Ab Initio Study of Molecular Properties and Decomposition Products of 1-Azidoalkynes—A Challenge for Experimentalists

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In this publication, a characterization of different azidoalkyne compounds using high-level ab initio quantum chemical methods is presented. For this purpose, the molecular structures and the ^{13}C NMR chemical shifts have been calculated at the MP2 and CCSD(T) level of theory and the influence of zero-point vibration as well as the solvent on the chemical shifts are discussed. Furthermore, a comparison of the energy barriers of the decomposition under N_2 separation for a set of 1-azidoalkynes with different functional groups has been carried out. The molecular structures and properties of the resultant decomposition products have been investigated. It is remarkable that large deviations of the NMR chemical shifts of ethylthioethynyl azide occur in comparison to the experiment. These deviations are far outside of the error bars. Electron correlation effects are of high importance if an accurate description of the chemical shifts of 1-azidoalkynes shall be obtained. A comparison of the energy barriers of the decomposition under N_2 separation of 1-azidoalkynes with different functional groups indicates that the stability of 1-azidoalkynes is not increased by typical donor or acceptor groups but rather by silyl or phenyl substituents. The molecular geometries of the decomposition products indicate that the equilibrium structures are of carbene character. Some of the results presented here are in contradiction to previous experimental publications and cast a new light on some open challenges for experimentalists.

I. Introduction

Since the 1950s, many groups have tried to generate 1-azidoalk-1-ynes, but these species are a mystery even today.[1−3] Several attempts at preparing the title compounds were unsuccessful or led to unwanted products.[4−6] For example, the reaction of (phenylethynyl)sodium or alkyl-1-ynyllithiums and tosyl azide yielded only 1,2,3-triazole derivatives instead of the target compounds.[7,8] Even in the case of generating 1-azido-2-phenylethyne (**2**) in situ, the sequential chemistry of such a short-lived intermediate is still unclear (Scheme 1). Thus, treatment of the precursor **1** with sodium azide in dimethyl sulfoxide (DMSO) was said to lead in low yield to product **4**, which was explained by formation of intermediate **2** followed by the loss of nitrogen and trapping of the nitrene **3** by DMSO.[9−11] Alternatively, starting material **5** is transformed under a variety of conditions and in high yield into *cis*- and *trans*-dicyanostilbenes **8**, which are formally dimers of the carbene **6**.[12,13] However, the known[14] trapping products of **6** including the cyclopropane framework could not be detected when **5** was treated in the presence of cyclohexene or diphenylacetylene. Therefore, the formation of **8** from **5** was explained by intermediates **2** and **7**.[12,13] But alternative routes leading from **5** to **8** without the intermediary 1-azidoalkyne **2** were also discussed because no stilbene derivative **8** was found in case of treating **1** with sodium azide.[10,11]

A way out of this unclear situation seems to be possible by a report on the isolation of the unstable azides **10**.[15,16] The reaction of precursor **9** with sodium azide in DMSO has been claimed to afford the title compound **10** and the heterocyclic product **11**. The ^{13}C NMR spectroscopic data of **10** are, however, very unusual compared to those of other functionalized acetylenes.[17] It is extremely surprising that **11** is reported to be stable without spontaneous isomerization to furnish an aromatic tautomer. Furthermore, the NMR spectroscopic data published[16] for **11** exclude the proposed 4*H*-1,2,3-triazole structure. Finally, several attempts to reproduce the generation of **10** and **11** from **9** have been unsuccessful.[18]

Although high-accuracy ab initio methods are powerful tools in the investigation of molecular species and in the prediction of spectroscopical properties of this class of compounds, no theoretical investigations on the unimolecular reactions of 1-azidoalkynes, or on structural modifications, which may lead to stabilization of these azides, have been carried out so far. Only calculations of the molecular structure and the heat of formation for 1-azido-2-nitroethyne have presently been reported.[19]

Nowadays, molecular properties like equilibrium geometries or nuclear magnetic resonance (NMR) chemical shifts can be calculated with high accuracy. Standard methods are, for example, the Møller−Plesset perturbation theory (MP2),[20] the coupled-cluster singles-and-doubles (CCSD),[21] or the coupled-cluster singles-and-doubles approach augmented by a perturbative treatment of triple excitations (CCSD(T)).[22] They are often used for the interpretation and support of experimental data or even for the prediction of molecular properties. A large number of computational investigations has shown that CCSD(T) yields near-quantitative accuracy provided that sufficiently large basis sets are used. [23−26] It has been demonstrated that combination of the CCSD(T) approach with Dunning's cc-pVTZ basis set[27] typically provides geometries with residual errors of

