessing an acidic terminal H atom undergo a facile base-promoted cyclization to triazoles.[5]
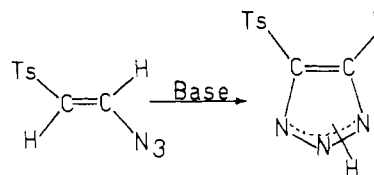
In addition to the vinyl azide cyclization of this study, the geometries found for vinyl azide and the transition state are then used as starting points to study the closing of protonated azidoazomethine **7** to protonated tetrazole **8**. This expectation
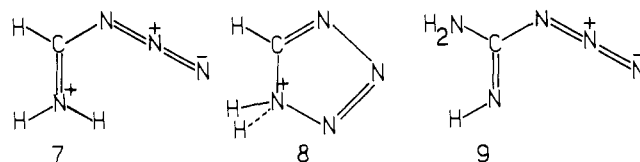
of similar transition states has been used to explain the stability of the azide form of substituted azidoazomethines in acid solution. Neutral guanyl azide **9** cyclizes spontaneously to 5-aminotetrazole[6] but the salts $[(NH_2)_2CN_3]^+X^-$ have the open azide structure.

In a previous study of the cyclization of azidoazomethine to 1*H*-tetrazole,[7] it was suggested that the reaction proceeds by an attack of the =NH lone pair on the other terminal nitrogen. Protonation of this lone pair by acidifying the media would lead then to another type of reaction, such as an electrocyclic reaction in which the π system must be disrupted by a turning of the terminal NH_2^+ group. This might then give a higher activation energy than the planar reaction by the nonprotonated species. Thus, the ring closing of azides 1 and 7 might be comparable to the ab initio theoretical results found for the electrocyclic reactions of 1,3-butadiene[8] and acrolein.[9]

Method

The calculations have been carried out by the ab initio SCF–LCAO–MO method, using the GAUSSIAN-70 series of computer programs.[10] The STO-3G minimal basis set of contracted Gaussians was used to construct that part of the potential energy hypersurface which includes the cyclization reaction. This basis set has been shown to give satisfactory geometries for a wide selection of organic compounds.[11] Nevertheless, several points were recalculated using the slightly more extended 4-31G basis set, which gives much better total energies for the compounds.[12]

In addition, localized molecular orbitals (LMO) were obtained employing the Boys procedure[13] adapted to the GAUSSIAN-70 program.[14] This procedure consists in a unitary transformation of the canonical molecular orbitals according to a criterion of a maximum sum of the squares of the distances of the orbital charge centroid from an arbitrarily defined origin of the molecular coordinate system,

$$D(\phi) = \sum_{i=1}^{n} [\langle \phi_i | r | \phi_i \rangle]^2$$

The LMO charge centroids clearly define the centers of gravity of electron charge for zones which in the past have been intuitively assigned as core, bonding, and lone pair regions. Furthermore, the change in the positions of the centroids can be used to measure the progression of a reaction, as has been shown for the concerted Diels–Alder cycloaddition of *cis*-butadiene to ethylene,[15] for 1,3-dipolar cycloadditions,[16] and for the neutral azidoazomethine–tetrazole isomerization.[7a] In the present case several points along the vinyl azide cyclization reaction path (STO-3G) are represented by centroids of charge.

Finally, configuration interaction has been shown to lower the barrier for the cyclization of 1,3-butadiene[8] from 46.7 to 40.1 kcal/mol. As the authors noted, however, CI is needed for more quantitative results but the SCF gives the qualitative features of the energy hypersurface. We have tested this assumption for the vinyl azide reaction with three types of limited CI. The configurations were constructed from the mono- and diexcitations from the highest occupied molecular orbital (HOMO) to the lowest unoccupied (LUMO) (3 configurations), from the 2 HOMOs to the 2 LUMOs (15 configurations), and from the 3 HOMOs to the 3 LUMOs (55 configurations).

Calculations

The reaction coordinate was chosen as the C_1N_5 distance (Figure 1) for the sole reason that it is across this space that a new bond would be formed in the vinyl azide cyclization reaction. Twelve C_1N_5 distances were chosen between those for the optimized azide and v-triazole geometries. Because this is a study of a possible cyclization reaction, the starting point for an optimization at a given C_1N_5 distance is the geometry found at the previous larger C_1N_5 distance and one can be reasonably sure that the cyclization reaction follows a valley on the potential energy hypersurface if, upon parabolic opti-
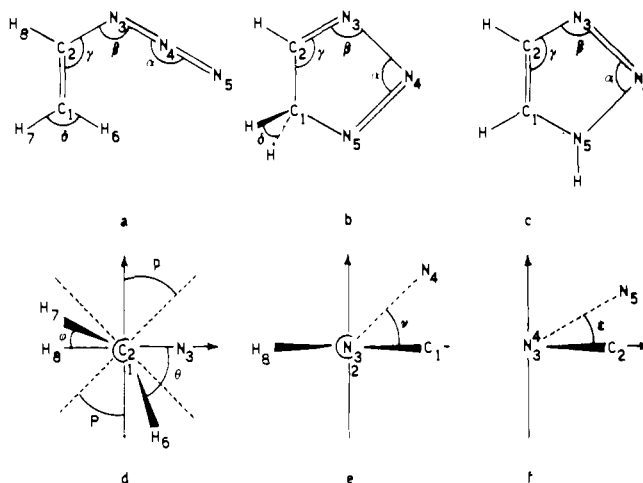

