Nitrogen Heterocycles | Hot Paper

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Detection of Cyclo-N_5^- in THF Solution

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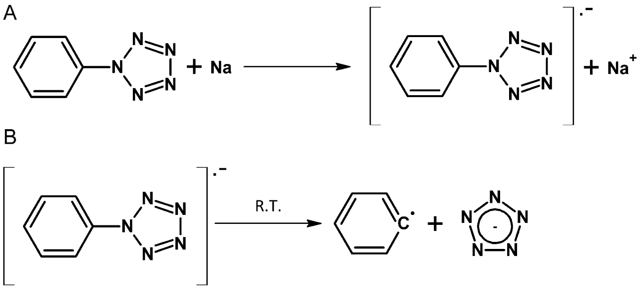
Abstract: *Compelling evidence has been found for the formation and direct detection of the cyclopentazole anion (cyclo-N_5^-) in solution. The anion was prepared from phenylpentazole in two steps: reduction by an alkali metal to form the phenylpentazole radical anion, followed by thermal dissociation to yield cyclo-N_5^-. The reaction solution was analyzed by HPLC coupled with negative mode mass spectrometry. A signal with m/z 70 was eluted about 2.1 min after injection of the sample. Its identification as N_5 was supported by single and double labeling with ^{15}N, which yielded signals at $m/z = 71$ and 72, respectively, with identical retention times in the HPLC column. MS/MS analysis of the $m/z = 70$ signal revealed a dissociation product with $m/z = 42$, which can be assigned to N_3^-. To our knowledge this is the first preparation of cyclo-N_5^- in the bulk. The compound is indefinitely stable at temperatures below −40 °C, and has a half-life of a few minutes at room temperature.*

The search for stable polynitrogen molecules is being actively pursued because they are assumed to have important applications as high energy density materials (HEDMs). They are also of considerable scientific significance, since nitrogen atoms do not tend to form stable long chains or multiatom rings. The cyclopentazole negative ion (cyclo-N_5^-) has attracted special attention since it was observed in the gas phase by mass spectrometry.[1,2] High-level theory predicts a rather high dissociation barrier (25 kcal mol^{-1}),[3] thus making it a lucrative candidate for experimental realization. It was also proclaimed to be a remarkably stable polynitrogen compound, possibly because of its aromatic stabilization.[4] Some simple derivatives, as well as bi(pentazole) were calculated to be stable species.[5] The successful production of cyclo-N_5^- in the bulk is a key step in making it of practical and commercial interest, as well as for the synthesis of even larger polynitrogen molecules. Despite some indirect evidence of its production in solution,[6,7] the race for its bulk production was considered not yet to be over;[8] indeed, direct detection of cyclo-N_5^- in the bulk has not thus far been reported. The main difficulty in preparing it from aryl pentazoles is assigned to the preponderance of a competing reaction (N_2 extrusion forming the corresponding azide). The energy barrier for the N_2 extrusion reaction is much smaller than for C–N bond cleavage, thereby causing the yield of cyclo-N_5^- to be negligibly small. The calculated gas-phase energy barrier for this reaction is on the order of 20–28 kcal mol^{-1}, much smaller than for cleavage of the C–N bond required to produce cyclo-N_5^- (86–98 kcal mol^{-1}).[9] The measured energy barrier to produce N_2 in liquid solutions is about 20 kcal mol^{-1}.[10] Östmark et al.[2] proposed that the radical anion (RA) of the aryl pentazole could be an intermediate species in the reaction, as the energy barriers for the N_2 extrusion and C–N bond-cleavage reactions in this negatively charged radical are similar. However, the origin of the radical anion in the experiments reporting the gas-phase production of cyclo-N_5^- was unclear. Attempts to reduce aryl pentazoles electrochemically or with alkali metals in solution did not lead to the detection of cyclo-N_5^-.[11,12] The proposed weakening of the C–N bond in the RA was supported by a recent theoretical study,[13] in which it was shown that the phenylpentazole radical anion (PPRA) is stable and observable at low temperatures in polar solvents. An important conclusion was that the yields of the C–N dissociation are very low in the gas phase because electron autodetachment is much more efficient, while in polar solvents, ionization is suppressed and the primary yields of the two competing molecular dissociation reactions are similar (about 25 kcal mol^{-1}). Herein, it is shown that the RA of phenylpentazole (PPRA) can be made in THF solution by reducing phenylpentazole with an alkali metal (Na or K). The PPRA is stable for days at −40 °C and below, thus permitting its detection by LC/MS and EPR spectroscopy. Warming the solution briefly to around room temperature results in formation of cyclo-N_5^-, as confirmed by LC/MS analysis. The two key steps proposed in the synthesis of cyclo-N_5^- from phenylpentazole are presented in Scheme 1.

