Formation of the *cyclo*-Pentazolate N_5^- Anion by High-Energy Dissociation of Phenylpentazole Anions

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The recent successful preparation of the *cyclo*-pentazolate N_5^- anion (*cyclo*-N_5^-) by the dissociation of the *p*-pentazolylphenolate anion using high-energy collisions is accounted for by considering the electronic structure of the system. It is shown that a symmetry-allowed conical intersection is involved, leading directly from an electronically excited state of the precursor to ground-state *cyclo*-N_5^-. The presence of the conical intersection is manifested by the structure of the thermal transition state of the C−N bond dissociation reaction, which is shown to be bent. A similar mechanism is proposed for the formation of *cyclo*-N_5^- from the dimethylaminophenylpentazole anion radical. High-level model calculations on the dissociation of these precursors and of the $HN_5^{\bullet -}$ anion radical, which is the parent molecule of the larger aromatic pentazolates, support the proposed model.

I. Introduction

Although the stability of the *cyclo*-pentazole N_5^- anion was recognized long ago by computations, attempts to prepare it (as well as that of the parent HN_5 molecule) were unsuccessful for many years. The task was finally achieved recently by two groups, both using precursors having a *cyclo*-pentazol group attached to an aromatic system. One is the selective dissociation of the C−N bond in substituted phenylpentazolate anions, stable compounds known since the work of Huisgen and Ugi 40 years ago.[1] The challenge is to keep the highly reactive N_5^- ring intact while breaking the C−N bond. Vij and co-workers[2] reported that dissociation of the *p*-pentazolylphenolate anion by *low-energy* collisions with an inert gas resulted in fragmentation of the pentazolate ring (by elimination of N_2) while *high-energy* collisions led to neat scission of the C−N bond and charge transfer to the pentazolate ring (Figure 1). No theoretical explanation to this seemingly counter-intuitive result (no fragmentation of the pentazolate ring upon higher energy collisions) was offered in the article.

More recently, Östmark and co-workers[3] showed that the *cyclo*-pentazolate anion can also be produced by laser desorption ionization (LDI) time-of-flight (TOF) mass spectroscopy of solid *p*-dimethylaminophenylpentazole. The proposed mechanism was electron attachment to form the dimethylaminophenylpentazole anion radical, which dissociates to form the pentazolate anion and a dimethylaminophenyl radical. This system is different from the *p*-pentazolylphenolate anion one in at least two ways: First, the reactant is an anion radical (open shell system) and not a closed shell one. Second, the negative charge is mostly residing on the pentazolate ring in both reactant and product, whereas in the *p*-pentazolylphenolate anion the charge is initially situated largely on the oxygen atom and is transferred to the N_5 ring in the course of the reaction.

In this paper we discuss a model that can account for these experimental findings. In particular it turns out that the apparently counter-intuitive result obtained for the *p*-pentazolylphenolate anion is actually expected considering the nature of the electronic states of the reactants and products.

The analysis presented in this paper is based on the idea that very rapid transitions from an electronically excited state to the ground-state surface are possible through conical intersections.[4−7] It is shown that in the reactive systems studied in refs 2 and 3, low-lying symmetry-allowed conical intersections[8] are present. A necessary condition for their existence is that the ground electronic state of the products be of different symmetry than that of the reactant. In the case of the closed shell anion system, the reactant anion has A_1 symmetry in the C_{2v} point group. The dissociation products are the totally symmetric *cyclo*-pentazolate anion plus a biradical (the oxocyclohexadienylidene biradical, abbreviated as OCH biradical, Figure 1). Spin conservation requires that the reaction will yield initially singlet states only, even though the biradical has a triplet ground state. Chung and co-workers[9] have recently shown that several singlet states of the OCH biradical are low lying, the lowest being of B_1 symmetry in C_{2v}. This happenstance led us to search for conical intersections in this system that might be involved in the high-energy reaction route. A similar symmetry-based argument holds for the anion radical system of ref 3.

The proper theoretical description of electronic structures of open-shell systems such as radicals, biradicals, and electronically excited states often requires more than one configuration. We therefore used the complete active space[10] (CASSCF) method to analyze the system. A relatively small model system, the $HN_5^{\bullet -}$ anion radical, whose size allows a rather complete analysis by using configuration interaction techniques, was chosen for an initial analysis. High-level ab initio calculations on this model system, as well as on the larger ones, support the proposed model.