Figure 1. Geometric parameters for the optimization along the vinyl azide closure reaction path (a, b, d, e) and for 1,2,3-triazole (c). The quantity ρ is one-half the sum of parameters ϕ and θ and can be taken as a measure of CH_2 rotation.

mization of each parameter, a barrier to other reactions is demonstrated. For instance, if at a given C_1N_5 distance a poorer total energy is obtained for N_3N_4 distances greater than, say 1.45 Å, a barrier to loss of nitrogen (N_4=N_5) can be shown. The height of such a barrier is not the object of this study, nor is the activation for nitrogen loss, even though it might be lower than that for cyclization.

All bond distances were optimized in steps of 0.02 Å except for the CH distances, which were kept at 1.08 Å. The other geometric parameters for the optimization of the vinyl azide closure are illustrated in Figure 1. The dihedral angles considered are $\theta = H_6C_1C_2N_3$, $\phi = H_7C_1C_2H_8$, $\nu = C_1C_2N_3N_4$, and $\epsilon = C_2N_3N_4N_5$, as shown in Figure 1. The only constraint among the angles was that atoms C_1, C_2, N_3, and H_8 remain planar with the line C_2H_8 bisecting angle γ. A step of 5° was taken in the optimization of each angle and the total energies for the points were fitted to a parabolic function to give an optimum value to 1°. Then that point was recalculated.

The procedure followed to obtain the optimum geometry for a given value of C_1N_5 consisted in repeating the following series of groups of optimizations. First, each of the four bond distances was varied along with angle α and then angles β and γ were varied. Next, the CH_2 group was rotated, and finally, the best combination of ν and ϵ was found for lifting N_4 and N_5 out of plane. The procedure for rotating the CH_2 group consisted in first defining the quantity ρ as one-half the sum of θ and ϕ. As can be seen in Figure 1c, ρ is the angle between the bisector of the projection of angle $H_7C_1H_6$ and the line which passes through C_1 perpendicularly to the plane $C_1C_2N_3$. The measure of the rotation of the CH_2 group can thus be given by ρ, where $\rho = 0°$ for the azide and 90° for triazole. The best values of ϕ, θ, and δ were found for different values of ρ and then the values for the best ρ were taken. Two repetitions of the four groups of geometry optimizations did not change bond lengths more than ±0.01 Å nor angles more than ±3° for a given value of C_1N_5. The energy lowering between two consecutive optimization cycles was never more than 1.2 kcal. Also, the range in the values of the parameters examined was great enough to include the optimized geometries of the points r_{15} on either side. This provides a certain assurance of the continuity in the exploration of the cyclization reaction hypersurface.

In the optimizations of the stable vinyl azide and triazole molecules, the C_1N_5 distance was not taken as an independent variable. The same sequence of optimizations was followed as for the intermediate points, the only difference being in the first group where the bond lengths and α were varied independently. This independence thus allowed the C_1N_5 distance to vary.

Table I. The Bond Lengths (Å), Angles (deg), and the Total Energy (+237 au) for Several Points Along the Vinyl Azide Closure Path

	r_{15}	r_{12}	r_{23}	r_{34}	r_{45}	α	β	γ	δ	θ	ϕ	ν	ϵ	E_{tot}
I[a]	3.60	1.32	1.45	1.31	1.16	189	112	129	116	0	0	0	0	−0.611 046
II	3.06	1.32	1.45	1.32	1.17	160	110	129	116	0	0	0	0	−0.599 149
III	2.76	1.32	1.45	1.34	1.19	145	109	129	116	0	0	0	0	−0.585 613
IV	2.62	1.32	1.45	1.35	1.20	138	109	129	116	0	0	0	0	−0.577 314
V	2.51	1.32	1.45	1.36	1.20	135	108	129	116	0	0	0	0	−0.572 730
VI	2.40	1.33	1.44	1.37	1.22	133	107	127	114	0	0	0	0	−0.565 279
VII	2.30	1.34	1.41	1.38	1.22	130	107	126	114	23	9	5	10	−0.560 373
VIII[b]	2.25	1.35	1.40	1.38	1.22	129	107	126	114	35	15	7	21	−0.558 547
IX	2.20	1.37	1.38	1.38	1.23	128	107	125	114	41	22	5	23	−0.558 996
X	2.15	1.39	1.37	1.39	1.23	126	107	125	114	57	31	3	23	−0.561 933
XI	2.10	1.41	1.35	1.40	1.24	124	107	124	114	69	40	0	19	−0.570 036
XII	1.95	1.46	1.33	1.41	1.25	120	107	123	112	106	64	0	0	−0.614 443
XIII	1.70	1.49	1.31	1.44	1.27	116	107	117	110	107	67	0	0	−0.677 306
XIV[c]	1.49	1.51	1.30	1.46	1.29	112	106	112	108	110	70	0	0	−0.700 535
XV[d]	1.38	1.35	1.39	1.31	1.39	106	108	109						−0.719 211

