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$_5^+$ anion radical, which is the parent molecule of the larger aromatic pentazoles, 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 phenylpentazole anions, stable compounds known since the work of Huisgen and Ugi 40 years ago. 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 pentazolylanion (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, Ostmark 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. It is shown that in the reactive systems studied in refs 2 and 3, low-lying symmetry-allowed conical intersections 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$_5^+$ 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 $^1$B$_1$ excited state
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. 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 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, in the present instance $B_1$. This coordinate may be found by the principle of maximum electronic structure, and hence the basic processes leading to 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 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 $s_{\text{CN}}$, the upward bend by $+\beta$, and the downward one by $-\beta$, the two reaction coordinates $R_{C_1}$ and $R_{C_2}$ may be written as $R_{C_1} = s_{\text{CN}} + \beta$ and $R_{C_2} = s_{\text{CN}} - \beta$.

These two reaction coordinates form a sign-inverting Longuet–Higgins loop that encircles a conical intersection. A loop similarly formed by two reaction coordinates was recently discussed for the cis–trans isomerization of the formaldiminium cation. The two symmetry-defined coordinates discussed above are obtained by the in-phase and out-of-phase combinations of $R_{C_1}$ and $R_{C_2}$.

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, 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$^-$ anion radical is the parent molecule of the dimethylaminophenylpentazolyl 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.
orbital. Thus, population of the $1\,^2\,A_1$ state leads to scission of the lowest energy antibonding state is repulsive as the extra electron is located mainly in the state. This species, which is formed by Franck-Condon electron attachment of HN$_5^-$, is not the most stable ground-state of the HN$_5$ neutral. The HN$_5^-$ anion radical is obtained by adiabatically adding an electron to the closed shell molecule HN$_5$. The extra electron finds itself in an antibonding $1\,^2\,A_1$ state of the HN$_5$ neutral. The HN$_5$ neutral, the HN$_5^-$ anion radical, and the N$_5^-$ anion radical have $2\,^2\,V_1$ symmetry in the ground state. The ground-state HN$_5$ neutral (FC stands for Franck-Condon excitation). The energy of the $1\,^2\,B_1\,^B$ state of the HN$_5^-$ anion at the geometry of the HN$_5$ neutral.

The stable form of HN$_5$ is calculated to be a closed shell molecule with $C_{3v}$ symmetry in the ground state. The ground state of the HN$_5^-$ anion radical is obtained by adiabatically adding an electron to the closed shell molecule HN$_5$. The extra electron finds itself in an antibonding $1\,^2\,B_1$ orbital, forming a $1\,^2\,B_1$ 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$_5^-$ anion radical—in fact, it is the transition state between two $C_i$ structures in which the H atom bends out of the pentazole ring plane. Electronically excited states of the anion radical (of $2\,^2\,A_1$ and $2\,^2\,A_2$ symmetry in $C_{3v}$) can also be formed adiabatically upon electron attachment of HN$_5$. The $1\,^2\,A_1$ state is repulsive as the extra electron is located mainly in the lowest energy antibonding $\sigma$ orbital, which is primarily a NH orbital. Thus, population of the $2\,^2\,A_1$ state leads to scission of the N–H bond and formation of a ground-state N$_5^-$ pentagon—the cyclo-pentazole 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 bond 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 $\pi$ orbitals (3 bonding ones and 2 antibonding) and two $\sigma$ 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 1: Calculated Energies of Species Relevant to the Dissociation of the HN$_5^-$ Anion Radical by Using CASSCF(9/7)/DZV with CISD/cc-pVDZ Values in Parentheses