II. Methodology

The singlet product ground state (OCH biradical + *cyclo*-pentazolate anion) correlates directly with the 1^1B_1 *excited state*

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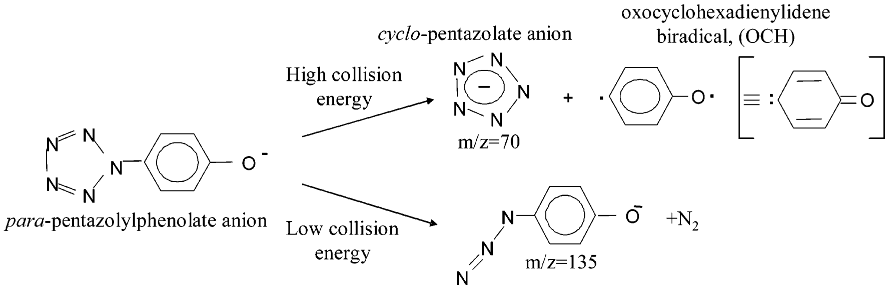
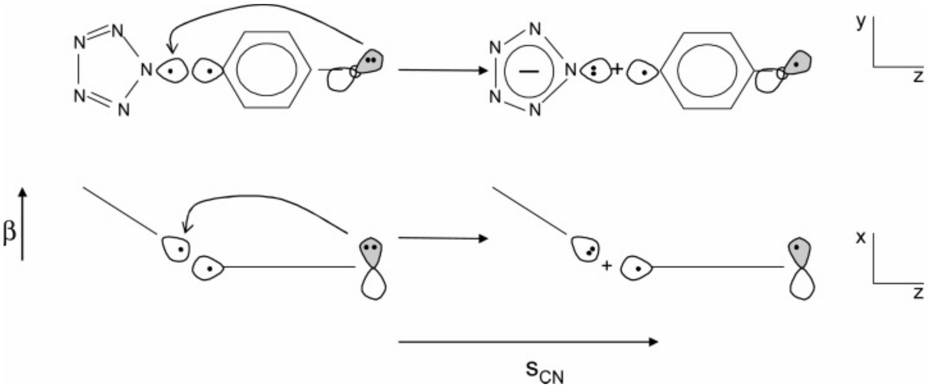


Figure 1. Dissociation patterns observed for the *p*-pentazolylphenolate anion: low-energy collisions lead to N_2 extrusion while high-energy collisions form the cyclopentazolate anion plus the 1,4-oxo-2,5-cyclohexadienylidene biradical (after ref 2). For the five VB structures representing the biradical (shown schematically in square brackets) see ref 9.

SCHEME 1: Schematic Representation of the C−N Bond-Breaking Reaction of the *p*-Pentazolylphenolate Anion[a]



[a] An electron is transferred from the oxygen p_x orbital to a sp^2 orbital of the nitrogen atom. This can only be possible if the two orbitals can interact, i.e., they must have the same symmetry. An out-of-plane bend of the pentazolate ring with respect to the phenyl ring reduces the symmetry to C_s, in which both orbitals have the same symmetry, A′. The top part shows the system projected on the *yz* plane, and bottom one the system on the *xz* plane. Note that the reaction can proceed "above" the phenyl ring plane, or "below" it. The first option only is depicted schematically by the solid line representing the pentazolate ring in the lower part of the figure. The second option requires an inversion of the oxygen p_x orbital; hence β is a sign-inverting coordinate. The coordinates s_{CN} and β are defined in the text.

of the reactant *p*-pentazolylphenolate anion. The first *excited state* of the product pair 1^1A_1 symmetry correlates directly with the *ground state* of the *p*-pentazolylphenolate anion. Thus, a symmetry-allowed curve crossing of the type $1^1A_1/1^1B_1$ is expected in this system; comparable situations have been extensively studied.[8,11] While the complete theoretical characterization of the potential energy surface of these polyatomic systems is obviously out of question, only two nuclear coordinates are required to determine the crossing region[12] leading to a conical intersection. One of them must be a totally symmetric one—the crossing can take place only along such a coordinate; the other (the coupling coordinate) is a deformation that transforms the two states to a common symmetry so that they can efficiently interact. The symmetry of this deformation is that of the direct product of the two irreducible representations of the electronically excited states,[8] in the present instance B_1. This coordinate may be found by the principle of maximum vibronic coupling: the energetic splitting of the adiabatic potentials at the conical intersection is a measure of the strength of the vibronic coupling. In this application, normal modes of the reactant are often used.[13]

We use a different approach: it was shown[6] that the coordinates leading to the conical intersection can be constructed from reaction coordinates of elementary chemical reactions that the reactant undergoes. In the present case an obvious choice is the coordinate that leads to the C−N bond dissociation and simultaneously to an electron transfer from the oxygen atom to the N_5 ring. The reaction coordinate clearly includes a C−N bond stretch that is a totally symmetric coordinate (a_1 symmetry in C_{2v}). A nonsymmetric component must also exist—it is an out-of-plane bend of b_1 symmetry. This deformation is required for the realization of the thermal reaction as it makes possible the interaction of the pentazolate ring with the oxygen atom: only by bending the pentazolate ring out of the plane of the phenyl ring can an electron be transferred from the oxygen p_x orbital to a sp^2 orbital of the nitrogen atom (Scheme 1).