Phenylpentazole is first reduced to the PPRA (Scheme 1 A) by interaction with an alkali metal (sodium and



Scheme 1. The two reactions assumed to lead to the solution-phase production of cyclo-N_5^-: Reduction of phenylpentazole by sodium metal (A) and decomposition of phenylpentazole radical anion to yield cyclo-N_5^- and a phenyl radical (B).

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potassium were used). The second step is the thermal dissociation of the radical anion (Scheme 1B) to yield the cyclo-N_5^- anion. This strategy formed the basis of the design of the reactions described below.

The whole sequence of reactions was carried out in a single pot. Phenylpentazole was dissolved in dry THF (for experimental details, please see the Supporting Information) cooled to −40 °C. A freshly cut small chunk of alkali metal, washed with dry THF, was added under mild stirring. In a few hours, the originally colorless solution became weakly yellow-orange, and a spongy gel appeared on the surface of the metal. After maintaining the solution under these conditions for a few days, 10 μL of the solution were analyzed by HPLC combined with mass spectrometry operated in the negative ion mode. A signal at $m/z = 147$ (the molecular mass of phenylpentazole) was recorded at an elution time of about 5.2 min (Figure 1). Substituting two ^{14}N atoms by ^{15}N led to the appearance of a signal at $m/z = 149$ with the same elution time. EPR measurements carried out at 200 K gave an EPR spectrum with three lines corresponding to the hyperfine splitting of a ^{14}N nucleus ($M_I = 1$), with a hyperfine value $a_N = 13.86$ G (Figure 2). No EPR signal was observed in the control sample to which no metal was added.

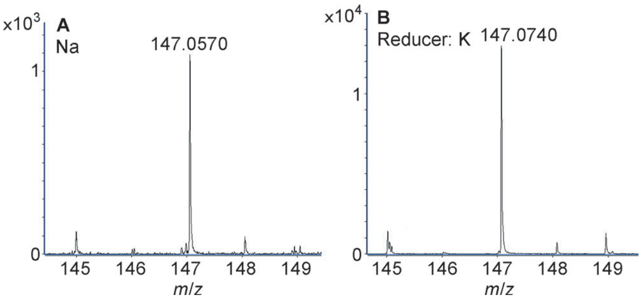

Figure 1. The mass spectrum of the phenylpentazole radical anion produced by the reduction of phenylpentazole with sodium metal (A) or potassium metal (B) in THF solution at −40 °C for 7 days, eluted 5.2 min after injection.

The solution was separated into two phases—gelatinous and clear—by centrifugation at room temperature. The EPR spectrum of both was the same within experimental error, although the signal intensity from the gel phase was rather poor. THF was added and strong stirring was applied. Thereupon the signal intensity increased significantly. A possible explanation is that the radical's motion is restricted within the gel, and the pairing of two radicals yields a diamagnetic dimer that cannot be observed by EPR spectroscopy. Dilution separates these pairs, and a strong signal results.

The solution was then warmed up briefly to room temperature (for a few minutes) and recooled to −40 °C. Injection into the same HPLC/MS apparatus yielded a signal with $m/z = 70$ at an elution time of 2.1 min. Replacing one or two ^{14}N atoms by ^{15}N generated signals at m/z 71 and 72, respectively, with the same retention time (Figure 3). The assignment of the structure to cyclo-N_5^- is based on the changes in the observed masses upon isotopic substitution—they must arise from molecules containing several nitrogen atoms. Since the only source of nitrogen atoms in this system is the five-membered nitrogen ring of phenylpentazole, the m/z 70 signal most likely corresponds to an anion consisting of five nitrogen atoms. Further confirmation was obtained by MS/MS analysis of the $m/z = 70$ signal 0.5–3.5 mins after injection, which yielded a fragment with $m/z = 42$, which is most likely due to the azide anion (N_3^-).

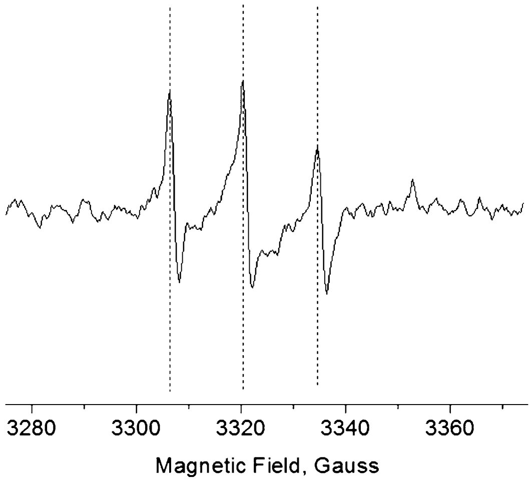

Figure 2. The EPR spectrum of phenylpentazole reduced by sodium metal in THF solution at −40 °C for 7 days. The spectrum, recorded at −73 °C, was obtained using the spongy orange fraction obtained subsequent to a short (30 s) centrifugation at room temperature.

