

Ethynyldiazonium Ions: Possible Precursors for the Generation of C-sp-Centered Carbenium Ions? An ab Initio Study of the Linear, Unimolecular Dissociation of the Parent Ethynyldiazonium Ion

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Abstract: The thermal dediazonation of ethynyldiazonium ions is examined as a possible reaction pathway for the generation of C-sp-centered carbenium ions, ethynyl cations RCC^+ . The possibility of the linear, unimolecular dissociation $\text{HCCNN}^+ (1) \rightarrow \text{HCC}^+ (2) + \text{N}_2$ is discussed on the basis of the structures obtained at the HF/6-31G* and the MP2/6-31G* levels, the energies calculated at levels up to MP4(SDQ)/6-31G**/MP2/6-31G*, and electron density analysis of **1** and several states of **2** and compared to the dissociations of vinylidiazonium ion, **3**, and methyldiazonium ion, **5**. **2** has several singlet states [$^1\Sigma^+(\pi^2) \approx ^1\Pi < ^1\Delta < ^1\Sigma^+(\pi^4)$] that are energetically close to the $^3\Pi$ ground state. The $^1\Sigma^+(\pi^4)$ state is correlated with the ground state of **1** by orbital symmetry. The primary reaction product, however, is **2** in its $^1\Sigma^+(\pi^2)$ state due to the occurrence of an avoided crossing. The dissociation toward **2**, $^1\Sigma^+(\pi^2)$, is endothermic by 96.2 kcal mol⁻¹ at the highest level. The activation barrier for the reaction is predicted to be closer to the binding energy of 150.2 kcal mol⁻¹ between molecular nitrogen and **2**, $^1\Sigma^+(\pi^4)$, since the avoided crossing is associated with a late transition state. The theoretical results suggest that the intrinsic stability of **1** is such that dediazonation does not occur.

1. Introduction

Alkanediazonium ions undergo facile unimolecular loss of nitrogen in solution.¹⁻³ Molecular nitrogen is a very good leaving group and allows also for the generation of unsaturated carbocations. Nucleophilic dediazonations of arenediazonium ions have long been known as a source of aryl cations.⁴ The thermal decomposition of arenediazonium ions has been observed in the gas phase⁵ and occurs in homogeneous solution quite readily at room or slightly elevated temperature. Extensive mechanistic studies established that a (solvated) aryl cation is formed in fluorinated solvents as an intermediate in the rate-determining step of the dediazonation.⁶ A related class of unsaturated carbocations, vinyl cations,^{7,8} can also be generated quite readily, given a sufficiently potent leaving group. A variety of olefinediazonium salts are known and their stability toward loss of nitrogen varies greatly.⁹ Vinyl cations generated by dediazonation have been discussed as intermediates in the deamination of vinylamines,

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(2) For a recent ab initio study see: Ford, G. P. *J. Am. Chem. Soc.* **1986**, *108*, 5104.

(3) The dissociation enthalpies of small alkanediazonium ions have been measured in the gas phase and the dediazonations are endothermic by about 40–50 kcal mol⁻¹: (a) Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1958**, *80*, 5472. (b) Foster, M. S.; Williamson, A. D.; Beauchamp, J. L. *Int. J. Mass. Spectrom. Ion. Phys.* **1972**, *15*, 429.

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(5) See for example: Zollinger, H. *Acc. Chem. Res.* **1973**, *6*, 335.

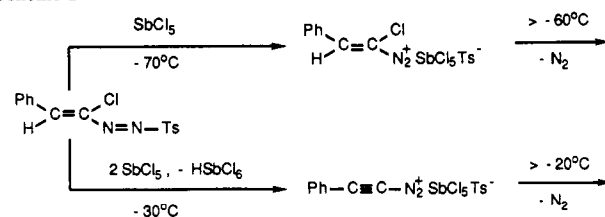
(6) See for example: (a) Bergstrom, R. G.; Wahl, G. H., Jr.; Zollinger, H. *Tetrahedron Lett.* **1974**, 2975. (b) Burri, P.; Wahl, G. H., Jr.; Zollinger, H. *Helv. Chim. Acta* **1974**, *57*, 2099. (c) Swain, C. G.; Sheats, J. E.; Harbison, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 783. (d) Swain, C. G.; Sheats, J. E.; Gorenstein, D. G.; Harbison, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 791. (e) Bergstrom, R. G.; Landells, R. G. M.; Wahl, G. H., Jr.; Zollinger, H. *J. Am. Chem. Soc.* **1976**, *98*, 3302. (f) Zollinger, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 141.

(7) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. *Vinyl Cations*; Academic Press: San Francisco, 1979; p 207.

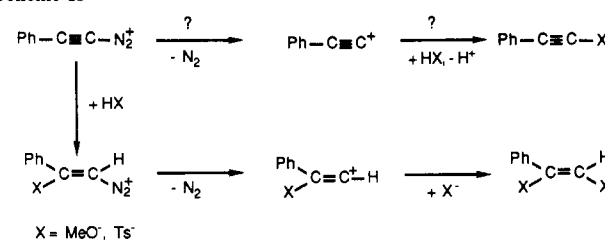
(8) (a) Hanack, M. *Acc. Chem. Res.* **1970**, *3*, 209; **1976**, *9*, 364. (b) Modena, G.; Tonellato, U. *Adv. Phys. Org. Chem.* **1971**, *9*, 185. (c) Stang, P. J. *Prog. Phys. Org. Chem.* **1973**, *10*, 305. (d) Stang, P. J. *Acc. Chem. Res.* **1978**, *11*, 107.

(9) For the preparation and synthetic exploitation of stable alkanediazonium salts see, for example: (a) Bott, K. *Angew. Chem.* **1979**, *91*, 279. (b) Saalfrank, R. W.; Weiss, B.; Peters, K.; Schnering, H. G. *Chem. Ber.* **1984**, *118*, 4026 and references therein.