By symmetry, two equivalent reaction channels are possible, bending the phenyl ring either "above" the plane of the pentazolate ring or "below" it. Denoting the C−N stretch coordinate by s_{CN}, the upward bend by $+\beta$, and the downward one by $-\beta$, the two reaction coordinates RC_1 and RC_2 may be written as $RC_1 = s_{CN} + \beta$ and $RC_2 = s_{CN} - \beta$.

These two reaction coordinates form a sign-inverting Longuet−Higgins loop that encircles a conical intersection.[14−16] A loop similarly formed by two reaction coordinates was recently discussed for the cis−trans isomerization of the formaldiminium cation.[17] The two symmetry-defined coordinates discussed above are obtained by the in-phase and out-of-phase combinations of RC_1 and RC_2.

The out-of-plane motion required in this type of reaction was noted also in similar reactions: in the recent work of Takeda et al. on the photodissociation of aryl halide anion radicals,[18] the transition state for the C−halogen bond dissociation reaction was found to have a bent carbon−halogen bond. This pattern may be taken as indicating the existence of a conical intersection.

III. Model System

The $HN_5^{\bullet-}$ anion radical is the parent molecule of the dimethylaminophenylpentazole anion radical; it has a similar electronic structure, and hence the basic processes leading to the formation of the pentazolate anion are expected to be similar.

TABLE 1: Calculated Energies of Species Relevant to the Dissociation of the $HN_5^{\bullet -}$ Anion Radical by Using CASSCF(9/7)/DZV with CISD/cc-pVDZ Values in Parentheses

species	energy (hartrees)	rel energy (eV)	symmetry	comments
$HN_5^{\bullet -}$ (GS)	−272.63197 (−273.385409)	0	C_s ($1^2A'$)	
$HN_5^{\bullet -}$	−272.626445 (−273.372805)	0.15 (0.34)	C_{2v} (1^2B_1)	TS between two C_s structures
$HN_3^- + N_2$	(−273.4419489)	(−1.54)	C_1	dissociation products
$HN_5^- \rightarrow H^\bullet + N_{5-\,(TS)}$	−272.602640 (−273.363634)	0.80 (0.59)	C_s ($1^2A'$)	transition state to $H^\bullet + N_5^-$
$H + N_5^-$	−272.632121 (−273.39042)	−0.004 (−0.14)	C_{2v} (1^2A_1)	dissociation products
$H + N_5^-$ (FC)	−272.38939 −272.38784	6.60 6.64	C_{2v} (1^2B_1)/ C_{2v} (1^2A_2)	excited states of dissociation products[a]
$HN_5^- \rightarrow HN_3^- + N_2$ (TS)	(−273.34107)	(1.20)	C_1	transition state to $HN_3^- + N_2$
HN_5 (GS)	−272.675165 (−273.425761)	−1.17 (−1.10)	C_{2v} (1^1A_1)	neutral
$HN_5^{\bullet -}$ (FC)	−272.610739 (−273.354727)	0.58 (0.83)	C_{2v} (1^2B_1)	*b*
$HN_5^{\bullet -}$ (FC)	−272.573674 (−273.309204)	1.58 (2.07)	C_{2v} (1^2A_2)	*c*
$HN_5^{\bullet -}$ (FC)	−272.511062 (−273.306748)	3.29 (2.14)	C_{2v} (1^2A_1)	*d*
$HN_5^{\bullet -}$ (CI)	−272.562550 (−273.335899)	1.88 (1.35)	C_{2v} ($^2B_1/^2A_1$)	conical intersection

[a] These excited states are derived from the degenerate excited state of the N_5^- anion (ref 25). [b] The energy of the 1^2B_1 state of the $HN_5^{\bullet -}$ anion at the geometry of the HN_5 neutral (FC stands for Franck−Condon excitation). [c] The energy of the 1^2A_2 state of the $HN_5^{\bullet -}$ anion at the geometry of the HN_5 neutral. [d] The energy of the 1^2A_1 state of the $HN_5^{\bullet -}$ anion at the geometry of the HN_5 neutral.