[a] Vinyl azide. [b] Transition state. [c] v-Triazole. [d] 1,2,3-Triazole.

Table II. The Geometries and Energies for the Optimization Cycles along the Reaction Path (r_{15})

r_{15}		r_{12}	r_{23}	r_{34}	r_{45}	α	β	γ	δ	θ	ϕ	ν	ϵ	E_{tot}, au
2.30	Start. point	1.35	1.40	1.38	1.22	130.0	107	128.0	112	0	0	0	0	−237.555 320
	1st opt	1.341	1.411	1.378	1.219	129.6	107	126.0	114	22	10	5	15	−237.558 843
	2nd opt	1.341	1.411	1.378	1.219	129.6	107	126.3	114	23	9	5	10	−237.560 373
2.25	Start. point	1.368	1.37	1.35	1.20	128.0	110	128	112	0	0	0	0	−237.545 915
	1st opt	1.352	1.398	1.387	1.227	128.9	110	126	114	34	20	6	20	−237.557 318
	2nd opt	1.352	1.398	1.379	1.221	128.7	107	125.8	114	35	15	7	21	−237.558 547
2.20	Start. point	1.368	1.37	1.35	1.20	127.0	110	128	112	0	0	0	0	−237.547 901
	1st opt	1.371	1.385	1.385	1.226	127.4	107	126.0	114	45	25	0	25	−237.557 066
	2nd opt	1.371	1.385	1.385	1.226	128.1	107	124.9	114	41	22	5	23	−237.558 996

An optimization of 1,2,3-triazole was undertaken in the same way as for v-triazole, although, of course, the parameters δ, ϕ, and θ do not exist here (Figure 1c). In this case, the CH and NH bonds were fixed as to bisect their immediate ring angles. The NH distance was left at 1.03 Å.

The three limited types of CI were employed in a further optimization near the cyclization transition state. A full reoptimization was not carried out but only the rotation angle ρ was tested for each level of CI. This angle was chosen because the vinyl azide π system is disrupted the most by a change in this angle.

After the geometries for stable vinyl azide and the cyclization transition state were found using the SCF method, these two geometries were taken as the starting points in a geometry search for protonated azidoazomethine and its cyclization transition state. These optimizations were carried out in the same manner as for vinyl azide and also employed the SCF method.

Results

Structural Analysis. The optimized geometries and corresponding total energies for several points along the vinyl-v-triazole reaction path are given in Table I. The total energies in Table I were obtained using the STO-3G basis set. On the whole, it is found that the changes in geometry are quite smooth. At first sight the rapid evolution of θ, ϕ, ν, and ϵ between points VI and VII might seem rather abrupt. The rotation of the CH₂ group is only 16°, however, and it seems reasonable that the π system will remain intact until a certain threshold in the distance between the terminal atoms is attained. So as to provide an idea of the limits of the geometrical optimization, we report in Table II the energy and geometry at the end of each optimization cycle for three points near the transition state.

Inspection of the geometries for the points in Table I shows three zones for this cyclization reaction. The first, points I–VI, can be called the azide zone since point VI resembles the reactant azide I, albeit an azide bent at N_4. Between points VI and XI there is a transition zone in which the CH₂ group rotates. The measure of this rotation, ρ (Figure 1), is 25° at point VIII and 44° at X. The triazole zone is then between points XI and XIV with a strong resemblance to v-triazole. This persistence of either π system and a narrow region in which the CH₂ group rotates has already been shown in the theoretical studies of the electronic reactions of 1,3-butadiene[8] and of acrolein.[9]

The progression of the reaction for vinyl azide can be represented by the displacements of the centroids of charge for localized molecular orbitals. Figure 2 gives these centroids calculated by the Boys procedure[13] for several points along the reaction coordinate. In this figure the nuclei are represented by C, N, and H; and the centroids for core electrons are also represented by the letters C and N since these centroids were always found to be within 0.003 Å of their respective nuclei. FF gives the position of the centroid and the symbols +, −, and * indicate whether an atom or centroid is above, below, or in the plane of the figure. The lines are simply used to join the centroids to the nearest nucleus or pair of nuclei and must not be thought of in the classical sense of a line representing an electron pair. The dashed lines are used to indicate the displacement of a centroid during the course of the cyclization reaction. The azide zone can thus be depicted by the centroids in Figure 2 as a process in which a lone pair is formed on N_4 while the π system for the molecule scarcely changes. Points X and XIV show how the aspect of the π system is maintained throughout the triazole region. As the distance C_1N_5 is stretched, atoms C_2, N_3, N_4, and N_5 remain planar as long as possible. Points VII–X describe the transition zone in which most of the major electronic reorganization takes place.

