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Tetrazolylpentazoles: Nitrogen-Rich Compounds

Anton Hammerl and Thomas M. Klapötke*

Department of Chemistry, University of Munich, Butenandtstrasse 5-13 (D),
D-81377 Munich, Germany

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Tetrazolylpentazole was identified as an intermediate in the reaction of tetrazolediazonium chloride with lithium azide by low-temperature ^{15}N NMR spectroscopy. The decomposition of ^{15}N-labeled tetrazolylpentazole to form ^{15}N-labeled tetrazoleazides and dinitrogen was followed by low-temperature ^{15}N NMR spectroscopy. The structures of the species involved in this decomposition were optimized at different levels of theory, and the structures of the transition states were identified. The activation barriers for the decomposition were calculated at different levels of theory.

Introduction

Nitrogen-rich or polynitrogen compounds are promising highly energetic materials with high energy densities that are environmentally acceptable.[1] The decomposition of these materials would ideally produce only the environmentally safe dinitrogen. Recently, new polynitrogen species like the remarkable N_5^{+} [2] and the $N_6^{-\bullet}$ radical anion[3] were investigated, and computational studies have identified several polynitrogen compounds as candidates for synthesis.[4] Perhaps apart from dinitrogen, azidopentazole is believed to be the most promising candidate for synthesis for a compound consisting only of nitrogen atoms.[4b,e] Other molecules like dipentazole containing the pentazole ring systems also have activation barriers that are sufficiently high to allow experimental observation.

Substituted phenylpentazoles, first synthesized by Huisgen and Ugi,[5] have been the subject of several studies.[6] Polyazapentalenes and related azidoazoles have been investigated by Elguero, Claramunte, et al.[5e] No new pentazole derivatives have been investigated since the first reports on pentazole compounds in the late 1950's. Pentazole N_5H,[7] its anion N_5^-, and several Li^+ salts of N_5^- [8] were the subject of various theoretical studies.

The motivation of this study was to find experimental evidence for a pentazole compound with the highest possible

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* To whom correspondence should be addressed. Fax +49-(0)89-21807492. E-mail: Thomas.M.Klapoetke@cup.uni-muenchen.de.

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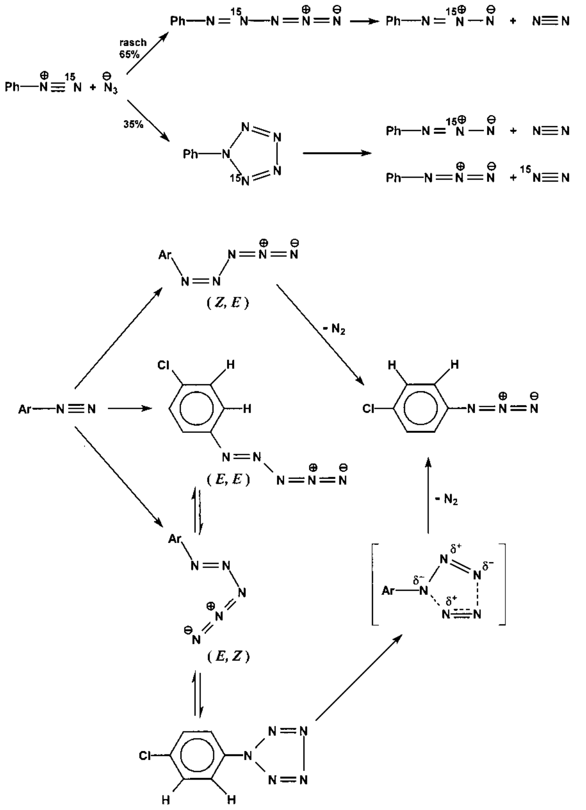
10.1021/ic0108134 CCC: $22.00

Scheme 1. Reaction of Phenyldiazonium Chloride with Sodium Azide[a]

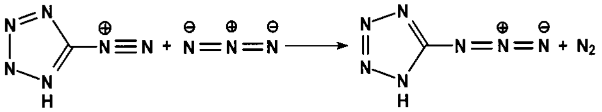


[a] Top: Suggested by Huisgen and Ugi.[5a−d] Bottom: Suggested by Butler et al.[5f]

nitrogen content, because in spite of all research only four solids with nitrogen contents greater than 90% (NH_4N_3,[9] $N_2H_5N_3$,[9] $N_2H_5N_3{\cdot}N_2H_4$,[1d] and $LiBN_{12}$[1b]) are known. Theoretical calculations were used to predict the stability of several tetrazolepentazole species.