Scheme I

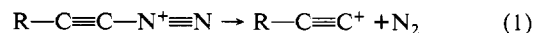


Scheme II



in the alkaline decomposition of 3-nitroso-2-oxazolidone, and in the decomposition of triazenes with acid.¹⁰

The successful preparation of (1-chloro-2-phenylethenyl)tosyldiazene has been reported recently by Hanack et al.¹¹ The addition of SbCl_5 to a dichloromethane solution of this compound at a temperature of -30°C results in the formation of the corresponding ethynyldiazonium salt. At temperatures above -20°C molecular nitrogen is evolved; see Scheme I. The reaction of the ethynyldiazonium compound with nucleophiles has been found to proceed via the ethenyldiazonium salt and the vinyl cation, formed by dediazonation, as shown in Scheme II. Although products formed by the addition of a nucleophile to the potential ethynyl cation intermediate have not been detected under the reaction conditions,¹¹ ethynyldiazonium ions can be considered as possible precursors for the generation of ethynyl cations by loss of molecular nitrogen (eq 1). Ethynyl cations have been detected



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Table I. Valence Bond Representations of the States of Ethynyl Cation That Arise from the Three Lowest Configurations

configuration	state	valence-bond representation ^{a,b}
[core] $\sigma^2\sigma^2\pi^4$	$^1\Sigma^+$	H—C≡C
		↓
[core] $\sigma^2\sigma^2\pi^3\sigma^1$	$^1\Pi$	H—C=C↑
		↑
	$^3\Pi$	H—C=C↑
[core] $\sigma^2\sigma^2\pi^2\sigma^2$	$^1\Delta$	H—C=C↑↓
		↑
	$^1\Sigma^+$	H—C—C↑↓
		↑
	$^3\Sigma^-$	H—C—C↑↓
		↑

^aThe charge is omitted. ^bUnpaired electrons in the states $^1\Sigma^+(\pi^2)$ and $^3\Sigma^-$ are in orthogonal π -orbitals.

in interstellar space¹² and under experimental conditions in the gas phase,¹³ but no examples for the unimolecular nucleophilic substitution at acetylenic carbon are known.^{14,15}

In light of this current research, it is tempting to ask the question as to whether C-sp-centered carbenium ions, ethynyl cations RCC^+ , could become accessible for the first time as highly reactive intermediates by thermal dediazonation of ethynyldiazonium ions in analogy to the formation of aryl and vinyl cations. The dissociation reaction shown in eq 1 has been investigated by ab initio methods for the simplest case in which the parent ethynyldiazonium ion, **1**, dissociates in a unimolecular fashion into the ethynyl cation, **2**, and molecular nitrogen. The reaction is compared to the dediazonation reactions $\text{H}_3\text{C}_2\text{N}_2^+ (\mathbf{3}) \rightarrow \text{H}_3\text{C}_2^+ (\mathbf{4}) + \text{N}_2$ and $\text{H}_3\text{CN}_2^+ (\mathbf{5}) \rightarrow \text{H}_3\text{C}^+ (\mathbf{6}) + \text{N}_2$. Earlier ab initio calculations of **2** are briefly reviewed, and the structure and relative energy of the $^1\Sigma^+(\pi^2)$ state are reported. The states of ethynyl cation are classified according to their orbital symmetry. It is shown that the dissociation of the diazonium ion toward the $^1\Sigma^+(\pi^4)$ state is the only allowed reaction pathway for the linear dediazonation according to the Woodward–Hoffmann rules.¹⁶ The existence of the lower lying $^1\Sigma^+(\pi^2)$ state of **2** should cause the occurrence of an avoided crossing in the state correlation. The reaction should therefore result in the formation of the ethynyl cation in its $^1\Sigma^+(\pi^2)$ state as the primary reaction product, which subsequently undergoes internal conversion and intersystem crossing in order to reach the $^3\Pi$ ground state of ethynyl cation. The occurrence of an avoided crossing causes an activation barrier along the dissociation path of **1**, whereas the dissociations of **3** and **5** proceed without activation barriers.²

2. Methods

Single-determinant spin-restricted Hartree–Fock (RHF) or unrestricted Hartree–Fock calculations (UHF) with the 6-31G* basis set¹⁷ have been used for the structural optimizations.¹⁸ The structures obtained for **1** and **2** have been refined subsequently with the Fletcher–Powell optimization¹⁹ procedure at the second-order Møller–Plesset (MP2) level in the frozen core approximation.²⁰ Vibrational frequencies have been calculated analytically at the HF/6-31G* level. Energies have been obtained

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Table II. Relative Energies (in kcal mol⁻¹) of States of Ethynyl Cation with Respect to Its Ground State $^3\Pi$

state	SCF ^a	CI ^a	SCF ^b	MP2 ^c	MP3 ^d
$^1\Sigma^+(\pi^4)$	97.6	63.7	105.3	61.9	67.7
$^1\Delta$	51.4	61.3	36.9 ^e		
$^3\Sigma^-$	22.8	35.3	7.6	6.6	2.4
$^1\Pi$	34.4	32.1			

^aA double- ζ basis set augmented by bond functions and the structure of ethynyl radical (CH = 1.063 Å, CC = 1.203 Å) were used, ref 25. ^bHF/6-31G*//HF/6-31G*, ref 26. ^cMP2/6-31G*//MP2/6-31G*, ref 28. ^dMP3/6-31G*//MP3/6-31G*, ref 26. ^eCRHF/6-31G*.

Table III. Structures (in Å) of States of Ethynyl Cation as Obtained at the HF/6-31G* and MP2/6-31G* Levels

state ^a	HF level		MP2 level	
	HC	CC	HC	CC
$^1\Sigma^+(\pi^4)$ ^b	1.075	1.173	1.090	1.207
$^1\Delta$ ^{b,c}	1.079	1.352		
$^3\Sigma^-$	1.080	1.345	1.093	1.372
$^1\Sigma^+(\pi^2)$	1.079	1.345	1.092	1.378
$^1\Pi$	1.075	1.253		
$^3\Pi$	1.074	1.253	1.085	1.237

^aData for $^1\Sigma^+$, $^1\Delta$, $^3\Sigma^-$, and $^3\Pi$ are taken from ref 26 and 28.

^bStates calculated at RHF; all other states are calculated at UHF.

^cUsing complex molecular orbitals.

Table IV. Vibrational Frequencies (in cm⁻¹) and Zero-Point Energies (ZPE, in kcal mol⁻¹) for Several States of **2**

state	σ, ν_{CH}	σ, ν_{CC}	π, δ	π, δ	ZPE
$^1\Sigma^+(\pi^4)$	3508.6	2315.8	1128.5		11.6
$^3\Pi$	3478.3	1809.5	936.3	551.8	9.7
$^1\Pi$	3458.8	1813.6	516.9	499.7	9.0
$^3\Sigma^-$	3396.0	1633.6	860.5	860.4	9.7
$^1\Sigma^+(\pi^2)$	3433.5	1641.4	971.3		10.0

at various levels of the Møller–Plesset perturbation formalism²⁰ (up to MP4(SDQ) in the frozen core approximation) to account in part for correlation effects. The correlation corrections allow also for a comparison between the energies of states whose zero-order wave functions have been computed by RHF or UHF, respectively.