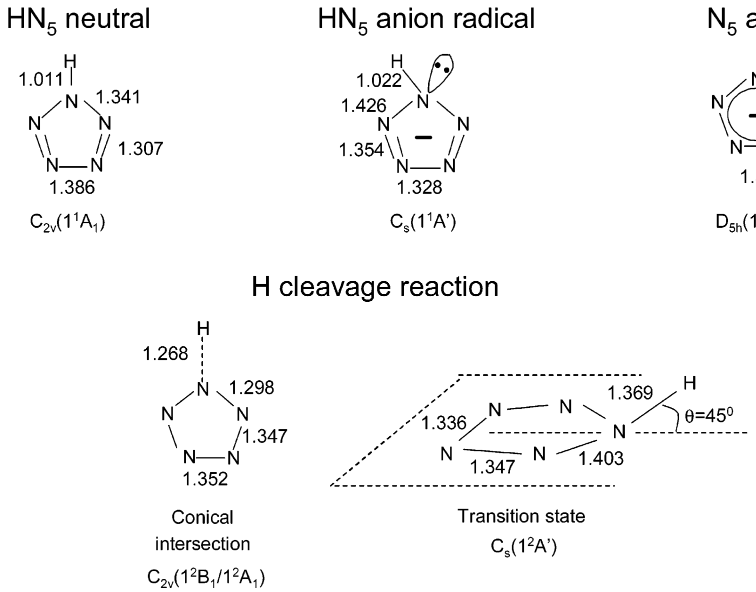


Figure 2. The calculated (CASSCF(9/7)/DZV) structures of some species relevant to the dissociation of $HN_5^{\bullet -}$: (top line from left) the ground-state HN_5 neutral, the $HN_5^{\bullet -}$ anion radical, and the N_5^- anion; (bottom line from left) the conical intersection and the N−H cleavage transition state.

The stable form of HN_5 is calculated to be a closed shell molecule with C_{2v} symmetry[19] in the ground state. The ground state of the $HN_5^{\bullet -}$ anion radical is obtained by adiabatically adding an electron to the closed shell molecule HN_5. The extra electron finds itself in an antibonding π^* orbital, forming a $^2B_1$ state. This species, which is formed by Franck−Condon electron attachment to the neutral, is not the most stable ground-state structure of the $HN_5^{\bullet -}$ anion radical—in fact, it is the transition state between two C_s structures in which the H atom bends out of the pentazolate ring plane. Electronically excited states of the anion radical (of $^2A_1$ and $^2A_2$ symmetry in C_{2v}) can also be formed adiabatically upon electron attachment of HN_5. The 1^2A_1 state is repulsive as the extra electron is located mainly in the lowest energy antibonding σ orbital, which is primarily a NH orbital. Thus, population of the $^2A_1$ state leads to scission of the N−H bond and formation of a ground-state N_5^- pentagon—the *cyclo*-pentazolate anion plus a hydrogen atom.

The rationale for choosing the active space of the CASSCF calculations was based on these considerations. However, even for this small molecule, it was impractical to find an active space that could be appropriate for the two dissociation modes: H−N bond scission and N_2 extrusion. We chose the active space that appeared to provide a valid physical basis for the H−N scission reaction, since a configuration interaction analysis is required to deal with the conical intersection. The active space employed in the CASSCF calculation consisted of seven molecular orbitals: all π orbitals (3 bonding ones and 2 antibonding) and two σ orbitals located primarily on the N−H bond, one bonding and one antibonding. Nine electrons were included, eight occupying the four bonding orbitals in the parent anion radical

TABLE 2: Calculated Energies of Species Relevant to the Dissociation of the *p*-pentazolylphenolate Anion ($OPh\text{-}N_5^-$) by Using CASSCF(12,11)/DZV with CISD/DZV//UCISD/D95V Values in Paretheses