Results and Discussion

Strategy. The reaction of tetrazolediazonium chloride with sodium azide gave sodium azidotetrazolate[10] (eq 1). The


(1)

similar reaction of phenyldiazonium chloride with sodium azide yielded phenyl azide and dinitrogen. Huisgen and Ugi isolated the first pentazole from this reaction and suggested the mechanism shown in Scheme 1.[5] Quite recently, Butler et al. reported on a combined theoretical and experimental NMR study elucidating the mechanism of the reaction of aryldiazonium chlorides with azide at −80 °C.[5f] They could show that an (*E*,*Z*)-arylpentazene is the key intermediate leading to the 1-arylpentazole product (Scheme 1).

Table 1. Energies of N_2 and N_3^- at Different Levels of Theory

	N_3^- $D_{\infty h}$	N_2 $D_{\infty h}$
	MP2/6-31G(d,p)	**MP2/6-31G(d,p)**
$-E$ [au]	163.789878	109.255278
zpe [kcal/mol]	6.0	3.1
ν_1 [cm^{-1}]	609.4	2174.6
	B3PW91/6-311G(2df,2p)	**B3PW91/6-311G(2df,2p)**
$-E$ [au]	164.204939	109.513931
zpe [kcal/mol]	7.1	3.5
ν_1 [cm^{-1}]	699.0	2458.4

We surmised that tetrazolylpentazole is formed in the first reaction. Tetrazole compounds are acidic; the hydrogen atom can occupy three positions (1*H*, 2*H*, and 3*H*). While the 3*H* tautomer is generally ignored in most discussions, the 1*H* and 2*H* are believed to be important. Therefore, we calculated the 1*H*, the 2*H*, and the anionic species of all compounds involved in this reaction as well as the structures of the transition states to find the most stable tetrazolepentazole species and to determine the activation barrier for the decomposition.

Quantum Chemical Calculations. The calculations were performed with the program package Gaussian 98.[11] All structures, energies, and vibrational data were calculated at the semiempirical PM3,[12] the ab initio HF[13] and MP2,[14] and the DFT-hybrid B3PW91[15] level of theory using polarized 6−31G(d,p) and 6−311G(2df,2p) double-ζ basis sets with diffuse functions and multiple polarization functions added.[16] All structures were fully optimized within the symmetry constraints stated in the respective tables and the vibrational frequencies computed at the optimized structures. All compounds have true minima on the potential energy surface with no imaginary frequencies. The transition states are of the first order and have one imaginary frequency. The energies for dinitrogen and the azide ion are summarized in Table 1.

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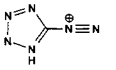
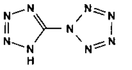
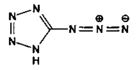
Table 2. Energies of 1*H*-Tetrazole Compounds[a]

			TS	
symmetry	C_s	C_1	C_1	C_1
		MP2/6-31G(d,p)		
$-E$ [a.u.]	365.815093	529.908156	529.880229	420.725686
zpe [kcal/mol]	27.6	38.3	35.6	31.2
ν_l [cm^{-1}]	155.3	21.9	–683.0 *i*	73.4
E_{rel} [kcal/mol]	–	45.7	63.2	0.0
		B3PW91/6-311G(2df,2p)		
$-E$ [a.u.]	366.745048	531.263300	531.233028	421.809421
zpe [kcal/mol]	28.2	38.9	36.5	31.9
ν_l [cm^{-1}]	183.7	53.8	–557.0 *i*	93.1
E_{rel} [kcal/mol]	–	37.7	56.6	0.0

[a] The relative energy for N_2 + 1*H*-N_3CHN_4 was set to zero.