Reaction Energies. The activation energy for the cyclization of vinyl azide to v-triazole using the minimal STO-3G basis set is calculated as the difference in total energy between points I and VIII, the value being 32.9 kcal/mol. The heat of reaction is −56.1 kcal/mol for the closing of vinyl azide to v-triazole,
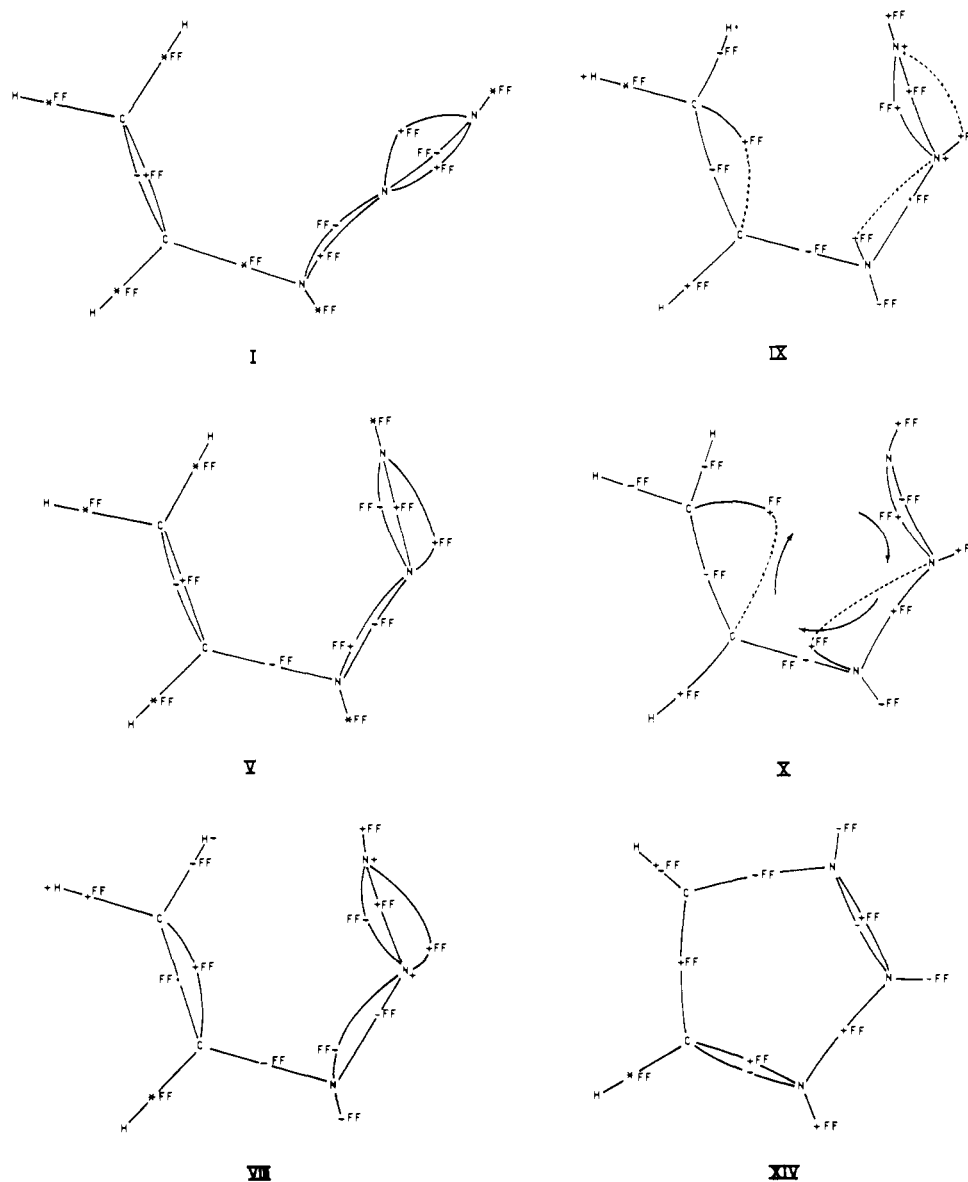
Figure 2. Centroids of charge (FF) for several points along the vinyl azide closure reaction path (+, −, * indicate the positive above, below, or in the plane of the page). Solid lines are put in simply to connect a centroid to one or two nearby nuclei and should not be thought of in the classical sense of a bond line. Broken lines are put in to recall a connection in previous points and the arrows in point X show the motion of the centroids.