species	energy (hartrees)	rel energy (eV)	symmetry	comments
$OPh\text{-}N_5^-$ (GS)	−576.47762 (−577.231383)	0	C_{2v} ($^1A_1$)	ground state of anion
$OPhN_3^- + N_2$	(−577.270004)	(−1.05)	C_s ($^1A'$)	separated products
$OPh\text{-}N_5^- \rightarrow OPhN_3^- + N_2$ (TS)	(−577.190741)	(1.11)	C_1	transition state for $OPhN_3^- + N_2$ formation
$^{\bullet}OPh^{\bullet} + N_5^-$ (GS)	576.39325 (−577.135782)	2.30 (2.60)	C_{2v} ($^1B_1$)	separated products
$OPh\text{-}N_5^-$ (FC)	−576.18609 (−576.91980)	7.93 (8.48)	C_{2v} (1^1B_1)	first excited state of B_1 symmetry
$OPh\text{-}N_5^-$ (CI)	−576.37574 (−577.110497)	2.77 (3.29)	C_{2v} ($^1B_1/^1A_1$)	conical intersection

and one in a π^* antibonding one. Having done that it was found that a single configuration is in fact dominant and this was the one chosen for a CISD analysis of both reactions.

IV. Computational Details

CASSCF calculations were performed with the GAMESS[20] electronic structure program, and CISD calculations with the GAUSSIAN suite of programs.[21] Initial computations were performed with CASSCF; in most cases it turned out that a single configuration was actually dominant, so that a single configuration method taking into account electron correlation such as CISD provided a satisfactory approximation. The CISD calculation was undertaken on the *ground-state potential surface* to locate minima and transition states. This was required as a complete active space that would be appropriate for all ground-state reactions was out of the question due to the size of the molecules. In particular we wanted to compare on a common basis the different competing ground-state dissociation channels. The N_2 extrusion channel requires several σ orbitals in addition to the π system, making the application of CASSCF impractical for this purpose. Several comparative runs were made with CASSCF and CISD, resulting in satisfactory agreement. The basis sets used were cc-pVDZ for HN_5, HN_5^-, and N_5^- and DZV for the *p*-pentazolylphenolate anion system.

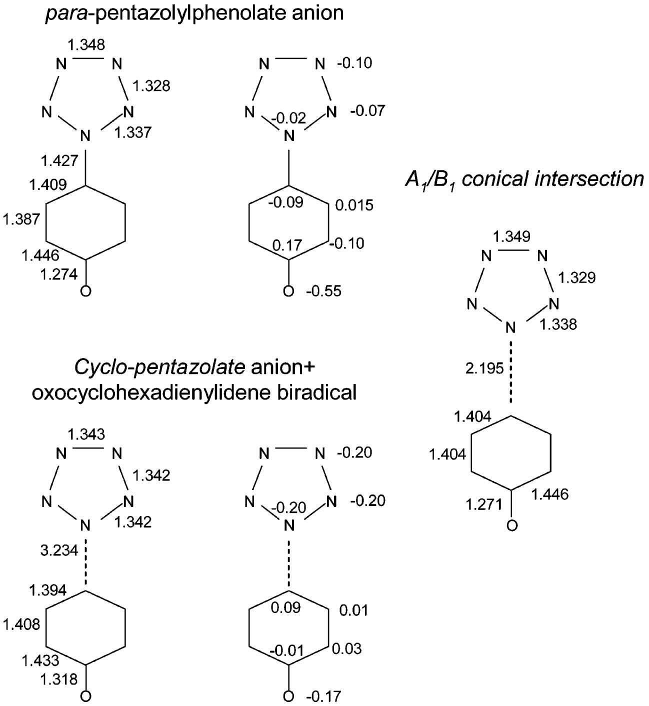


Figure 3. The calculated (CASSCF(12,11)/DZV) structures (left) and charge distribution (Löwdin, middle) of the *p*-pentazolylphenolate anion (top part) and its products (bottom part) following C−N bond scission. The structure of the conical intersection is shown on the right-hand side. The distance between the two rings in the bottom part is larger than 3 Å; the value shown was used for this illustration.

V. Results

The $HN_5^{\bullet-}$ Anion Radical: A Model System. This anion radical was chosen to simulate the dissociation of the dimethylaminophenylpentazole anion radical implicated in the experiments of ref 3. As explained in Section III, this smaller anion radical is expected to undergo a similar reaction (a C−N bond scission is replaced by a H−N one); moreover, since the C−N bond dissociation reaction of the closed shell *p*-pentazolylphenolate anion leads to an open shell system, it turns out that this parent anion radical is also a good model for the latter.

The calculated energies of the three lowest electronic states of the $HN_5^{\bullet-}$ anion radical and other species relevant to the reactivity of the system (products, transition states, conical intersection) are reported in Table 1. Some calculated structures are shown in Figure 2.

Comparing the data obtained by the CASSCF and CISD methods shows reasonably good agreement, justifying the use of the latter.