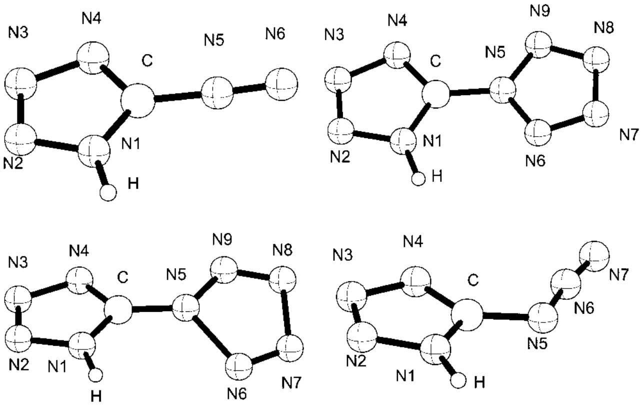


Figure 1. Structures of the calculated 1*H*-tetrazole compounds at the B3PW91 level of theory.

Table 3. Reaction Enthalpies and Activation Energies (without and with Zpe Correction) for the Decomposition of 1*H*-Tetrazolylpentazole to 1*H*-Azidotetrazole and Dinitrogen

	MP2	B3PW91
$\Delta H°$	−47.6	−39.1
E_{act}	17.5	18.9
E_{act}(zpe)	14.8	16.1

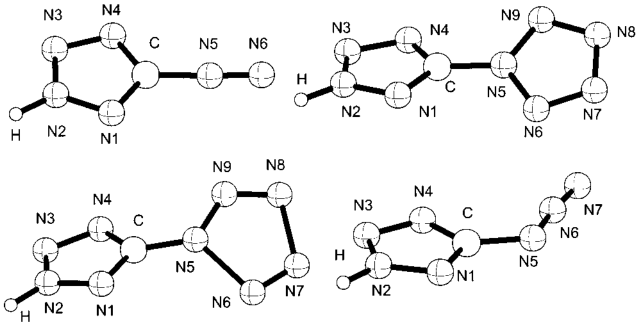
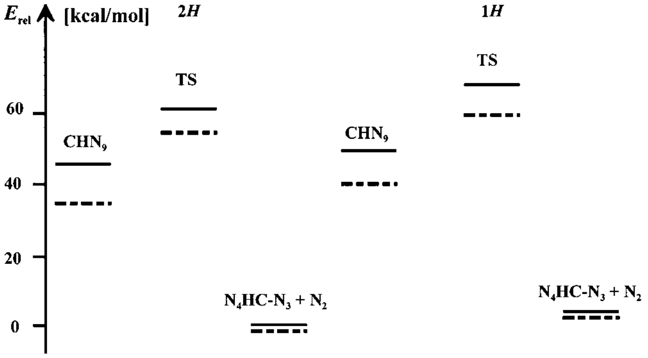


Figure 2. Structures of the calculated 2*H*-tetrazole compounds at the B3PW91 level of theory.

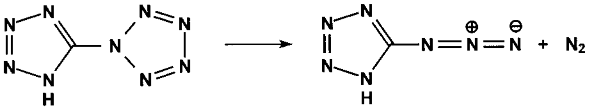
Scheme 2. Reaction Scheme of the Decomposition of 1*H*- and 2*H*-Tetrazolylpentazole to the Respective 1*H*- and 2*H*-Tetrazolylpentazoles and Dinitrogen at the MP2(FC)/6-31G(d,p) (—) and B3PW91/6−311(2df,2p) (- - -) Levels of Theory[a]



[a] The relative energy of azidotetrazole and dinitrogen was set to 0.

The structures, energies, and vibrational frequencies of all compounds involved in the formation and decomposition were computed at PM3, HF, MP2(FC), and B3PW91 levels of theory. The results are summarized in Tables 2, 4, and 6; the structures (B3PW91/6−311G(2df,2p) of the compounds are given in Figures 1, 2, and 3. As expected for an exothermic process and nicely in accord with Hammond's postulate,[17] the transition states resemble still more the starting materials rather than the reaction products and N_2.

1*H*-Tetrazolylpentazole. The reaction energy for the decomposition of 1*H*-tetrazolylpentazole to yield 1*H*-azidotetrazole and N_2 (eq 2) (Scheme 2) was calculated and, after zero point energy correction (Δzpe) and corrections for the translational ($\Delta U^{tr}(1) = {}^3/_2RT$) and rotational terms ($\Delta U^{rot}(1) = RT$) and for the work term ($p\Delta V(1) = RT$), converted into the reaction enthalpy value. The reaction barriers for the decomposition reaction for the MP2(FC) and B3PW91 levels of theory are shown in Table 3. The



(2)

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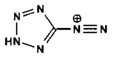
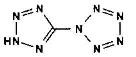
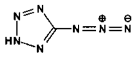
[17] (a) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 344. (b) Lendvay, G. *J. Phys. Chem.* **1994**, *98*, 6098.