using the same basis set. Since this basis set does not treat linear forms as well as cyclic forms in regard to total energy, the heat of reaction should be calculated with at least the equivalent of an extended basis set. Points I, VIII, and XIV have thus been recalculated using the 4-31G basis set. The total energies are respectively −240.309 792, −240.243 727, and −240.326 952 au, thus giving an activation energy of 41.4 kcal/mol and a heat of reaction of −10.8 kcal/mol. The former must now be treated with caution since the transition state geometry might be rather different using the extended basis set. The results of the energetics of this reaction are represented graphically in Figure 3, along with the results for the closure of neutral azidoazomethine in the STO-3G[7a] and 4-31G[7b] basis sets. Point XV was also recalculated using the 4-31G basis set and the total energy was found to be −240.370 574 au. The difference between this point and point XIV gives 27.4 kcal/mol in favor of point XV, using this basis set.

In optimizing the CH_2 rotation with the three CI methods it was found that ϕ and θ both increase by 3° with each of the methods. The geometry for point VIII was used as the starting point of the optimization. In this case, the angle of CH_2 rotation ρ is 28° with CI, compared to 25° with only SCF. The activation energies were found to be lowered 1, 3, and 4 kcal/

mol when 3, 15, and 55 configurations, respectively, were employed. This result can be compared to the cyclization of *cis*-butadiene[8] where CI lowered the barrier from 46.7 to 40.1 kcal/mol but where the SCF still gives the qualitative features of the energy hypersurface.

It was found that the geometries for protonated azidoazomethine were the same, within 2° and 0.02 Å, as their vinyl azide counterparts for points I, VIII, and IX. Point IX in this case is slightly higher in energy than point VIII. Using IX then gives an activation energy of 42.9 kcal/mol for this cyclization reaction, using the STO-3G basis set. The values for the total energies for these three points are I, −253.789 512; VIII, −253.721 727; IX, −253.721 132 au.

Population Analyses. Table III gives the values for the bond overlap populations[17] (P_{AB}) for several points on the vinyl azide cyclization reaction path. The bond energies (E_{AB}) associated with these populations can be calculated by the formula[16]

$$E_{AB} = a_{AB}P_{AB}{}^3 + b_{AB}P_{AB}{}^2 + c_{AB}P_{AB}$$

The coefficients a_{AB}, b_{AB}, and c_{AB} have been obtained for several reference compounds and are given in ref 16. The evolution of a particular bond AB can then be evaluated for a
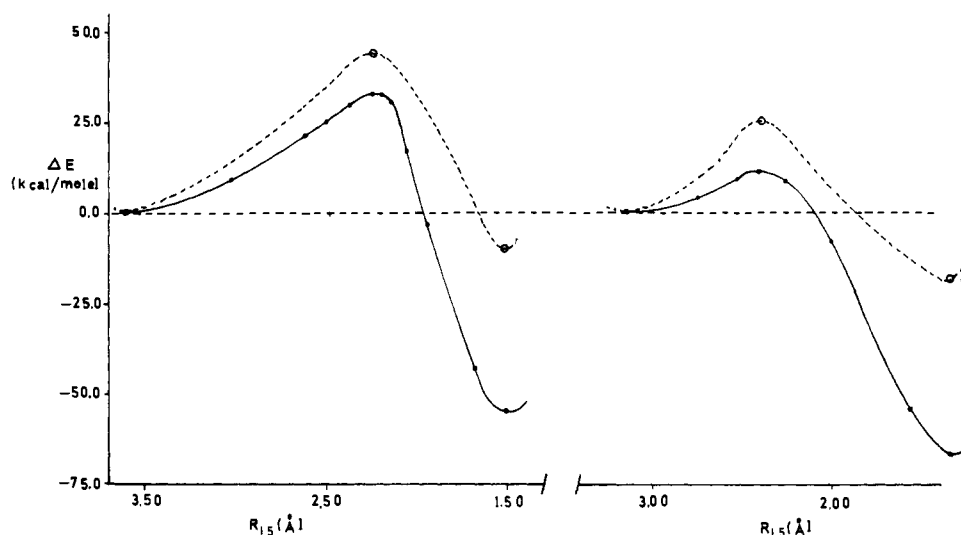
Figure 3. The energies along the vinyl azide (on the left) and neutral azidoazomethine (on the right) cyclization pathways are given for the STO-3G (solid lines) and the 4-31G (dashed lines) basis sets. The points actually optimized are given as solid circles. In the 4-31G cases (open circles) the corresponding geometries optimized in STO-3G were employed.

point i on the vinyl azide cyclization reaction path by the relation[16]

$$T_{AB}(i) = 100 \frac{E_{AB}(i) - E_{AB}(\text{I, vinyl azide})}{E_{AB}(\text{XIV}, v\text{-triazole}) - E_{AB}(\text{I})}$$

These results, also given in Table III, indicate that in the azide zone only the bond N_4N_5 has evolved in going from points I to VIII. The narrow transition zone from VIII to X contains the major part of the electronic evolution. Also the transition state VIII shows only a small percentage of bonding across C_1N_5, even though the CH_2 group is rotated 25° (ρ, Figure 1).