The *p*-Pentazolylphenolate Anion System. The energies of the *p*-pentazolylphenolate anion, its two dissociation products, and the transition state for N_2 extrusion were calculated by using the CISD method. The results, along with the CASSCF(12,11)/DZV data where available, are listed in Table 2.

The calculation of the transition state for C−N bond scission turned out to be superfluous, as we were interested in the relative energy barriers of the two reactions. The barrier of the C−N bond scission reaction is higher than the exothermicity of the reaction, which was found to be much larger than the barrier for the N_2 extrusion (2.60 vs 1.11 eV, Table 2).

The active space used for the calculation of the conical intersection included 10 π orbitals (6 occupied and 4 virtual) and one σ orbital (the antibonding σ^*_{CN} orbital) that is important in the C−N dissociation reaction. The calculated structures and charge distributions of the ground state system are shown in Figure 3. While the negative charge is largely concentrated on the oxygen atom in the *p*-pentazolylphenolate anion, it is essentially completely transferred to the *cyclo*-pentazolate ring when the C−N bond is stretched. We have also calculated the energy of the separated fragments in the first excited state (the $^1A_1$ state). The energy difference between the ground state and this excited state is due to the electronic excitation of the oxocyclohexadienylidene biradical that has a very low-lying excited state. The results agreed very well with those of Chung et al.,[9] and are therefore not described here in detail: for instance, the energy separation between the $^1B_1$ and $^1A_1$ states at the CASSCF(10/12)DZV level was about 12 kcal/mol, matching the result of ref 9 (performed with a smaller active

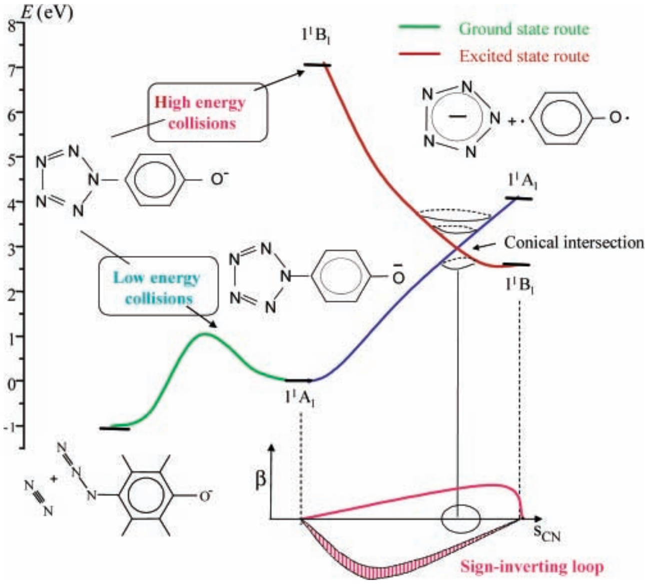


Figure 4. A scheme showing the energy levels of the *p*-pentazolylphenolate anion prepared by collisions of electrons with the neutral precursor. Low-energy collisions lead primarily to the ground state of the anion, which preferentially extrudes N_2, while high-energy collisions form an excited state that dissociates to the cyclopentazolate anion via a conical intersection. The coordinates s_{CN} and β of the sign-inverting loop (see Methodology Section) encircling the conical intersection (cherry color) are described in Scheme 1. Calculated numerical values are reported in Table 2.

space). The structure and energy of the conical intersection are also shown in Figure 3 and listed in Table 2.

VI. Discussion

Dissociation of the *p*-Pentazolylphenolate Anion. The thermodynamically most stable primary products are N_2 + *p*-azidophenolate anion (which dissociates further by N_2 release). The barrier for this reaction was calculated to be 1.1 eV. Scission of the C−N bond leads to formation of *cyclo*-N_5^- and the OCH biradical. The barrier for this reaction is much higher, as the reaction is endothermic ($\Delta H = 2.6$ eV). In this reaction an electron is transferred from the p-orbital of the oxygen atom to the pentazolate ring (a sp^2 orbital of the nitrogen atom formerly bound to the phenyl ring), leaving a biradical species (Scheme 1). The electronic symmetry of the products is determined by the OCH biradical whose properties have been extensively studied.[9,22,23] The lowest lying singlet (B_1 symmetry) was calculated to lie at about 10 kcal/mol higher than the triplet ground state while the energy of the first excited singlet state (A_1 symmetry) is 10−20 kcal/mol higher, depending on the level of calculation. The fact that the ground state of the products is an open-shell system (even though the reactant is a closed shell one) makes this system akin to the smaller $HN_5^{\bullet-}$ discussed above.