<table>
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<tr>
<th>species</th>
<th>energy (hartrees)</th>
<th>rel energy (eV)</th>
<th>symmetry</th>
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<tr>
<td>HN$_5^-$ (GS)</td>
<td>$-272.63197$</td>
<td>0</td>
<td>$C_2v(1^2A')$</td>
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<td>HN$_5^-$</td>
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<td>$C_{3v}(1^2B_1)$</td>
<td>TS between two $C_i$ structures</td>
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<td>HN$_5^-$ + N$_2$</td>
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<td>HN$_5^-$ $\rightarrow$ H$^+$ + N$_5^-$ (TS)</td>
<td>$-272.602640$</td>
<td>0.80</td>
<td>$C_{1v}(1^2A')$</td>
<td>transition state to H$^+$ + N$_5^-$</td>
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<td>H + N$_5^-$</td>
<td>$-272.632121$</td>
<td>0.004</td>
<td>$C_{3v}(1^2A_1)$</td>
<td>dissociation products</td>
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<td>H + N$_5^-$ (FC)</td>
<td>$-273.30942$</td>
<td>(−0.14)</td>
<td>$C_{3v}(1^2B_1)$</td>
<td>excited states of dissociation products$^d$</td>
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<td>HN$_5^-$ $\rightarrow$ HN$_3^-$ + N$_2$ (TS)</td>
<td>$-273.341571$</td>
<td>0.60</td>
<td>$C_{2v}(1^2A_2)$</td>
<td>transition state to HN$_3^- +$ N$_2$</td>
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<td>HN$_5$ (GS)</td>
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<td>$C_{3v}(1^2A_1)$</td>
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<td>1.58</td>
<td>$C_{2v}(1^2A_2)$</td>
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<td>HN$_5^-$ (CI)</td>
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<td>2.07</td>
<td>$C_{2v}(1^2B_1/1^2A_1)$</td>
<td>conical intersection</td>
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</table>

$^a$ 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$_5^-$ 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$_5^-$ anion at the geometry of the HN$_5$ neutral. $^d$ The energy of the $1^2A_1$ state of the HN$_5^-$ 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$_5^-$: (top line from left) the ground-state HN$_5$ neutral, the HN$_5^-$ 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 $C_{3v}$ symmetry in the ground state. The ground state of the HN$_5^-$ anion radical is obtained by adiabatically adding an electron to the closed shell molecule HN$_5$. The extra electron finds itself in an antibonding $\pi^*$ orbital, forming a $1^2B_1$ 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$_5^-$ anion radical—in fact, it is the transition state between two $C_i$ structures in which the H atom bends out of the pentazole ring plane. Electronically excited states of the anion radical (of $2^2A_1$ and $2^2A_2$ symmetry in $C_{3v}$) 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 $\sigma$ orbital, which is primarily a NH orbital. Thus, population of the $2^2A_1$ state leads to scission of the N–H bond and formation of a ground-state N$_5^-$ pentagon—the cyclo-pentazole 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 $\pi$ orbitals (3 bonding ones and 2 antibonding) and two $\sigma$ 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.
and one in a π* antibonding one. Having done 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 electronic structure program, and CISD calculations with the GAUSSIAN suite of programs. 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 CASSCF 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 N2 extrusion channel requires several 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 HN5, HN5−, and N5− and DZV for the p-pentazolylphenolate anion system.

V. Results

The HN5− 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 HN5− 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 N2 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 N2 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 1A1 state). The energy difference between the ground state and this excited state is due to the electronic excitation of the oxycyclohexadienylidene 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 1B1 and 1A1 states at the CASSCF(10,12)/DZV level was about 12 kcal/mol, matching the result of ref 9 (performed with a smaller active

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**TABLE 2: Calculated Energies of Species Relevant to the Dissociation of the p-pentazolylphenolate Anion (OPh-N5−) by Using CASSCF(12,11)/DZV with CISD/DZV//UCISD/D95V Values in Parentheses**

<table>
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<th>rel energy (eV)</th>
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<tr>
<td>OPh-N5− (GS)</td>
<td>−576.47762</td>
<td>0</td>
<td>C2v (1A1)</td>
<td>ground state of anion</td>
</tr>
<tr>
<td>OPh-N5− + N2</td>
<td>−577.231383</td>
<td>−1.05</td>
<td>C2v (1A′)</td>
<td>separated products</td>
</tr>
<tr>
<td>OPh-N5− ← OPhN5− + N2 (TS)</td>
<td>−577.190741</td>
<td>1.11</td>
<td>C1</td>
<td>transition state for OPhN5− + N2 formation</td>
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<tr>
<td>'OPh' + N5− (GS)</td>
<td>−576.39325</td>
<td>2.30</td>
<td>C2v (1B1)</td>
<td>separated products</td>
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<tr>
<td>OPh-N5− (FC)</td>
<td>−576.18609</td>
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<td>first excited state of B1 symmetry</td>
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<tr>
<td>OPh-N5− (CI)</td>
<td>−576.91980</td>
<td>8.48</td>
<td>C2v (1B1/1A1)</td>
<td>conical intersection</td>
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**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.
VI. Discussion