All ab initio calculations have been carried out on our VAX-11/750 system with the programs GAUSSIAN 80 UCSF²¹ and GAUSSIAN 82.²² Cross sections of the electron densities have been computed with the program PROJ.²³

3. Low-Lying States of Ethynyl Cation

There are three electron configurations of the ethynyl cation in which only bonding orbitals are occupied. These configurations give rise to the six lowest lying states of **2**, and the symmetry species of these states together with their valence-bond representations are shown in Table I. It is easily seen why HCC^+ is intrinsically unstable; the π^4 state contains a cationic center at an sp-hybridized carbon and most of the other states are biradical in nature. All of these states with the exception of the $^1\Sigma^+(\pi^2)$ state have been studied previously at the ab initio level.^{24–28}

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Table V. Energies ($-E$ in atomic units) of the Cations **1**–**6** and N_2 at Various Levels of Theory (All Values Are Based on the HF/6-31G* Structures and Calculated with the 6-31G* Basis Set)

molecule	SCF	MP2	MP3	MP4(DQ)	MP4(SDQ)
1 , $^1\Sigma^+$	184.797 72	185.350 24	185.346 46	185.350 83	185.359 21
2 , $^3\Pi$	75.785 55 ^a	75.940 89 ^a	75.960 08 ^a	75.962 23	75.965 97 ^a
3 , $^1A'$	186.059 35	186.608 80	186.619 55	186.625 31	186.632 31
4 , 1A_1	77.086 73	77.306 57	77.327 46	77.329 75	77.333 74
5 , 1A_1	148.216 06 ^b	148.645 85 ^b	148.653 68 ^b	148.660 11	148.665 31
6 , $^1A_1'$	39.230 64 ^c	39.325 14 ^c	39.341 58 ^c	39.344 33 ^c	39.344 67 ^c
N_2 , $^1\Sigma_g^+$	108.943 95 ^d	109.248 08	109.245 27	109.249 30	109.253 14

^aReference 28. ^bReference 2. ^cReference 31. ^dReference 32.

Table VI. Relative Energies^a (in kcal mol⁻¹) of Excited States of **2** with Respect to the Ground State $^3\Pi$ (All Values Are Based on the HF/6-31G* Structures and Calculated with the 6-31G* Basis Set^b)

method	$^3\Sigma^-$	$^1\Pi$	$^1\Sigma^+(\pi^2)$	$^1\Delta$	$^1\Sigma^+(\pi^4)$
SCF	7.6	15.0	21.6	36.9 ^c	107.0
MP2	6.7	15.1	18.4	66.0	70.5
MP3	2.5	14.2	13.5	70.5	69.8
MP4(DQ)	1.4	13.7	12.1	69.8	69.1
MP4(SDQ)	2.8	13.6	13.5	69.1	

^aIncluding vibrational zero-point energy corrections. Zero-point energies are scaled³³ (factor 0.9). The states $^1\Sigma^+(\pi^4)$ and $^1\Delta$ are calculated with RHF, all other states at UHF. ^bEnergies of the states $^3\Sigma^-$, $^1\Delta$, and $^1\Sigma^+(\pi^4)$ are taken from ref 28. ^cUsing CRHF. Not corrected for vibrational zero-point energy.

In 1977 Shih et al.²⁵ reported calculations of five states of the ethynyl cation, and the relative energies of these states with respect to the ground state $^3\Pi$ are summarized in the first two columns of Table II. In 1981 Krishnan et al.²⁶ reported Hartree-Fock calculations at the 6-31G* basis set level for the states $^3\Pi$, $^3\Sigma^-$, $^1\Delta$, and $^1\Sigma^+(\pi^4)$ that were based on optimized structures (see Table III). Note that the structure of the $^1\Sigma^+(\pi^4)$ state is in excellent agreement with the geometry obtained by Montgomery et al.²⁷ from optimization with a DZ+P basis set. With the exception of the $^1\Delta$ state, geometry optimizations were also performed with third-order Møller-Plesset perturbation theory. Again, the ground state was found to be the $^3\Pi$ state and the same ordering of states was found as was reported by Shih et al.²⁵ In a subsequent paper by Raghavachari et al.,²⁸ various HF and MP energies of the states $^3\Pi$, $^3\Sigma^-$, and $^1\Sigma^+$ were reported. The relative energies of the states with respect to the ground state are summarized in Table II. From an inspection of the data presented in these papers the conclusion can be drawn that there is only very little influence of the utilized basis sets on the energy splitting within each treatment. It also can be seen that the relative energies of the states are only moderately changed in going from second-order Møller-Plesset perturbation theory to higher orders. Evidence for the adequacy of the perturbation approach in calculating the states of the ethynyl cation comes also from the good agreement between the calculated²⁶ and the experimental²⁹ values for the heat of formation of ethynyl cation.³⁰

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(30) Although the calculations of the splitting between the $^3\Pi$ and the $^1\Sigma^+$ states resulted in comparable values at the HF level and when electron correlation is taken into account by subsequent CI or perturbation calculations, there still remains some uncertainty regarding the energy gaps between the ground state and the other states. Recently, electronic transitions in the ethynyl cation were observed by high-resolution translational energy spectroscopy: O'Keefe, A.; Derai, R.; Bowers, M. T. *Chem. Phys.* **1984**, *91*, 161. The observed transitions (3.4 and 1 eV) were assigned to the transitions $^1\Sigma^+ - ^1\Delta$ and $^3\Sigma^- - ^3\Pi$. While these transitions are in reasonable agreement with the energy differences calculated at the HF level only the CI derived transition energy for the second transition is in reasonable agreement. All other theoretical predictions based on post-SCF methods resulted in far too small transition energies.

(31) *The Carnegie-Mellon Quantum Chemistry Archive*, 3rd ed.; White-side, R. A.; Frisch, M. J.; Pople, J. A., Eds.; Department of Chemistry, Carnegie-Mellon University: Pittsburgh, Pennsylvania.

(32) (a) The bond lengths of N_2 at the levels HF/6-31G* and MP2/6-31G* are 1.078 and 1.131 Å, respectively: DeFrees, D. J.; Levi, B. A.; Pollack, S. K.; Hehre, W. J.; Binkley, J. S.; Pople, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4085. (b) Note, short NN bond lengths have also been found for aliphatic diazonium ions: Vincent, M. A.; Radom, L. *J. Am. Chem. Soc.* **1978**, *100*, 3306.

Table VII. Energies ($-E$ in atomic units) of the Cations **1**, **2** ($^3\Pi$, $^1\Sigma^+(\pi^2)$, and $^1\Sigma^+(\pi^4)$), and N_2 at Various Levels of Theory (All Values Are Based on the MP2/6-31G* Structures and Calculated with the 6-31G* Basis Set)

molecule	MP2	MP3	MP4(DQ)	MP4(SDQ)
1	185.364 21	185.346 16	185.352 96	185.364 10
2 , $^3\Pi$	75.941 52 ^a	75.960 68	75.962 77	75.966 25
2 , $^1\Sigma^+(\pi^2)$	75.913 19	75.940 33	75.944 71	75.946 47
2 , $^1\Sigma^+(\pi^4)$	75.842 95 ^a	75.852 35	75.856 55	75.862 55
N_2	109.255 28 ^b	109.245 92	109.251 97	109.257 01

^aReference 28. ^bReference 32.