Table 4. Energies of 2*H*-Tetrazole Compounds[a]

			TS	
symmetry	C_s	C_1	C_1	C_1
		MP2/6-31G(d,p)		
$-E$ [a.u.]	365.842805	529.917691	529.889142	420.731748
zpe [kcal/mol]	28.4	38.9	36.1	32.0
ν_1 [cm^{-1}]	173.3	41.2	-703.7 *i*	72.4
E_{rel} [kcal/mol]	–	43.5	61.4	0.0
		B3PW91/6-311G(2df,2p)		
$-E$ [a.u.]	366.768702	531.269248	531.239034	421.813062
zpe [kcal/mol]	28.9	39.9	37.0	32.3
ν_1 [cm^{-1}]	189.0	33.3	-557.9 *i*	88.8
E_{rel} [kcal/mol]	–	36.2	55.2	0.0

[a] The relative energy for N_2 + 2*H*-N_3CHN_4 was set to zero.

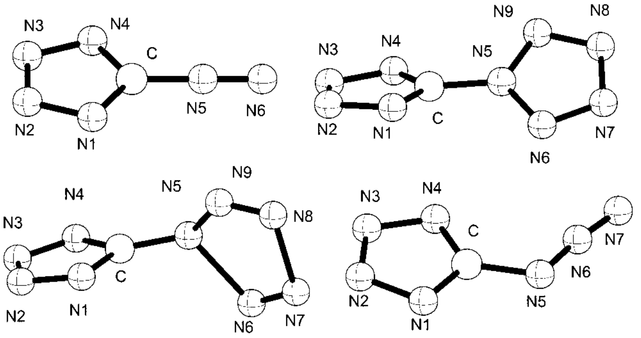


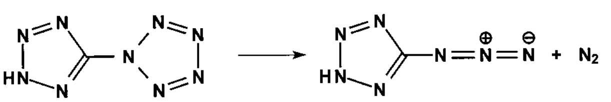
Figure 3. Structures of the calculated tetrazolate compounds at the B3PW91 level of theory.

Table 5. Reaction Enthalpies and Activation Energies (without and with Zpe Correction) for the Decomposition of 2*H*-Tetrazolylpentazole to 2*H*-Azidotetrazole and Dinitrogen

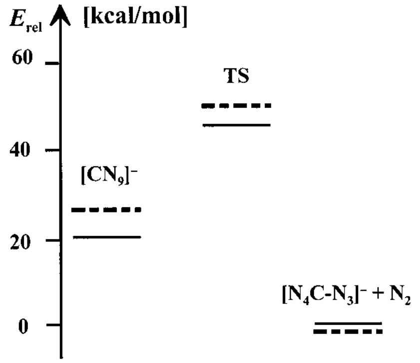
	MP2	B3PW91
$\Delta H°$	−45.2	−37.6
E_{act}	17.9	19.0
E_{act}(zpe)	15.1	16.1

activation barriers for the decomposition are 14.8 (MP2) and 16.1 (B3PW91) kcal mol^{-1} with zpe correction.

2*H*-Tetrazolylpentazole. The reaction energy for the decomposition of 2*H*-tetrazolylpentazole to yield 2*H*-azidotetrazole and N_2 (eq 3) was calculated and, after zero point energy correction (Δzpe) and corrections for the translational ($\Delta U^{tr}(1) = {}^3/_2RT$) and rotational terms ($\Delta U^{rot}(1) = RT$) and for the work term ($p\Delta V(1) = RT$), converted into the reaction enthalpy value. The reaction barriers for the decomposition reaction for the MP2(FC) and B3PW91 levels of theory are shown in Table 5. At both levels the activation barriers are 15.1 (MP2) and 16.1 (B3PW91) kcal mol^{-1} with zpe correction.