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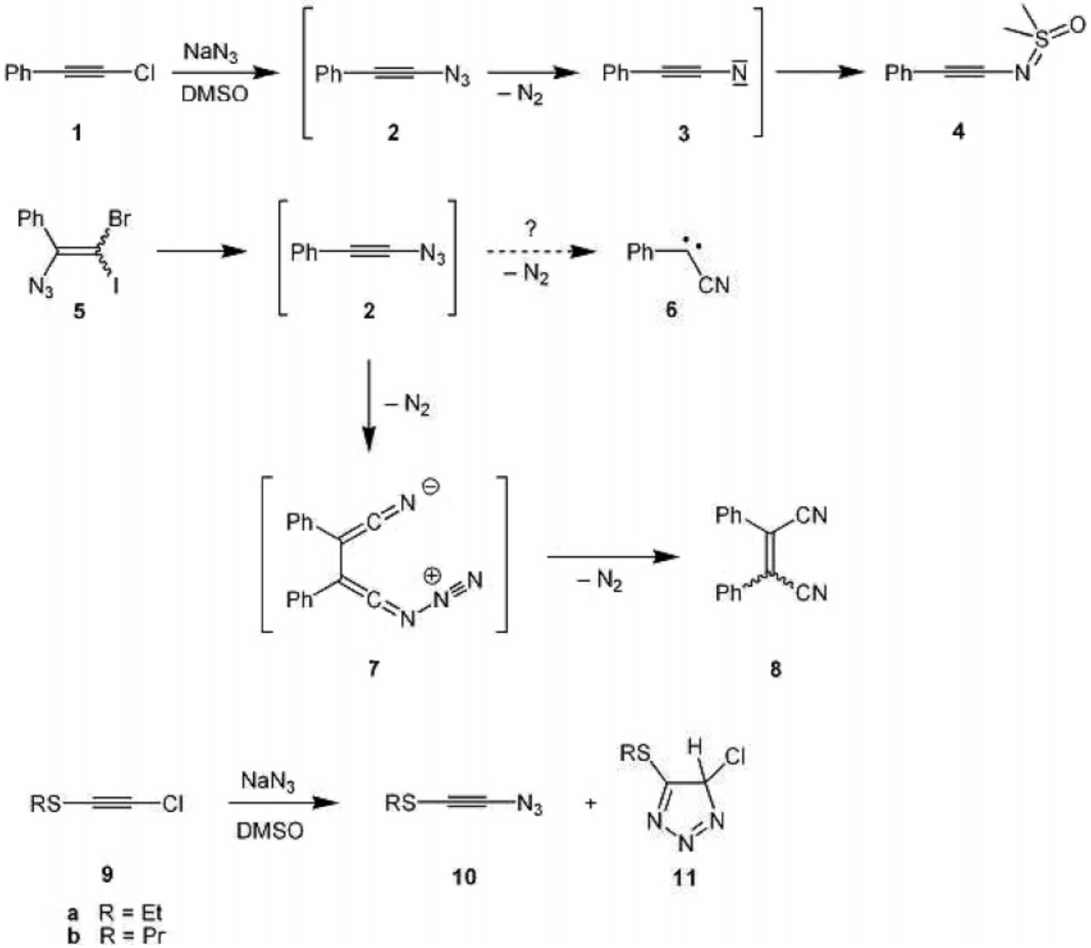
SCHEME 1: Attempts to Generate 1-Azidoalk-1-ynes



less than 0.005 Å for bond distances and a few tenths of a degree for bond angles.[28−30]

In experimental investigations, NMR spectroscopy is one of the most frequently used tools for the characterization of molecular structures. As NMR spectroscopy yields only indirect information about the geometry of a molecule, quantum chemical calculations can be used as a link between NMR chemical shifts and molecular structures (for some examples, see refs 31−36). An important prerequisite for the application of such calculations is that they are capable of providing results of sufficient accuracy. Benchmark calculations for ^{13}C chemical shifts have indicated that large basis set CCSD(T) calculations including zero-point vibrational corrections yield results with mean deviations to the experiment of less than 6 ppm.[37] Most experimental NMR spectra are obtained in solution. Whereas the prediction of solvent effects is a very difficult task for computational chemistry, often measurements of NMR chemical shieldings in solvents with varying dielectric constants can give an estimate of the solvent dependence.