Discussion

The cyclizations of vinyl azide and protonated azidoazomethine present enough structural and electronic similarities in their transition states to be discussed as one type of reaction. The three zones found for the vinyl azide–triazole potential energy hypersurface indicate the structural similarity to the cyclization of 1,3-butadiene[8] and acrolein,[9] which have been classed as electrocyclic reactions.[18] However, the reactions studied here present electronic properties which permit a comparison with the cyclization of neutral azidoazomethine.[7] The comparison is presented below by means of the principal types of bond reorganizations drawn from an analysis of the movement of the LMO charge centroids.

azido–tetrazole isomerization 8 electrons involved	vinyl azide–triazole isomerization 6 electrons involved
$\bar{\pi}_{4,5} - n_4$	$\bar{\pi}_{4,5} - n_4$
$\pi_{3,4} - \pi_{2,3}$	$\pi_{3,4} - \pi_{2,3}$
$\pi_{1,2} - \pi_1$	$\pi_{1,2}$
(electron pair on N_1)	
$n_1 - \sigma_{1,5}$	$\searrow \sigma_{1,5}$

In the two cases the formation of a lone pair is observed on N_4 at the expense of the orthogonal $\bar{\pi}_{4,5}$ bond, and this reorganization takes place well before the transition state (in the azide zone). This effect can also be seen from the evolution of the bond N_7N_5 for point VIII ($T_{N_4N_5}$ (VIII) of Table III) which has already reached 75.5%. For its part, the neutral azidoazomethine cyclization proceeds via the displacement of the lone pair on atom N_1 toward atom N_5. This attack is the driving force for the reaction and the reorganization of the π system is a simple consequence of this first electronic move-

ment. Protonated azidoazomethine and vinyl azide do not possess this lone pair and thus the π system must participate directly in the formation of the σ bond between atoms 1 and 5. This electronic reorganization along the reaction pathway is described in Figure 4 (see Figure 5 of ref 7a for the corresponding diagram in the neutral azidoazomethine cyclization reaction). The free azide anion has been classed as a 1,3 dipole.[19] Similarly, the various resonance forms for the reactant vinyl azide permit it to be classed as a 1,5 dipole. In the linear azide one may write these forms with a + on N_4 indicating the participation of an electron pair on this atom in the π system of the molecule. As the azide part bends, forming a lone pair on N_4 at the expense of the orthogonal $\bar{\pi}_{4,5}$ bond, new resonance forms may be written for vinyl azide in which the + sign is on N_5. The cyclization reactions for vinyl azide and protonated azidoazomethine can thus be classified as 1,5-dipolar
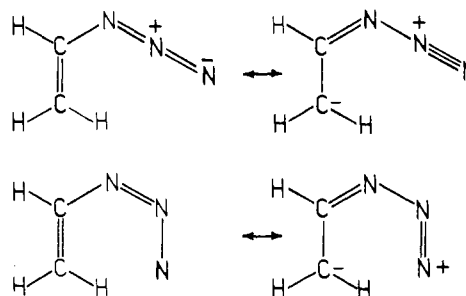
electrocyclic reactions. As stated above, the experimental activation energies for the decomposition of several substituted vinyl azides to azirines range between 26 and 30 kcal/mol.[3] These activations may be for such proposed mechanisms as **2b** (cyclization to v-triazole with subsequent loss of nitrogen) or **2c** (direct attack of C_1 on N_3 with concerted loss of nitrogen). The minimal basis set activation energy of 32.9 kcal/mol plus the lowering of this value by 4 kcal/mol with the (55 × 55) CI tends to give acceptance to **2b** as a possible route. The 4-31G barrier of 41.4 kcal/mol seems too high to permit this mechanism but it too is expected to be determined by CI. This value is suspect also because the geometries used were optimized with the STO-3G basis set. The difference in the geometries optimized in the two basis sets might account for several kcal/mol when the optimized geometry of one is used indiscriminantly in the other.