(3)

Scheme 3. Reaction Scheme of the Decomposition of Pentazolyltetrazolate to Pentazolyltetrazolate and Dinitrogen at the MP2(FC)/6-31G(d,p) (—) and B3PW91/6−311(2df,2p) (- - -) Levels of Theory[a]



[a] The relative energy of azidotetrazolate and dinitrogen was set to 0.

All 2*H*-tetrazole compounds have slightly lower energies than 1*H*-tetrazole compounds (1−3 kcal mol^{-1}). In general, in solid tetrazole compounds the 1*H* tautomers are stabilized by intermolecular hydrogen bonds and, therefore, more stable than the 2*H* tautomers. In the gas phase the intermolecular hydrogen bonds are not formed and the 2*H* tautomers are more stable.[18] The activation barriers for the decomposition of the 1*H* and the 2*H* are equal with 16.1 kcal mol^{-1} at B3PW91.

Pentazolyltetrazolate. The reaction energy for the decomposition of pentazolyltetrazolate to yield azidotetrazolate and N_2 (eq 4) (Scheme 3) was calculated and, after zero point energy correction (Δzpe) and corrections for the translational ($\Delta U^{tr}(1) = {}^3/_2RT$) and rotational terms ($\Delta U^{rot}(1) = RT$) and for the work term ($p\Delta V(1) = RT$), converted into the reaction

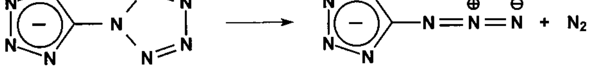

(4)

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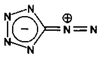
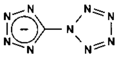
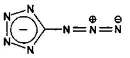
Table 6. Energies of Tetrazolate Compounds[a]

			TS	
symmetry	C_s	C_1	C_1	C_1
		MP2/6-31G(d,p)		
$-E$ [a.u.]	365.503926	529.406305	529.369416	420.193195
zpe [kcal/mol]	19.6	30.3	27.8	23.3
ν_1 [cm^{-1}]	146.9	45.1	$-184.0\ i$	61.2
E_{rel} [kcal/mol]	–	26.4	49.6	0
		B3PW91/6-311G(2df,2p)		
$-E$ [a.u.]	366.432526	530.752970	530.713010	421.271237
zpe [kcal mol^{-1}]	20.1	30.9	28.3	23.7
ν_1 [cm^{-1}]	180.6	41.0	$-552.7\ i$	80.9
E_{rel} [kcal mol^{-1}]	–	20.2	45.3	0

[a] The relative energy for $N_2 + N_3CN_4^-$ was set to zero.

Table 7. Reaction Enthalpies and Activation Energies (without and with Zpe Correction) for the Decomposition of Pentazolyltetrazolate to Azidotetrazolate and Dinitrogen

	MP2	B3PW91
$\Delta H°$	−28.2	−21.8
E_{act}	23.1	25.1
E_{act}(zpe)	20.6	22.5

enthalpy value. The reaction barriers for the decomposition reaction for the MP2(FC) and B3PW91 levels of theory are shown in Table 7. At both levels the activation barriers are 20.6 (MP2) and 22.5 (B3PW91) kcal mol^{-1} with zpe correction.

All three tetrazolepentazole compounds are stable toward the loss of dinitrogen with activation energies of about 15 kcal mol^{-1} for the protonated compounds and 22.5 kcal mol^{-1} for pentazolyltetrazolate at the B3PW91 level of theory. PM3 underestimates and HF overestimates the activation barriers whereas MP2 and B3PW91 nicely agree on the activation barriers. This is not surprising because the electron correlation is even more important for the calculation of transition states and reactions that include the breaking of bonds than for the calculation of ground states.

While an activation barrier of 15−20 kcal mol^{-1} is no huge barrier, it is sufficient for experimental observation. The anionic compound would be the best candidate, since the activation barrier for the decomposition is slightly higher than in the protonated compounds.

NBO Analysis for Pentazolyltetrazolate. A NBO analysis[19] for the most stable compound, pentazolyltetrazolate, was performed.