In this paper, a theoretical study of 1-azidoalkynes is presented. Sections II and III describe the NMR investigation and the computational details. In the first part of section IV, the molecular properties of ethylthioethyne, which serves as a benchmark example, and ethylthioethynyl azide are studied, and the results are compared to the experiment. In the second part, the energy barrier of the decomposition of this class of molecules under N_2 separation is investigated in order to assess the stability of 1-azidoalkynes. The equilibrium geometries of a set of possible decomposition products, which have also been discussed in the literature, have been investigated in the third part in order to characterize the nature of these molecules.

II. Details of the NMR Investigation

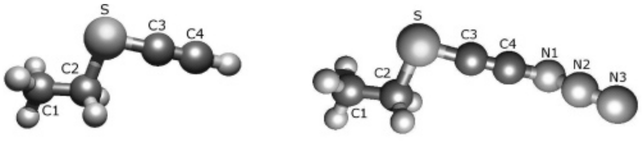
Ethylthioethyne (**12**) was prepared according to a known[38] procedure. ^{13}C NMR spectra of this compound in different solvents (ca. 100 mg/mL) were measured at 100.6 MHz using a Unity Inova Varian spectrometer at 293 K. All data were referenced to TMS ($\delta = 0$).

III. Computational Details

In this work, geometry optimizations have been carried out at the MP2 and CCSD(T) levels using Dunning's cc-pVTZ basis sets. All geometries were converged to at least 10^{-7} Å bond length.[39] The equilibrium structures for compounds, which are likely to not have a closed-shell wavefunction, have been optimized by unrestricted MP2 calculations. All equilibrium structures were confirmed by normal-mode analyses.

The calculations of the ^{13}C chemical shifts have been performed at the MP2 and CCSD(T) levels of theory using the tz2p and qz2p basis sets.[40,41] To avoid the gauge-origin problem in the calculation of NMR chemical shifts, we used the gauge including atomic orbitals (GIAO)[42−44] approach.

The geometry optimizations of cyanophenylcarbene as well as the transition-state searches were performed using the quantum chemistry package TURBOMOLE.[45] For the most time-consuming coupled-cluster (CC) NMR calculations, a parallel pilot version of the Mainz−Austin−Budapest version of the ACES II package has been used.[46] The calculations of



12 **10a**

Figure 1. Benchmark molecule ethylthioethyne (**12**) and the investigated compound ethylthioethynyl azide (**10a**).

TABLE 1: Important Bond Lengths and Angles of Ethylthioethyne 12 and Ethylthioethynyl Azide 10a Obtained at the Geometry Optimizations

	ethylthioethyne (**12**)		ethylthioethynyl azide (**10a**)
	MP2	CCSD(T)	MP2
	cc-pVTZ	cc-pVTZ	cc-pVTZ
		bond length (Å)	
C_1C_2	1.51	1.52	1.51
C_2 S	1.82	1.83	1.82
SC_3	1.68	1.69	1.68
C_3C_4	1.22	1.21	1.22
C_4N_1			1.34
N_1N_2			1.24
N_2N_3			1.14
		bond angle (deg)	
C_1C_2S	108.33	108.50	108.27
C_2SC_3	99.21	99.36	100.14
SC_3C_4	180.00	180.00	177.37
$C_3C_4N_1$			171.78
$C_4N_1N_2$			119.72
$N_1N_2N_3$			170.30

the other equilibrium geometries, the NMR chemical shifts, the zero-point vibrational corrections, and the energy barriers at the CCSD(T) level of theory have been carried out using the ACES II program.[47]

IV. Results and Discussion

A. Molecular Properties of Ethylthioethyne 12 and Ethylthioethynyl Azide 10a. Although all attempts to get direct proof of 1-azidoalkynes were unsuccessful or highly doubtful and succeeding reactions of such azides are presently unclear, until now no high-accuracy ab initio methods have been applied in order to investigate 1-azidoalkynes. For such investigations, especially CC and perturbative methods have proven to be powerful tools in the prediction of molecular properties.

To assess the accuracy of the calculated molecular properties of ethylthioethynyl azide (**10a**), we have also calculated the geometry and NMR chemical shifts for ethylthioethyne (**12**) (see Figure 1). This experimentally well-characterized system serves as benchmark molecule in this investigation.