Table VIII. Selected Vibrational Frequencies^a (in cm⁻¹) and Zero-Point Energies (ZPE in kcal mol⁻¹) of the Diazonium Compounds **1**, **3**, and **5**

molecule	ν_{CC}	ν_{CN}	ν_{NN}	ZPE
1	2407.2	985.1	2768.1	19.0
3	1784.7	761.7	2764.6	34.3
5		642.9	2814.7	30.7

^aAll other frequencies of **1**–**6** are listed in ref 39.

Vibrational frequencies of the low-lying states of **2** (except $^1\Delta$) are listed in Table IV. The energies of the ground state of **2** calculated at various levels of perturbation theory with the HF/6-31G* structure are collected in Table V and the relative energies of the excited states are given in Table VI.

The $^1\Pi$ state, not considered in the work of Raghavachari et al., has been optimized at the HF/6-31G* level. The resulting structural data are given in Table III, and the relative energies obtained at the different levels of perturbation theory are listed in Table VI with respect to the ground state. Shih et al.²⁵ placed the $^1\Pi$ state below the $^3\Sigma^-$ state, whereas in our work the $^1\Pi$ state lies significantly above the $^3\Sigma^-$ state at all levels. The inversion of the ordering between these states is presumably a consequence of the use of non-optimized structures by Shih et al.; note that the difference between the CC bond lengths in ethynyl radical and the optimized structure of the $^3\Sigma^-$ state is about 0.14 Å.

No calculations of the $^1\Sigma^+$ state arising from the configuration [core] $\sigma^2\sigma^2\pi^2\sigma^2$ have been reported in the literature. The optimized structures of this state obtained at the UHF/6-31G* and the MP2/6-31G* levels are given in Table III, and its relative energies with respect to the ground state are listed in Table VI. At the MP4(SDQ)/6-31G*/HF/6-31G* level a value of 13.5 kcal mol⁻¹ has been obtained. At the highest level applied, MP4(SDQ)/6-31G*/MP2/6-31G*, and using the zero-point energies calculated at HF/6-31G* the $^1\Sigma^+(\pi^2)$ state is 12.7 kcal mol⁻¹ above the ground state (see Tables IV and VII); the inclusion of correlation effects to second-order in the structural optimization has only little effect on the relative energy. The $^1\Sigma^+(\pi^2)$ state is thus placed close to the $^1\Pi$ state but significantly below the $^1\Sigma^+(\pi^4)$ state. The $^1\Sigma^+(\pi^2)$ state is 55.6 kcal mol⁻¹ and 54.0 kcal mol⁻¹ below the $^1\Sigma^+(\pi^4)$ state at the MP4(SDQ)/6-31G* level based on the HF- and MP2-optimized structures, respectively. The $^1\Delta$ state was calculated using a complex RHF wavefunction, since a real single determinant wavefunction would not contain the appropriate symmetry of this state. The energies of the states $^1\Delta$ and $^1\Sigma^+$ can therefore not be compared directly. It appears that the $^1\Delta$ state

(33) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Gordon, M. S.; DeFrees, D. J.; Pope, J. A. *J. Phys. Chem.* **1982**, *77*, 3654.

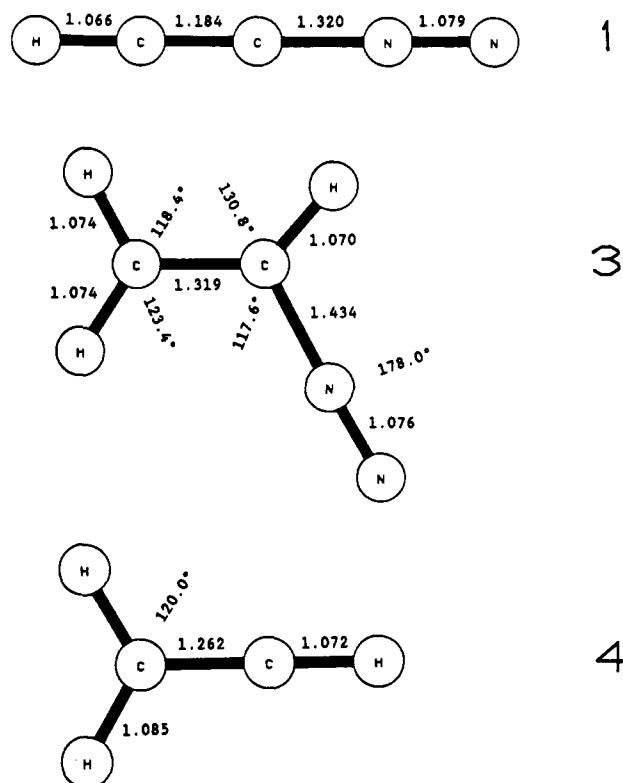


Figure 1. The optimized structures of ethynyldiazonium ion, **1** ($C_{\infty v}$), vinylidiazonium ion, **3** (C_2), and vinyl cation, **4** (C_{2v}), as obtained at HF/6-31G*.

lies energetically between the $^1\Sigma^+$ states. The resulting ordering of the singlet states is $^1\Sigma^+(\pi^2) \approx ^1\Pi < ^1\Delta < ^1\Sigma^+(\pi^4)$.

4. The Structures of the Ethynyldiazonium and Vinylidiazonium Ions

The CC bond length in the ethynyldiazonium compound³⁴ (see Figure 1) is virtually identical with the CC bond lengths calculated for acetylene and butadiyne at the same level.³⁶ The CH bond length compares quite well with the value observed in acetylene³⁷ (1.061 Å). The CN bond length of **1** indicates a bond order of almost two,³⁸ and it is significantly shorter than the CN bond lengths calculated for vinylidiazonium ion (**3**, bond order ≈ 1.5)

(34) The structures of **1**, **3**, and **4** have first been optimized with the 3-21G basis set.³⁵ The obtained structural parameters are very close to the 6-31G* results. **1**: HC = 1.059 Å, CC = 1.185 Å, CN = 1.307 Å, and NN = 1.084 Å; $E(\text{RHF}, 3-21\text{G}) = -183.75492$ hartrees. **3**: Z matrix; C1/C2 1 1.317/H1 2 1.067 1 129.838/H2 1 1.072 2 118.388 3 0.000/H3 1 1.072 2 123.702 3 180.000/N1 2 1.440 1 118.919 3 0.000/X 6 1.000 2 90.000 3 0.000/N2 6 1.081 7 88.409 2 180.000, and $E(\text{RHF}, 3-21\text{G}) = -184.997067$ hartrees. **4**: Z matrix; C1/C2 1 1.259/X 2 1.000 1 90.000/H1 2 1.068 3 90.000 1 180.000/H2 1 1.086 2 120.893 3 0.000/H3 1 1.086 2 120.893 3 180.000, and $E(\text{RHF}, 3-21\text{G}) = -76.655774$ hartrees.

(35) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. *J. Am. Chem. Soc.* **1982**, *104*, 2797.