The tetrazolate and the pentazole ring system formally have 6 π electrons. Five orbitals are not fully populated: π (N2−N3) (1.887 e), π (N1−C5) (1.834 e), π (N7−N8) (1.862 e), π (N9−N10) (1.887 e), and the free electron pair of N4 with 1.257 e. Therefore, four antibonding orbitals are partially filled: π^* (N2−N3) (0.475 e), π^* (N1−C5) (0.511 e), π^* (N7−N8) (0.400 e), and π^* (N9−N10) (0.400 e). The strongest intramolecular interactions (negative hyperconjugation) in the NBO picture are p-LP(N4) → π^* (N2−N3), s-LP(N6) → π^* (N7−N8), s-LP(N6) → π^* (N9−N10), and π^* (N2−N3) → π^* (N1−C5).

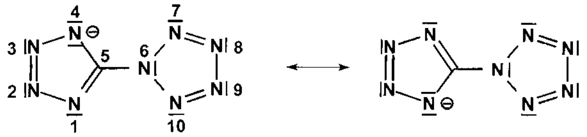


Figure 4. Resonance structures of pentazolyltetrazolate.

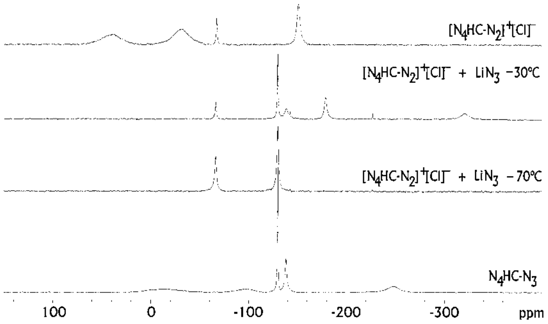


Figure 5. ^{14}N NMR spectra of the reaction of tetrazolediazonium chloride with lithium azide at different temperatures.

A simple NBO analysis does not describe the bonding situation in an aromatic system accurately. The bonding situation is better described by the resonance displayed in Figure 4.

Syntheses. An ethereal solution of tetrazolediazonium chloride was reacted with a solution of lithium azide in methanol. At 0 °C a rapid gas evolution occurred. At lower temperature the gas evolution was slower. The ^{14}N NMR spectrum of the reaction mixture at −70 °C shows only two signals, the signal of dinitrogen and a signal of azidotetrazole. At −30 °C more species are observed. The ^{14}N NMR spectra show that a reaction takes place at −70 °C. Unfortunately,

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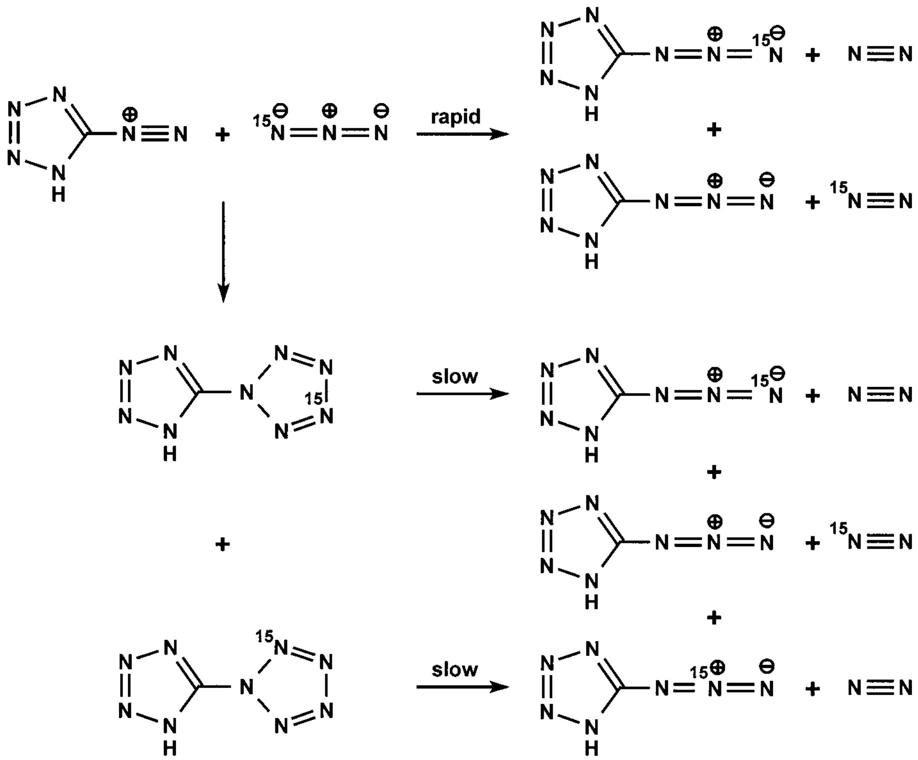
(19) (a) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (b) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

Scheme 4. Reaction Paths of the Reaction of ^{15}NNN with Tetrazolediazonium Chloride



the ^{14}N NMR spectra give no evidence for a pentazole compound.