The apparent counter-intuitive dissociation pattern of the anion under high-energy collisions—preferential C−N bond dissociation over the lower barrier N_2 forming one—may be rationalized by the energy level diagram of Figure 4.

High-energy collisions with the inert gas molecules are likely to promote the anion to an electronically excited state. A conical intersection between the 1^1A_1 and 1^1B_1 states allows the rapid crossing to the ground state, forming the *cyclo*-N_5^- and the OCH biradical. Low-energy collisions, on the other hand, are likely to vibrationally excite the anion in its electronic ground state, which preferentially dissociates by N_2 extrusion. Thus, the model presented conforms nicely with the experimental observations.

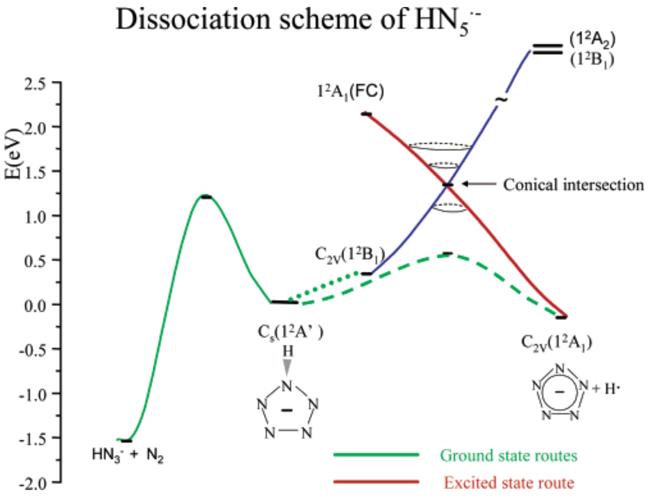


Figure 5. A partial energy scheme showing the main calculated dissociation routes of the $HN_5^{\bullet-}$ anion radical, starting at the C_s ($1^2A'$) minimum. The green lines denote thermal routes: full line, extrusion of N_2; dashed line, formation of N_5^-; dotted line, umbrella inversion to a second C_s ($1^2A'$) minimum (not shown) via C_{2v} transition state. The red line shows the formation of the pentazolate anion by a route starting in an electronically excited state (1^1A_1), which is formed by Franck−Condon excitation of the HN_5 neutral.

Dissociation of the Dimethylaminophenylpentazole Anion Radical. In contrast with the pentazolylphenolate anion reaction, the N_5^- anion is the preferred product by both thermal and photochemical routes in the case of the $HN_5^{\bullet-}$ anion radical and probably also by its phenyl derivatives. Comparison of the data reported in Tables 1 and 2 shows that the barriers to N_2 extrusion from $HN_5^{\bullet-}$ and from $OPhN_5^-$ are very similar (around 1.1 eV). In contrast, the barrier to C−N bond dissociation is rather high for the closed shell $OPhN_5^-$ anion (>2.6 eV), while the barrier for H−N bond rupture is quite small (~0.6 eV) for the $HN_5^{\bullet-}$ anion radical. The higher barrier in the case of the pentazolylphenolate anion is due to the extra energy required to convert a closed shell system to an open shell biradical one.

The situation depicted in Scheme 1 applies to anion radical systems as well: a coupling coordinate of b_1 symmetry is required to transfer the σ electrons of the NH bond to the electron that occupies the antibonding b_1 π orbital. Just as the electronic reorganization involved in the C−N bond-scission reaction necessitates an out-of-plane distorted transition state, here the same holds for the H−N bond fracture. The NH out-of-plane bending coordinate deforms the molecule reducing the symmetry of the system from C_{2v} to C_s. Therefore in the thermal transition state the H atom is bent out of plane (Figure 2). By symmetry, two such transition states can be operative (above and below the N_5^- ring), and they form the sign-inverting loop,[14−16] together with the anion radical and the products, that encircles the conical intersection.

The energy level diagram and the routes leading to H−N bond dissociation on one hand and N_2 extrusion on the other are depicted in Figure 5.[24]

VII. Summary

The recently reported formation of the *cyclo*-pentazolate anion from two precursors[2,3] can be readily explained on the basis of the electronic structure of the precursors. The existence of a conical intersection in these systems accounts for the neat cleavage of the C−N bond in the anion (or anion radical) keeping the fragile cyclopentazolate ring intact. The two systems differ in detail: In the closed shell anion, the barrier for the C−N bond dissociation reaction is much higher than the barrier for the N_2 extrusion reaction, while in the open shell anion radical systems, the barriers are similar. Another difference is that in the closed shell molecule, the negative charge is largely centered on the oxygen atom and the reaction therefore involves electron transfer to the pentazolate ring. In the anion radical precursor, the negative charge is situated on the N_5 ring and no charge-transfer accompanies the reaction. Model calculations on $HN_5^{\bullet -}$ show that this as yet unobserved anion radical is expected to show a similar reaction pattern.