Another factor which effects the value of the calculated activation energies is the optimization process itself. Owing

Table III. Bond Overlap Populations (P_{AB}), Bond Energies (E_{AB}, kcal/mol), and Rates of Evolution (T_{AB}, %) of the Bonds for Several Points on the Vinyl Azide Cyclization Reaction Path

	C_1N_5	C_1C_2	C_2N_3	N_3N_4	N_4N_5
P_{AB} I[a]	0.000	0.592	0.329	0.304	0.549
VIII[b]	0.027	0.549	0.367	0.283	0.445
XI	0.105	0.458	0.430	0.257	0.436
XIV[c]	0.295	0.369	0.492	0.242	0.399
E_{AB} I[a]	0.0	138.3	64.8	45.6	156.2
VIII[b]	3.4	127.8	75.3	40.6	95.2
XI	15.3	116.8	93.9	35.2	91.0
XIV[c]	55.9	81.7	113.6	32.3	75.4
T_{AB} VIII[b]	6.1	18.4	21.0	37.3	75.5
XI	27.4	39.2	59.7	78.5	80.7

[a] Vinyl azide. [b] Transition state. [c] v-Triazole.

to the limitations of the procedure chosen one can only say that the calculated E_a is the lowest of only those paths that were explored. Taking this fact into account along with the effects of basis set size and of CI we estimate that the E_a for the cyclization of vinyl azide is between 30 and 40 kcal/mol. This theoretical estimate is for molecules in the gas phase at 0 K and 0 variational mode while the experimental values were for reactions carried out in solution at 300 K or more. Thus, the cyclization mechanism **2b** remains a candidate for the decomposition of vinyl azides to azirines unless a fuller exploration of the potential energy hypersurface would show that another mechanism, such as **2c,** presents a much lower barrier.

Still, an activation barrier of 42.9 kcal/mol (STO-3G, single configuration) is quite significant for the cyclization of N_1 protonated azidoazomethine. This value can be compared with that found for the cyclization of the neutral species, 12.3 kcal/mol,[7a] using the same theoretical method. The difference of 30 kcal/mol might well explain the stability of certain substitutes azidoazomethines in acidic solution which would otherwise cyclize to tetrazoles.[6]

As stated above the STO-3G minimal basis set does not treat linear forms as well as cyclic forms, thus giving a heat of reaction too negative (−56.1 kcal/mol). The value obtained with the more extended 4-31G basis set (−10.8 kcal/mol) cannot of course be compared with experiment since *v*-triazole and its isoelectronic analogues have never been trapped. The closest comparison might be the cyclization of **9** to 5-aminotetrazole for which the heat of reaction was measured at −17.8 kcal/mol.[20] A comparison of theoretical results can be made with the cyclization of neutral azidoazomethine to 1*H*-tetrazole. Here, the heat of reaction is calculated to be −18 kcal/mol with the 4-31G basis set[7b] using geometries optimized in STO-3G (as in the case of vinyl azide cyclization to *v*-triazole). Tetrazole is an aromatic compound, however, which might well explain the more negative heat of reaction than with *v*-triazole, a nonaromatic compound. The heat of reaction for the isomerization of *v*-triazole to 1,2,3-triazole was found to be −27.4 kcal/mol in 4-31G, which can in part be taken as a delocalization energy. In this case the heat of reaction of vinyl azide to 1,2,3-triazole can be calculated as −37.8 kcal/mol in 4-31G using geometries optimized in STO-3G.

The formation of *v*-triazole and its subsequent loss of nitrogen might not be important in the formation of azirines from vinyl azides—even if the lowest passage were to be by the cyclization transition state. The barrier to loss of nitrogen is probably less somewhere between the cyclization transition state and the *v*-triazole form. One can not be sure of this without a search at further points on the full hypersurface which explores this barrier. However, evidence that this is so is suggested by an examination of the bond energies, $E_{AB}(i)$, and of the centroids of charge.

The bond energies are weak for C_1N_5 and N_3N_4 in *v*-triazole (E_{AB} (XIV) in Table II) and it is across these single bonds that
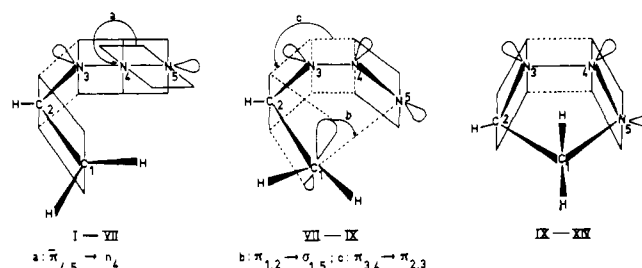

Figure 4. Successive steps in the electronic reorganization during the cyclization of vinyl azide.

nitrogen would be lost. Between points VIII and XI, $E_{N_3N_4}$ decreases while $E_{C_1N_5}$ has increased only slightly. As for the centroids (Figure 2), between points VIII and X one centroid has left N_3N_4 while a centroid has not fully left C_1C_2 to join C_1N_5.