also shown in Figure 3 and listed 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 N₂ + p-azidophenolate anion (which dissociates further by N₂ release). The barrier for this reaction was calculated to be 1.1 eV. Scission of the C–N bond leads to formation of cyclo-N₅⁻ and the OCH biradical. The barrier for this reaction is much higher, as the reaction is endothermic (ΔH = 2.6 eV). In this reaction an electron is transferred from the π-orbital of the oxygen atom to the pentazolate ring (a sp² 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. The lowest lying singlet (B₁ 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 (A₁ 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 HN₅⁻ and probably also by its phenyl derivatives. Comparison of the data reported in Tables 1 and 2 shows that the barriers to N₂ extrusion are much lower than for HN₅⁻ and from OPhN₅⁻ are similar (around 1.1 eV). In contrast, the barrier to C–N bond dissociation is rather high for the closed shell OPhN₅⁻ anion (>2.6 eV), while the barrier for H–N bond rupture is quite small (~0.6 eV) for the HN₅⁺ 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 b₁ symmetry is required to transfer the σ electrons of the NH bond to the electron that occupies the antibonding b₁ or 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 C₃₀ to C₁. 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 N₅⁻ ring), and they form the sign-inverting loop, 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 N₂ extrusion on the other are depicted in Figure 5.24

VII. Summary

The recently reported formation of the cyclo-pentazolyl anion from two precursors 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 stable cleavage of the C=N bond in the anion (or anion radical) keeping the fragile cyclopentazolate ring intact. The two systems

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 N₂, while high-energy collisions form an excited state that dissociates to the cyclopentazolate anion via a conical intersection. The coordinates ε₉ 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.

Figure 5. A partial energy scheme showing the main calculated dissociation routes of the HN₅⁻ anion radical, starting at the C₁ (1¹A₁) minimum. The green lines denote thermal routes: full line, extrusion of N₂; dashed line, formation of N₅⁻; dotted line, umbrella inversion to a second C₁ (1³A¹) minimum (not shown) via C₂ transition state. The red line shows the formation of the pentazolate anion by a route starting in an electronically excited state (1¹A₂), which is formed by Franck–Condon excitation of the HN₅ neutral.

Dissociation of the Dimethylaminophenylpentazole Anion Radical. In contrast with the pentazolylphenolate anion reaction, the N₅⁻ anion is the preferred product by both thermal and photochemical routes in the case of the HN₅⁻ anion radical and probably also by its phenyl derivatives. Comparison of the data reported in Tables 1 and 2 shows that the barriers to N₂ extrusion from HN₅⁺ and from OPhN₅⁻ are very similar (around 1.1 eV). In contrast, the barrier to C–N bond dissociation of the pentazolylphenolate anion is due to the extra energy required to convert a closed shell system to an open shell biradical one.

The apparent counter-intuitive dissociation pattern of the anion under high-energy collisions—preferential C–N bond dissociation over the lower barrier N₂ 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 1¹A₁ and 1¹B₁ states allows the rapid crossing to the ground state, forming the cyclo-N₅⁻ 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 N₂ extrusion. Thus, the model presented conforms nicely with the experimental observations.

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VII. Summary

The recently reported formation of the cyclo-pentazolyl anion from two precursors 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 stable 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 N₂ 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 N₅ ring and no charge-transfer accompanies the reaction. Model calculations on HN₅⁺ show that this as yet unobserved anion radical is expected to show a similar reaction pattern.

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References and Notes

(24) A possible decay route of the HN₅⁺ anion radical is ejection of an electron to form the neutral HN₅. 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).