(36) (a) The structure³¹ of $\text{H}-\text{C}\equiv\text{C}-\text{H}$ at RHF/6-31G*: CH = 1.057 Å, CC = 1.185 Å. (b) The structure and energy of $\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{H}$ at RHF/6-31G*: CH = 1.057 Å, $\text{C}\equiv\text{C} = 1.187$ Å, C-C = 1.389 Å, $E = -152.497928$ hartrees.

(37) Streitwieser, A., Jr.; Heathcock, C. H. *Introduction to Organic Chemistry*, 2nd ed.; Macmillan: New York, 1981; p 334.

(38) A single CN bond is about 1.47 Å, as in methylamine, and a CN double bond is about 1.27 Å, as in methyleneimine. The bond shortening associated with a change in hybridization from a $\text{C}(\text{sp}^2)-\text{N}(\text{sp}^2)$ to a $\text{C}(\text{sp})-\text{N}(\text{sp})$ double bond can be estimated to be about 0.03 Å.³⁷

(39) Frequencies (in cm^{-1}) and vibrational zero-point energies (ZPE, in kcal mol^{-1}) calculated at 6-31G*. For **1**: ZPE = 19.0, 251.0 (π), 589.2 (π), 927.8 (π), $\nu_{\text{CN}} = 985.1$ (σ), $\nu_{\text{CC}} = 2407.2$ (σ), $\nu_{\text{NN}} = 2768.1$ (σ), $\nu_{\text{CH}} = 3600.6$ (σ). For **3**: ZPE = 34.3, 270.0 (a'), 389.7 (a''), 598.9 (a'), 755.9 (a''), $\nu_{\text{CN}} = 761.7$ (a'), 1015.4 (a''), 1158.7 (a'), 1201.9 (a''), 1418.2 (a'), 1533.4 (a'), $\nu_{\text{CC}} = 1784.7$ (a'), $\nu_{\text{NN}} = 2764.6$ (a'), 3369.5 (a'), 3462.8 (a'), 3474.4 (a'). For **4**: ZPE = 23.9, 516.7 (b_2), 695.8 (b_1), 1060.3 (b_1), 1178.9 (b_2), 1378.0 (a_1), $\nu_{\text{CC}} = 1836.9$ (a_1), 3244.9 (a_1), 3338.2 (b_2), 3502.4 (a_1). For **5**: ZPE = 30.7, 374.3 (e), $\nu_{\text{CN}} = 642.9$ (a_1), 1248.5 (e), 1546.3 (a_1), 1574.5 (e), $\nu_{\text{NN}} = 2814.7$ (a_1), 3267.0 (a_1), 3408.0 (e). For **6**:³¹ ZPE = 21.2, 1516.8 (a_2''), 1538.8 (e'), 3261.7 (a_1'), 3471.5 (e'). For N_2 :³¹ ZPE = 3.9, 2761.5 (σ_g).

Table IX. Energy Differences (in kcal mol^{-1}) between the Diazonium Ions and the Ground States of the Dissociation Products as Obtained at the SCF Level and at the Various Levels of Perturbation Theory^a

method	$1 \rightarrow 2 + \text{N}_2$	$3 \rightarrow 4 + \text{N}_2$	$5 \rightarrow 6 + \text{N}_2$
SCF	37.1 (42.8)	12.1 (18.0)	21.0 (26.0 ^b)
MP2	96.3 (101.2)	28.1 (34.0)	40.6 (45.6)
MP3	83.6 (88.5)	23.5 (29.4)	36.9 (41.9)
MP4(DQ)	82.5 (87.4)	23.1 (29.0)	36.7 (41.7)
MP4(SDQ)	83.0 (87.9)	22.5 (28.4)	37.4 (42.4)

^a Vibrational zero-point energy corrections are included (uncorrected values are given in parentheses); vibrational zero-point energies are scaled (factor 0.9) to account for their overestimation.³³ All values were calculated on the basis of the HF/6-31G* structures and with the 6-31G* basis set. ^b Reference 2.

Table X. Electron Assignments for the Low-Lying States of Ethynyl Cation in the Point Groups $C_{\infty v}$ (C_{2v} for the Π states) and C_2

state	axial symmetry		planar symmetry	
	elec assign	state	elec assign	state
$^1\Sigma^+(\pi^4)$	8a, 4e	$^1A'$	10a', 2a''	
$^1\Pi$	9a, 2b ₁ , 1b ₂	$^1A''$	11a', 1a''	
	9a, 1b ₁ , 2b ₂	$^1A'$	10a', 2a''	
$^3\Pi$	9a, 2b ₁ , 1b ₂	$^1A''$	11a', 1a''	
	9a, 1b ₁ , 2b ₂	$^1A'$	10a', 2a''	
$^1\Delta$	10a, 2b ₁	$^1A'$	12a'	
	10a, 2b ₂	$^1A'$	10a', 2a''	
$^1\Sigma^+(\pi^2)$	10a, 2e	$^1A''$	11a', 1a''	
$^3\Sigma^-$	10a, 2e	$^1A''$	11a', 1a''	

and methyldiazonium ion (**5**, 1.510 Å,² bond order ≈ 1.0). The relative strengths of the CN bonds in the diazonium compounds **1**, **3**, and **5** are also reflected in the frequencies of the CN stretching vibrations; see Table VIII. The NN bond length increases only slightly with the degree of unsaturation. The NN bond length in **1** is practically identical with the bond length³² in N_2 and close to the experimental bond length⁴⁰ of N_2 (1.098 Å).

Optimization of **1** at the MP2/6-31G* level affects primarily the CC and the NN bond lengths. The CC bond length increases to a value of 1.23 Å. The NN bond length becomes 1.15 Å at this level, and the increase is of the order of the bond length increase found for N_2 in going from the HF to the MP2 level.³² The CH bond length is found to be 1.08 Å and the CN bond length is decreased by 0.02 Å in comparison to the HF result.

The calculated structure and the relative changes of bond lengths with respect to ethynyl cation can be rationalized with the following simplified bonding scheme. This bonding scheme is best discussed by considering the association instead of the dissociation reaction. The nitrogen molecule approaches **2** along the linear least motion path and a nitrogen lone pair is used to form a σ -donor bond with the terminal carbon atom of **2**. **2** has to provide a σ -LUMO and its electronic structure in the bond-forming process should therefore be dominated by the configuration $[\text{core}]\sigma^2\sigma^2\pi^4$ (vide infra). The overlap of the π system in HCC^+ and N_2 results in two orthogonal 4-center-4-electron π systems. In addition to the bond order of one, due to the σ bond, each of the π systems contributes a bond order of about 0.5 to the CN bond. The increase in the CC bond length of **1** as compared to **2** could be explained on the basis of π -electron delocalization and is probably also related to the position of the charge. The charge of HCC^+ polarizes the molecule to a great extent, thereby shifting electron density from the CH region into the CC bond. This argument explains the long CH distance and the short CC distance in this cation. In **1** the charge is no longer concentrated on the carbon atom. The polarization effects in the HCC part of the molecule should therefore be less pronounced. The calculations show indeed that the CH bond becomes shorter and that the CC bond is lengthened in **1** as compared to **2**.