Changing the polarity of the solvent by adding petroleum ether does not result in the precipitation of a pentazole compound. Therefore, we followed the reaction of tetrazolediazonium chloride with Li(^{15}NNN) with ^{15}N NMR spectroscopy (Scheme 4). According to Huisgen's scheme (Scheme 1), the main reaction should give ^{15}N$_\gamma$-azidotetrazole. A side reaction can give ^{15}N-marked tetrazolylpentazole. With both terminal nitrogen atoms of the azide anion being equal, two differently marked pentazole compounds should be formed. The decomposition of these compounds with dinitrogen loss would give either ^{15}N$_\gamma$- or the ^{15}N$_\beta$-azidotetrazoles.

The reaction was carried out at −70 °C and followed by low-temperature ^{15}N{^{1}H} NMR spectroscopy (Figures 6 and 7). The ^{15}N NMR spectrum at −70 °C shows signals for HN_3 ($\delta = -325.2$ H*N*NN and $\delta = -183.5$ HNN*N*), dinitrogen ($\delta = -71.8$), and ^{15}N$_\gamma$-azidotetrazole ($\delta = -144.7$). Two signals at $\delta = -29.7$ and 7.7 are also observed. The ^{15}N NMR spectra were recorded with hydrogen decoupling. Here the NOE effect is responsible for changes in amplitude of the signals that can result in negative amplitudes because of the negative gyromagnetic ratio of ^{15}N.[20]

The solution was allowed to reach −50 °C, and another ^{15}N NMR spectrum was recorded. Here the signals at $\delta = -29.7$ and 7.7 lose intensity while the dinitrogen signal gains intensity. The magnification shows a small signal at $\delta =$

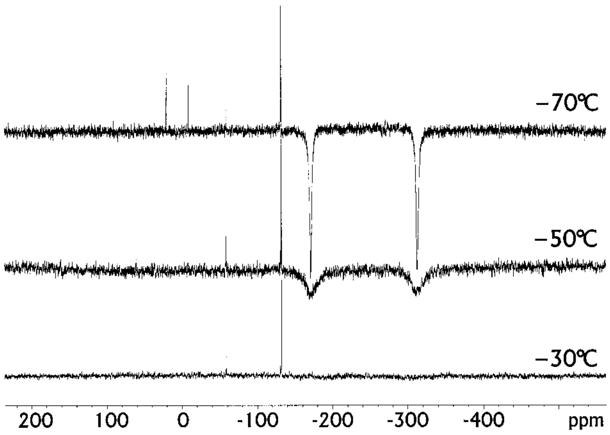


Figure 6. ^{15}N{^{1}H} NMR spectra of the reaction of tetrazolediazonium chloride with Li(^{15}NNN) at different temperatures.

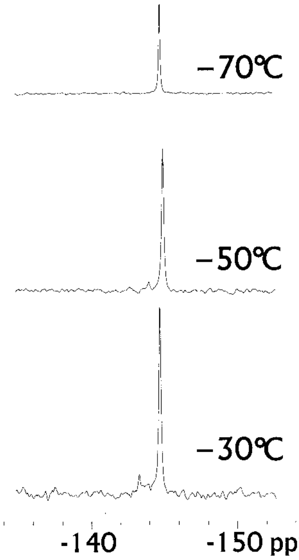


Figure 7. Magnification of the signals of ^{15}N$_\beta$- and ^{15}N$_\gamma$-azidotetrazole.

−143.4 next to the signal of $^{15}N_\gamma$-azidotetrazole, which corresponds to $^{15}N_\beta$-azidotetrazole (lit.: 145.7 (DMSO)[21]). After warming up to −30 °C only the signals of dinitrogen and $^{15}N_\beta$- and $^{15}N_\gamma$-azidotetrazole were observed.