Conclusion

In taking into account the effects of basis set size, CI, and geometry optimization limitations, we estimate the activation energy for the cyclization of vinyl azide to be between 30 and 40 kcal/mol. This range is not too much higher than that found experimentally for the decomposition of substituted vinyl azides to azirines (26–30 kcal/mol),[3] and so the cyclization mechanism cannot be discounted on this point.

In decreasing the distance C_1N_5 and in optimizing the other parameters to this distance a barrier was found for loss of nitrogen. (The starting point of an optimization at one C_1N_5 distance was the optimized geometry for the previous longer C_2N_5 distance.) This barrier, which is probably lowest between points VIII and X, has not been measured and so one cannot be sure if crossing this barrier before VIII (the cyclization transition state) would lead to a smaller activation energy.

The activation energy for the cyclization of N_1 protonated azidoazomethine was found to be 42.9 kcal/mol (STO-3G, single configuration), and the geometry of the transition state was found to be similar to that for vinyl azide. Although the same comments can be made for the effects of basis set size and CI and although the geometry optimization was not as advanced as in the case of vinyl azide, one can compare this activation energy to that for the cyclization of neutral azidoazomethine[7a] (12.3 kcal/mol), which was calculated with the same method (STO-3G, single configuration) as the protonated case.

Owing to the many resonance structures that can be proposed for the linear and bent forms of the azide moiety, many different and contradictory mechanisms for the cyclization reaction can be represented a priori by bent arrows and "electron pushing" (see ref 7a for the four different mechanisms proposed for neutral azidoazomethine). We present one bond reorganization scheme for the different phases of the cyclization reaction studied here. The bond reorganizations

are based on the displacements of LMO centroids of charge during the reaction and thus theoretical support is given to one set of bond reorganizations or "electron pushing". A comparison of the bond reorganizations for the azidoazomethine and vinyl azide cyclizations demonstrates the importance of the terminal lone pair in forming a new bond with a subsequent rearrangement of the π system for the former case. In the case of vinyl azide and protonated azidoazomethine the π system must be disrupted in order to participate directly in the formation of a new bond.

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A Theoretical Study of Substituted CHNO Isomers

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Abstract: A detailed ab initio molecular orbital study using minimal and split-valence basis sets has been carried out for singlet isomers of R(CNO), R = Li, BH_2, CH_3, NH_2, OH, F, Cl, CN, C_6H_5, p-$NH_2C_6H_4$, and p-$NO_2C_6H_4$. Calculated structures are in reasonable agreement with available experimental data. The predicted equilibrium structures generally resemble those of the parent compounds (R = H). Only the lithium substituent leads to large structural distortions: LiNCO, LiOCN, and LiONC are all predicted to be linear molecules. Methyl fulminate (CH_3ONC) is predicted to be quite stable toward intramolecular rearrangement and of comparable thermodynamic stability to acetonitrile oxide (CH_3CNO). There is no theoretical evidence that any of the substituted oxazirines RC̄N̄O are kinetically stable compounds. The calculations suggest that hydroxycarbonyl- and fluorocarbonylnitrene are low-energy isomers but with relatively small barriers toward intramolecular rearrangement. Other substituted singlet carbonyl nitrenes (R = Li, CH_3, Cl) rearrange without activation to the corresponding isocyanate.

Introduction

In a previous paper,[2] we presented an ab initio molecular orbital study of the isomers of CHNO and the reaction pathways which interconnect them. We found that the most stable isomer is HNCO (isocyanic acid) followed by HOCN (cyanic acid), HCNO (formonitrile oxide), and HONC (carboxime). Detailed investigation of the CHNO potential surface suggested that, in addition to the two experimentally characterized molecules isocyanic acid and formonitrile oxide, two additional isomers, namely, cyanic acid and carboxime, are likely to be reasonably stable species and should be observable under suitable conditions. Other conceivable CHNO isomers such as singlet formylnitrene and oxazirine were found to collapse with little or no activation to more stable structures. From a structural point of view, an important result was that HNCO, HOCN, and HONC are all predicted to be trans-bent molecules. This result has been confirmed in other independent calculations.[3]

The main objective of the present work is to determine theoretically the effect of substituents on the structures and stabilities of CHNO isomers and, in particular, on the stabilities of the lesser known isomers, viz., fulminates (RONC), oxazirines (RC̄=N̄-O), and carbonylnitrenes (RC(O)N). For the latter class of compounds, there is some experimental information against which the theoretical results may be judged.

Methods and Results

Two Gaussian-type basis sets were used in this study. The simpler of these, the minimal STO-3G set,[4] was employed for geometry optimizations and direct calculations of transition states using procedures described previously.[5] The transition states are characterized as stationary points in the surface with one negative eigenvalue of the energy second derivative matrix. Single calculations at STO-3G optimized geometries were then carried out using the split-valence 4-31G basis set.[6] Finally,