(40) *CRC Handbook of Chemistry and Physics*, 63rd ed.; CRC Press: Boca Raton, FL, 1982/83; p F-181.

5. Thermal Dissociation

1. Orbital Symmetry and Electron Assignment. In order to apply the Woodward–Hoffmann rules¹⁶ to the discussion of the possibility of reaching one of the states of **2** by thermal dissociation of **1**, the states have to be classified according to their orbital symmetries. In doing so we follow the systematic approach on how to construct state correlation diagrams given by Yamabe et al.^{41,42} The symmetry rule can then be expressed as the criterion that the electron assignment must be conserved in the reactions.

In the case of states where the molecular symmetry is preserved in the symmetry of the electronic wave function, the molecular orbitals are either totally symmetric, *a*, or they belong to the degenerate representation *e*. In the Π states the degeneracy of the π orbitals vanishes, the symmetry of the electronic wave function is reduced from $C_{\infty v}$ to C_{2v} , and the set of π orbitals splits into molecular orbitals of symmetry b_1 and b_2 . The electron assignment of a given state is then obtained by counting the number of electrons in each symmetry orbital. The electron assignments obtained in this way are shown in Table X. The electron assignments are given with respect to the point group $C_{\infty v}$ (or C_{2v} for the Π states) and its subgroup C_s for reasons discussed later.

The electron assignments for the diazonium compound are (18a,8e) in the point group $C_{\infty v}$ and (22a',4a'') in the point group C_s , respectively. The nitrogen molecule has an electron count of (10a,4e) in $D_{\infty h}$ and of (12a',2a'') in C_s symmetry, respectively. For thermal dissociation proceeding along the linear least motion reaction path to be allowed according to the Woodward–Hoffmann rule the ethynyl cation then has to have the electron assignment (8a,4e). If the dissociation proceeds only with the retention of a symmetry plane in the course of the reaction, then the electron count of the ethynyl cation has to be (10a',2a'') in order for the reaction to be allowed by orbital symmetry.

The electron assignments given in Table X show that only the dissociation of **1** to the $^1\Sigma^+(\pi^4)$ state of **2** is symmetry allowed in the least motion reaction pathway. Assuming a nonlinear dissociation in which all atoms remain in a common plane, the dissociation is also symmetry allowed with respect to the states $^1\Delta$ and $^1\Pi$. However, nonlinear dissociations toward these states should be accompanied by large activation barriers due to unnecessary motion of atoms. A fast scan of the energy surface of **1** starting at nonlinear geometries with fixed CN bond lengths in the range between 1.4 and 2.0 Å with a smaller basis set³⁵ revealed that **1** returns to linearity in all cases.⁴³ The nonlinear dissociation path has therefore not been considered further. Dissociation toward the remaining states is forbidden by orbital symmetry, and in the case of the triplet states, $^3\Pi$ and $^3\Sigma^-$, the dissociation is spin forbidden as well.

2. Least Motion Dissociation. The least motion dissociation of **1** into N_2 and **2**, in its $^1\Sigma^+(\pi^4)$ state, is allowed by orbital symmetry. Assuming a reaction without barrier (the zero-point energy corrected) activation energy is endothermic by 144.1 kcal mol⁻¹ at the RHF level (see Tables VI, VII, and IX). The dissociation energy is increased when correlation corrections are taken into account. At the MP4(SDQ)/6-31G*//HF/6-31G* level the dissociation energy is 152.1 kcal mol⁻¹, and at the highest level applied, MP4(SDQ)/6-31G*//MP2/6-31G*, a dissociation energy of 150.2 kcal mol⁻¹ has been obtained.

At this point it is important to consider how the presence of the $^1\Sigma^+(\pi^2)$ state of the ethynyl cation affects the least motion

path dissociation. This state does not have the orbital symmetry required that makes the dissociation toward this state allowed according to the Woodward–Hoffmann rule. However, this state has the same total symmetry as the higher lying $^1\Sigma^+(\pi^4)$ state, and such a unique electron assignment as given in Table X is incorrect in a strict sense.⁴¹ The electron assignment is only a valid approximation if the contaminations introduced by other electron assignments are small. In other words the two $^1\Sigma^+$ states can mix and an avoided crossing can occur. According to the systematic approach by Yamabe et al. such an avoided crossing has to be given when two lines between states of the same symmetry but of different electron assignment cross.⁴¹ By taking the occurrence of this avoided crossing into account the dissociation of **1** leads to fragments in which HCC⁺ in its $^1\Sigma^+(\pi^2)$ state is the product. Consequently, the energy required for the orbital symmetry allowed dissociation represents an upper limit for the activation energy of the dissociation following the least motion path. The lower limit is determined by the difference between the energy of the diazonium compound and the combined energies of N_2 and HCC⁺ in its $^1\Sigma^+(\pi^2)$ state; this limit is 96.6 kcal mol⁻¹ at the MP4(SDQ)/6-31G*//HF/6-31G* level and 96.2 kcal mol⁻¹ at the MP4/6-31G*//MP2/6-31G* level, respectively. The actual activation energy is expected to be substantially above this lower limit for the following reasons.

In order to reach the lower $^1\Sigma^+$ state of ethynyl cation an electron redistribution has to occur along the dissociation path which places two π electrons of **1** in the carbon's σ lone pair. Such electron redistributions are accompanied by large activation energies. Moreover, it is more than likely that the transition state of the dissociation reaction toward the $^1\Sigma^+(\pi^2)$ state is a late transition state. In order for this electronic redistribution in the HCC fragment to occur, the terminal carbon has to provide an empty σ orbital. This carbon σ orbital is used for the CN σ bond of **1** and, hence, the electronic redistribution can only occur at a point on the reaction coordinate where the bond to the N_2 fragment is almost completely broken. The activation energy for the dissociation reaction leading to the ethynyl cation in its $^1\Sigma^+(\pi^2)$ state is therefore expected to be much closer to the value of the binding energy of N_2 and HCC⁺, $^1\Sigma^+(\pi^4)$, than to the binding energy of N_2 and HCC⁺, $^1\Sigma^+(\pi^2)$.

The significance of the reaction energies lies in their large order of magnitude as compared to the dissociation energies of 22.5 and 37.4 kcal mol⁻¹ calculated for **3** and **5**, respectively, at the MP4(SDQ)/6-31G*//HF/6-31G* level (see Tables V and IX). The binding energy of 150.2 kcal mol⁻¹ obtained at the highest applied level for the combination of N_2 and $^1\Sigma^+(\pi^4)$, defining the upper limit of the activation energy, is so high that a thermal least motion path dissociation can safely be excluded as a possible reaction channel, even in the unlikely event that the avoided crossing would reduce the activation barrier by 30 kcal mol⁻¹. The temperature required by such activation energies would promote the homolytic cleavage of the CH bond and would lead to decomposition of **1**. From a comparison of the calculated binding energies between molecular nitrogen and the ethynyl cation in its $^1\Sigma^+$ states with typical bond energies for CN bonds⁴⁴ one again reaches the conclusion that the CN bond in the diazonium ion **1** is a rather strong one with a bond order close to that of a double bond.