The $^{15}N\{^1H\}$ NMR spectra at −70 and −50 °C show an intermediary in the reaction of tetrazolediazonium chloride with Li(^{15}NNN). It decomposes at −50 °C to form dinitrogen, $^{15}N_\gamma$- and $^{15}N_\beta$-azidotetrazole. The ^{15}N NMR signals have chemical shifts of $\delta = -29.7$ and 7.7 and correspond to the reported ^{15}N NMR shifts of *p*-dimethylaminophenylpentazole ($\delta = -27.1$ (N2) and 4.9 (N3)).[6b] Therefore, the intermediate is a tetrazolepentazole.

Conclusion

The structures of 1*H*- and 2*H*-tetrazolylpentazole and pentazolyltetrazolate were optimized at different levels of theory. All compounds have true minima on their potential energy surfaces. The corresponding decomposition reactions to form the respective azidotetrazole compounds and dinitrogen were calculated. The activation energies for the decomposition have values of about 15 kcal mol^{-1} (MP2) and 16.1 kcal mol^{-1} (B3PW91) for the 1*H* and 2*H* tautomers and values of 20.6 kcal mol^{-1} (MP2) and 22.5 kcal mol^{-1} (B3PW91) for the anionic compound.

A ^{15}N NMR spectroscopical investigation of the reaction of tetrazolediazonium chloride with Li(^{15}NNN) at low temperatures showed a tetrazolepentazole compound to be present which decomposes at −50 °C to form dinitrogen and $^{15}N_\beta$- and $^{15}N_\gamma$-azidotetrazole.

Experimental Section

CAUTION! Tetrazolediazonium salts and azidotetrazole are very sensitive to electrostatic discharge, friction, and impact. During this work many explosions occurred; safety precautions like protective clothing, face shields, and ear plugs have to be taken at all times. All reaction were carried out in Teflon equipment.

General. NMR spectra were recorded on a JEOL Eclipse 400 instrument. Chemical shifts (δ scale) were recorded with respect to CH_3NO_2 ($^{14/15}$N). Tetrazolediazonium chloride was prepared in ethereal solution after a literature procedure.[22] Na(^{15}NNN) was used as provided by Prof. W. Beck and converted to Ag(^{15}NNN) by reaction with $AgNO_3$. Li(^{15}NNN) was synthesized from Ag^{15}NNN and lithium chloride.

General Procedure. To an ethereal solution of tetrazolediazonium chloride at −78 °C was added slowly a solution of Li(^{15}NNN) in methanol that was cooled to −78 °C. An NMR tube was then filled with the reaction mixture and inserted in the precooled spectrometer. After a first measurement the sample was allowed to reach higher temperatures in the spectrometer. ^{14}N NMR measurements: −30 °C, ^{14}N NMR, $\delta = -324$ (H*N*NN), −182 (HNN*N*), −145 (N_4HC−NN*N*), −132 (N_4HC−N*N*N), −66 (N_2); −70 °C, ^{14}N NMR, $\delta = -135$ (N_4HC−N*N*N), −66 (N_2); sodium azidotetrazolate, ^{14}N NMR (room temperature), $\delta = -253$ (N_4HC−*N*NN), −144 (N_4HC−NN*N*), −135 (N_4HC−N*N*N).

Studies with Li^{15}NNN: ^{15}N NMR (Et_2O, CH_3OH), −70 °C, $\delta = -325.2$ (H*N*NN), −183.5 (HNN*N*), −144.7 (N_4HC−NN*N*), −71.8 (N_2), −29.7 (N_5:N_β), 7.7 (N_5:N_α); −50 °C, −325.2 (H*N*NN), −183.5 (HNN*N*), −144.7 (N_4HC−NN*N*), −143.4 (N_4HC−N*N*N), −71.8 (N_2), −29.7 (N_5:N_β), 7.7 (N_5:N_α); −30 °C, −144.7 (N_4HC−NN*N*), −143.4 (N_4HC−N*N*N), −71.8 (N_2); room temperature, −144.7 (N_4HC−NN*N*), −143.4 (N_4HC−N*N*N); ^{14}N NMR (room temperature), $\delta = -253$ (N_4HC−*N*NN), −144 (N_4HC−NN*N*), −135 (N_4HC−N*N*N).

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