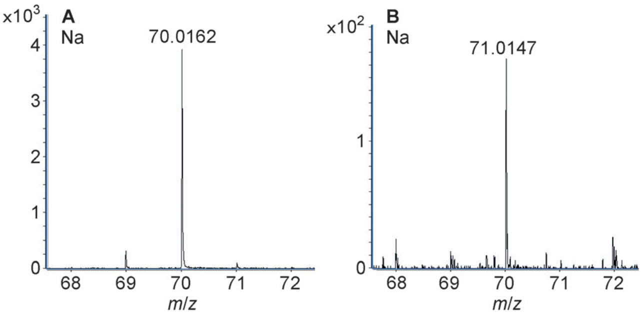

Figure 3. The HPLC/MS mass spectrum observed upon heating a solution of the phenylpentazole radical anion in THF to room temperature for a short period of time (30–300 s); the spectrum was recorded 2.1 min after injection into the HPLC column: A) using the all-^{14}N phenylpentazole, the spectrum is assigned to cyclo-$^{14}N_5^-$, B) using $^{14}N_4{}^{15}N_1$-phenylpentazole, the spectrum is assigned to cyclo-$^{14}N_4{}^{15}N^-$.

Storage of the reaction mixture for several weeks at −40 °C resulted in the recorded mass spectra remaining unchanged, which indicates that the species is stable at that temperature. At room temperature, the $m/z = 70$ signal disappeared after a few minutes. These findings indicate an activation energy of 20–25 kcal mol^{-1}, in good agreement with the theoretical prediction.[3] It is interesting to compare this result with the conclusions of Butler et al.,[7] who proposed on the basis of NMR spectra that cyclo-N_5^- (or HN_5) is unstable and does not build up in the solutions even at −40 °C. These authors used cerium(IV) ammonium nitrate (CAN) to N-dearylate a series of *N*-(*p*-anisyl)azoles in acetonitrile or methanol solvents. This reaction resulted in ^{15}N NMR signals of the azide being observed, but none corresponding to cyclo-N_5^-. It is possible that the discrepancy in the conclusion is the result of a reaction between CAN and cyclo-N_5^-, or another factor that results in the anion being unstable under the conditions used in the CAN experiment (for example, different solvents were used).

The data are consistent with the formation of the proposed phenylpentazole radical anion intermediate in Scheme 1. More work is required to establish whether this is the only process leading to the production of cyclo-N_5^- and what other products are formed. Attempts to produce cyclo-N_5^- by the same method from dimethylaminophenylpentazole led to a different pattern. No immediate products were observed, and gel formation was much slower—it was only clearly observed several weeks after introducing the metal chunk.

The EPR signal is weak and bands are broad in the presence of the gel, thus suggesting limited rotation and probably also restricted translation. The gel, therefore, acts like a matrix, preventing or reducing recombination, and thus allowing the production of cyclo-N_5^-. If gel formation is diminished when dimethylaminophenylpentazole is used instead of phenylpentazole, the back reaction will be faster, and most RAs will react by N_2 extrusion.

In conclusion, the race for the first successful synthesis and observation of cyclo-N_5^- in the condensed phase is over: the formation of this anion in THF solution has been demonstrated. It is a relatively stable polynitrogen compound as it survives a trip in a separating column at room temperature. It is thus amenable for chemical manipulations at practical temperatures (in the −20 to +20 °C range). Evidence for the formation of the proposed phenylpentazole radical anion intermediate is also presented. In principle, this finding opens the way to the practical use of cyclopentazolate salts and other derivatives.

Experimental Section

CAUTION: Aryl pentazoles and some of their reaction products are sensitive to heat and potentially explosive. Proper protection gear is required, as well as extreme caution.

Phenylpentazole was synthesized by a slightly modified version of Huisgen and Ugi[14] as described in Ref. [15]. It was stored at −40 °C until used. The reduction by an alkali metal was carried out in a small glass vial with a Teflon-coated rubber plug at −20 to −40 °C. The vial containing the reduced composition was also kept at −40 °C until used. HPLC/MS measurements were carried out at room temperature, so some loss of the reactive species (PPRA, cyclo-N_5^-) may have taken place. For complete details, please see the Supporting Information.

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Keywords: cyclopentazolate anion · high energy density materials · nitrogen heterocycles · phenylpentazole · radical anions

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Communications

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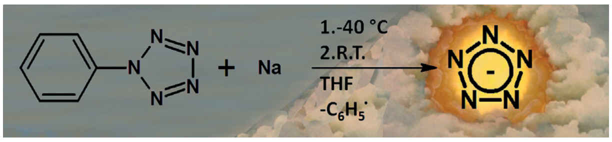

N-circled: The cyclopentazolate anion (cyclo-N_5^-), which is thought to be important for further development of polynitrogen chemistry, has been synthesized in THF and detected by HPLC/MS. The anion is generated by the reduction of phenylpentazole with an alkali metal in THF followed by thermal dissociation. The compound is indefinitely stable below −40 °C, and has a half-life of a few minutes at room temperature.