6. Electron Density Analysis

The singlet states $^1\Sigma^+$ of the ethynyl cation are rather unique with respect to their electronic structures. In the electronic structure of the π^4 state the terminal carbon is extremely electron deficient. This carbon atom participates only in an electron sextet and, even worse, only two of the electrons of this sextet occupy σ orbitals. The electronic structure of the π^2 state is most peculiar in that it may be regarded as a combination of an unsaturated singlet carbene with a vinyl cation and both of the carbon atoms are formally assigned sextets. In order to gain some insight into

(41) (a) Yamabe, S.; Minato, T.; Osamura, Y. *Int. J. Quantum Chem.* **1980**, *18*, 243. (b) Osamura, Y. Ph.D. Dissertation, Osaka City University, 1979.

(42) For some further applications see: (a) Yamabe, S.; Minato, T.; Osamura, Y. *J. Am. Chem. Soc.* **1979**, *101*, 4525. (b) Osamura, Y.; Nishimoto, K. *Theor. Chim. Acta* **1979**, *51*, 257. (c) Minato, T.; Osamura, Y.; Yamabe, S.; Fukui, K. *J. Am. Chem. Soc.* **1980**, *103*, 581.

(43) The structures (in Å) and the energies (in kcal mol⁻¹) as compared to the equilibrium energy) of **1** for a given CN bond length are as follows. CN = 1.4, CH = 1.059, CC = 1.183, NN = 1.081, and *E* = 4.8; CN = 1.6, CH = 1.059, CC = 1.179, NN = 1.079, and *E* = 32.7; CN = 1.8, CH = 1.059, CC = 1.177, NN = 1.079, and *E* = 64.4; CN = 2.0, CH = 1.060, CC = 1.177, NN = 1.080, and *E* = 91.2.

(44) Typical bond energies of CN bonds: C–N 73 kcal mol⁻¹, C≡N 147 kcal mol⁻¹, C=N 213 kcal mol⁻¹; see ref 37, p 1195.

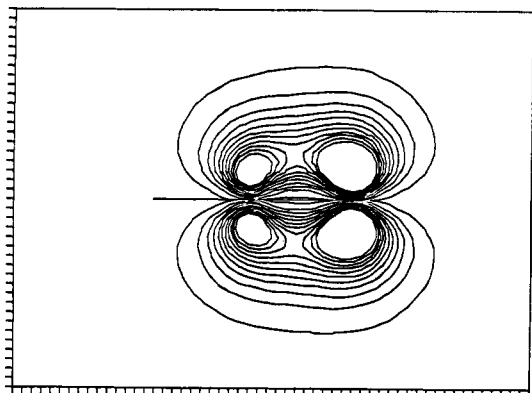
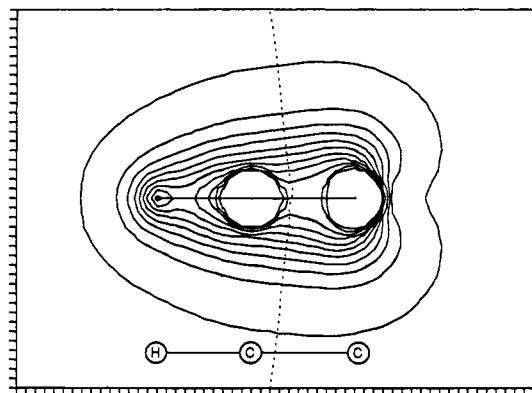


Figure 2. Contour maps of the cross sections of the total (top) and the π electron densities of ethynyl cation (**2**) in its $^1\Sigma^+(\pi^4)$ state. The contour levels are (in $e\text{ au}^{-3}$) from 0.005 to 0.405 by 0.04 for the total density and from 0.005 to 0.105 by 0.01 for the π density.

the electronic structures of these states cross sections of the electron density are presented. Correlation effects certainly affect the quantitative features since both $^1\Sigma^+$ states are contaminated by other configurations, but the general characteristics of the electron distributions are presumably maintained.

In Figure 2 contour maps of the cross sections of the total density and of the π density are shown for the π^4 state. The highly electronegative terminal carbon atom (C_t) polarizes the electron density in the CC-bonding region to a very large extent. The cross section of the zero-flux surface of the gradient of the density⁴⁵ with the molecular plane is shown as a dotted line. The bond critical point⁴⁵ along the CC bond path appears only 0.44 Å away from the central carbon atom (density is 0.346 e au^{-3}) and shows the extreme polarization of the CC- σ density toward the sextet carbon. This polarization of σ density is accompanied by polarization of the π density in the same direction, as evidenced by the contour map of the π density. Polarization of electron density of the π^2 state is less severe and it affects electron density shifts in the *opposite* direction as compared to the π^4 state; the C_t carbon is less electron deficient than the other carbon in this electronic state. The bond critical point (see Figure 3) appears 0.75 Å away from the central carbon atom (density is 0.342 e au^{-3}), only moderately dislocated from the center of the bond and shifted toward the terminal carbon atom. Most of the π density is accumulated at the central carbon atom (C_c).

The cross sections of the electron density of **1**, shown in Figure 4, confirm the electronic structure of the molecule as discussed earlier on the basis of its optimized geometry. In the above discussed simplified bonding scheme the CN bond is formed by filling the "sp-hole" of the HCC fragment with nitrogen lone pair density. Nevertheless, the C_t carbon still remains electron deficient as evidenced by the analysis of the bonds to this atom. The bond

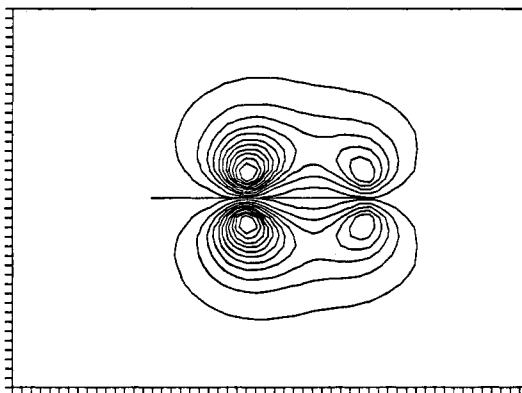
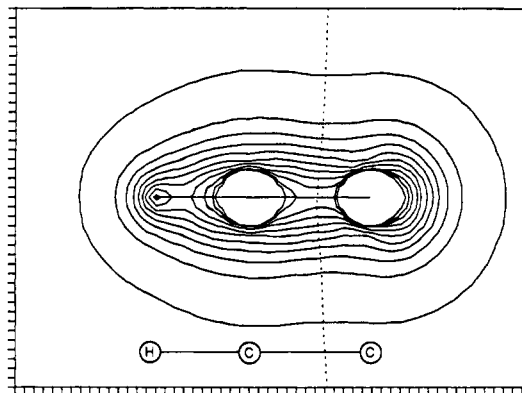


Figure 3. Contour maps of the cross sections of the total (top) and the π electron densities of ethynyl cation (**2**) in its $^1\Sigma^+(\pi^2)$ state. Contour levels are as in Figure 2.