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References and Notes

(1) Huisgen, R.; Ugi, I. *Chem. Ber.* **1957**, *90*, 2914. Huisgen, R.; Ugi, I. *Angew. Chem.* **1956**, *68*, 705.

(2) Vij, A.; Pavlovich, J. G.; Wilson, W. W.; Vij, V.; Christe, K. O. *Angew. Chem., Int. Ed.* **2002**, *41*, 3051.

(3) Östmark, H.; Wallin, S.; Brinck, T.; Carlqvist, P.; Claridge, R.; Hedlund, E.; Yudina, L. *Chem. Phys. Lett.* **2003**, *379*, 539.

(4) Klessinger, M.; Michl, J. *Excited states and photochemistry of organic molecules*; VCH: New York, 1995.

(5) Bernardi, F.; Robb, M. A.; Olivucci, M. *Chem. Soc. Rev.* **1996**, *25*, 321.

(6) Zilberg, S.; Haas, Y. *Chem. Phys.* **2000**, *259*, 249.

(7) Ben-Nun, M.; Martinez, T. J. *Chem. Phys.* **2000**, *259*, 237.

(8) Köppel, H.; Domcke, W.; Cederbaum, L. S. *Adv. Chem. Phys.* **1984**, *57*, 59.

(9) Chung, G.; Pack, M. V.; Reed, D. A.; Kass, S. R.; Gordon, M. S. *J. Phys. Chem. A* **2000**, *104*, 11822.

(10) Roos, B. O. *Adv. Chem. Phys.* **1987**, *69*, 399.

(11) Sobolewski, A. L.; Woywood, C.; Domcke W. *J. Chem. Phys.* **1993**, *98*, 5627.

(12) Teller, E. *J. Phys. Chem.* **1937**, *41*, 109.

(13) See for instance: Viel, A.; Krawczyk, R. P.; Manthe, U.; Domcke, W. *Angew. Chem., Int. Ed.* **2003**, *42*, 3434.

(14) Zilberg, S.; Haas, Y. *Eur. J. Chem.* **1999**, *5*, 1755.

(15) Haas, Y.; Zilberg, S. *Adv. Chem. Phys.* **2002**, *124*, 433.

(16) Herzberg, G.; Longuet-Higgins, H. C. *Disciss. Farady Soc.* **1963**, *25*, 321. Longuet-Higgins, H. C. *Proc. R. Soc. London* **1975**, *A334*, 147.

(17) Zilberg, S.; Haas, Y. *Photochem. Photobiol. Sci.* **2003**, *2*, 1256.

(18) Takeda, N.; Poliakov, P. V.; Cook, A. R.; Miller, J. R. *J. Am. Chem. Soc.* **2004**, *126*, 4301.

(19) Ferris, K. F.; Bartlett, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 8302.

(20) Schmidt, M. W.; Baldridge, K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(21) Frisch, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M.; Wong, C. Y.; Peng, A.; Nanayakkara, C.; Gonzalez, M.; Challacombe, P. M. W.; Gill, B. G.; Johnson, W.; Chen, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

(22) Wassermann, E. W.; Murray, R. *J. Am. Chem. Soc.* **1964**, *86*, 4203.

(23) Sole, A.; Olivella, S.; Bofill, J. M.; Anglanda, J. M. *J. Phys. Chem.* **1995**, *99*, 5934.

(24) A possible decay route of the $HN_5^{\bullet -}$ anion radical is ejection of an electron to form the neutral HN_5. The data in Table 1 indicate that this is an exothermic reaction that may be faster than bond dissociation. However, dynamic correlation is not included in the CASSCF calculations. We have used the CASMP2 correction to calculate the energies of the radical anion and the neutral. Using a (9/7) active space (8/7 for the neutral) and DZV basis set, the energy of the radical anion is calculated to be −273.14052 hartrees, and that of the neutral −273.13382 hartrees. Thus the reaction is endothermic (by 4 kcal/mol at this level). Zero-point energy adds 2 kcal/mol to the difference. (We thank a referee for his comments on this point).

(25) Nguyen, M. T. *Coord. Chem. Rev.* **2003**, *244*, 93.