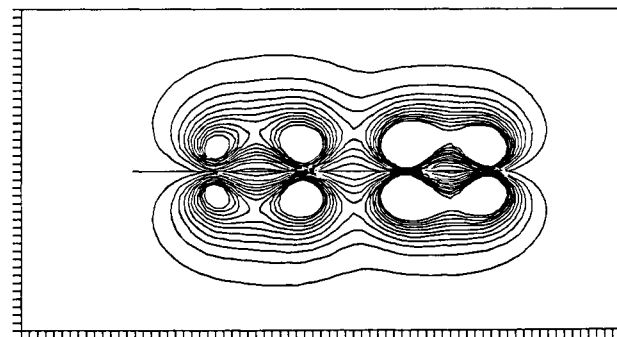
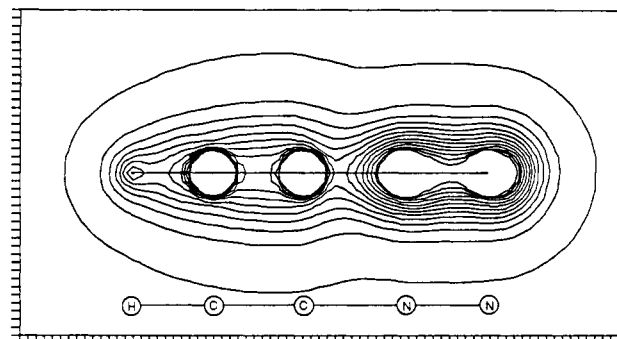


Figure 4. Contour maps of the cross sections of the total (top) and the π electron densities of ethynyldiazonium ion (**1**). Contour levels for the total density are (in $e\text{ au}^{-3}$) from 0.005 to 0.605 by 0.04 and the contour level settings for the π density are as in Figures 2 and 3.

critical point of the CN bond (density is 0.277 e au^{-3}) is located much closer to carbon than to nitrogen, 0.41 and 0.91 Å away from C and N, respectively. The bond critical point of the CC

(45) Bader, R. F. W.; Anderson, S. G.; Duke, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 1389 and references therein.

bond (density is 0.340 e au^{-3}) remains further away from the C_i carbon (0.70 \AA) than from the central C atom (0.48 \AA) and indicates a polarization of the σ density in a way as to reduce the electron deficiency of the C_i carbon. A similar polarization is found in the π density; π density is shifted from the HC fragment to the C_i carbon atom. Within the NN fragment of the diazonium ion the expected features can be observed. As a result of the delocalization of N_p density an electron shift from the N(N) atom to the N(C) atom occurs in the σ and in the π systems. The bond critical point of the NN bond (density is 0.641 e au^{-3}) appears 0.58 \AA away from the N(C) atom.

The electron density diagrams presented show that the electron distribution of the HCC fragment in **1** greatly resembles the electron distribution of **2** in its $^1\Sigma^+(\pi^4)$ state. The electron distribution in this fragment is characterized by strong polarization of the bonds toward the electron deficient C_i carbon. Upon the initial elongation of the CN bond the electron deficiency of the C_i atom should increase and the electron distribution of the HCC fragment should become even more similar to the density distribution in ethynyl cation in its $^1\Sigma^+(\pi^4)$ state. The subsequent reorganization of the electronic distribution of the HCC fragment toward the density distribution of the $^1\Sigma^+(\pi^2)$ state involves the displacement of two π electrons into a σ orbital and the reorganization of the density results in the inversion of the direction of the electron density polarization. The analysis of the electron density distribution thus provides a rationale for and supports the assumed late transition state for the reaction $\mathbf{1} \rightarrow \mathbf{2} [^1\Sigma^+(\pi^2)] + \text{N}_2$ and its high activation barrier.

7. Conclusion

The dissociation reaction $\text{HCCNN}^+ (\mathbf{1}) \rightarrow \text{HCC}^+ (\mathbf{2}) + \text{N}_2$ has been investigated. Since the total spin multiplicity is maintained in the reaction, **2** is formed in a singlet state. For the low-lying singlet states the ordering $^1\Sigma^+(\pi^2) \approx ^1\Pi < ^1\Delta < ^1\Sigma^+(\pi^4)$ has been obtained. Dissociation toward the states $^1\Delta$ and $^1\Pi$ involves nonlinear reaction pathways and should therefore be associated with large activation barriers. Only the $^1\Sigma^+(\pi^4)$ state is correlated to the ground state of **1** by orbital symmetry. The linear least-motion dissociation leads, however, to ethynyl cation in its $^1\Sigma^+(\pi^2)$ state as the primary reaction product since the two

$^1\Sigma^+$ states mix and cause an avoided crossing. The lower and upper limits to the activation energy for the thermal dissociation are given by the binding energies of N_2 with **2** in its $^1\Sigma^+(\pi^2)$ and $^1\Sigma^+(\pi^4)$ states, respectively. At the MP4(SDQ)/6-31G*/MP2/6-31G* level values of 96.2 and $150.2 \text{ kcal mol}^{-1}$ have been calculated, respectively. The calculation of the actual activation energy requires a multiconfiguration calculation which is beyond our computational capabilities. However, simple arguments based on bond formation in the association reaction and electron density redistribution considerations strongly suggest a late transition state for the dissociation reaction. The activation energy is therefore predicted to be much closer to the upper rather than to the lower limit.

The significance of the reaction energies lies in their large magnitude as compared to the dissociation energies of the vinylidiazonium and the methyldiazonium ions. Even if the avoided crossing would only be associated with a small barrier, which is not likely, the activation energy would still be such that the thermal unimolecular dissociation does not occur. The ethynyldiazonium ion is not sufficiently unstable to compensate for the high intrinsic instability of **2**. The CN bond in **1** is rather strong as evidenced by the calculated bond length of 1.32 \AA , the frequency of the CN stretching vibration, and the high electron density at the bond critical point. Stabilizing substituents and solvent effects could help to increase the thermodynamic stability of the products more than that of the diazonium ion, but it appears unlikely that such modest alteration should make the reaction possible.

If C-sp-centered carbenium ions should ever become accessible, other precursors have to be thought of that fulfill two requirements. The precursor has to have a higher intrinsic instability and its fragmentation has to yield one or more small molecules with very high thermodynamic stability. Theoretical investigations of precursors that fulfill these requirements are in progress.

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