The geometries of **12** and ethylthioethynyl azide **10a** have been optimized at the MP2/cc-pVTZ level. Additionally, the geometry of the smaller benchmark molecule **12** has been optimized at the CCSD(T) level of theory in order to test the accuracy of MP2 geometries for this class of molecules. The optimized structural parameters of **12** and **10a** are summarized in Table 1. Only small changes in the molecular structure are observed if the geometries of **12** obtained at the MP2 and CCSD(T) level of theory are compared. Electron correlation effects beyond MP2 result in geometry changes of at most 0.01 Å and 0.2°.

If the ^{13}C chemical shifts obtained by using the MP2 and CCSD(T) geometry are compared, then differences of about 1 ppm can be observed (see Table 2). As has been proven for a number of ^{13}C chemical shifts,[37] it appears to be sufficient to use the MP2/cc-pVTZ geometry for the calculation of the ^{13}C chemical shifts for this class of compounds. The chemical shifts are not influenced to a large extent by the basis sets used for the calculations. If the spectra obtained by using the tz2p and qz2p basis sets are compared, then changes of about 1 ppm occur.

TABLE 2: Relative ^{13}C Chemical Shifts for Ethylthioethyne (12) for the Investigated Methods and Basis Sets[a]

geometry	^{13}C chemical shifts (ppm)	C_1	C_2	C_3	C_4
*MP2/cc-pVTZ	MP2/tz2p	14.5	35.7	84.2	76.0
	MP2/qz2p	14.5	35.8	84.9	75.0
	CCSD(T)/qz2p	14.5	34.8	79.9	80.9
	B3-LYP/tz2p	14.5	39.9	84.7	89.1
*CCSD(T)/cc-pVTZ	MP2/tz2p	14.5	36.1	83.2	75.6
	MP2/qz2p	14.5	36.2	83.9	74.6
	CCSD(T)/qz2p	14.5	35.1	79.3	79.9
	experiment	14.5	29.0	74.4	82.8

[a] Relative shifts were obtained by converting the computed shielding constants σ via $\delta = \sigma_{C_1} - \sigma + \delta_{C_1,\mathrm{exp}}$ to relative shifts with C_1 as the internal standard.[48] The experimental shifts are measured in C_6D_6.

Although MP2 calculations of chemical shifts often yield results of good accuracy, the results for compound **12** obtained at the MP2/tz2p and MP2/qz2p level of theory even fail to reproduce the experimental spectrum qualitatively as the chemical shifts of C_3 and C_4 appear in the wrong order. However, CCSD(T) calculations of the NMR chemical shifts yield correct relative shifts for C_3 and C_4. According to this, correlation effects beyond MP2, which are on the order of 5 ppm, seem to play an important role in such ethynyl azides. This is most likely due to effects of the sulfur atom on the electronic structure. Because of the more-delocalized electronic structure of **10a** in comparison to **12**, correlation effects might even be stronger in **10a**.

Although the results obtained at the B3-LYP/tz2p level of theory give a correct assignment of the carbon atoms in the ethynyl group, the deviations from the experiment of up to 13 ppm are relatively high. Because of this discrepancy, one should be hesitant to use DFT methods for the prediction of the NMR chemical shifts of this class of molecules.

Thus, it is very difficult to obtain a qualitatively correct description without a high-level treatment of correlation effects.[49] Therefore, calculations at the CCSD(T)/qz2p level of theory using the MP2/cc-pVTZ geometry can be expected to yield results with an accuracy of about 5−6 ppm in comparison to the experiment.

B. A Note on Solvent Effects and Zero-Point Vibration. Experimental values are normally taken from measurements in solution and also always include zero-point vibrational effects. Former publications[37] have demonstrated that external effects on the ^{13}C chemical shifts should not be disregarded if accurate predictions of NMR chemical shifts should be obtained. Thus, for a comparison of theory and experiment, at least zero-point vibrational and solvent effects should be regarded.[50]

On this account, zero-point vibrational corrections have been calculated using a perturbative approach as described in ref 37. Because of the high computational effort associated with the calculation of vibrational corrections, only calculations at the MP2/tz2p level of theory are feasible. The calculation for **12** allows an estimation of the order of magnitude of the corrections which are at most 3−4 ppm.[67] Although this gives an estimate for the size of the residual error due to zero-point vibrational effects, the MP2 values cannot be considered highly accurate because of the correlation effects as discussed in the previous section.

Although several approaches for the calculation of solvent effects on magnetic properties are known in the literature,[35,52]

TABLE 3: Experimental ^{13}C Chemical Shifts of Ethylthioethyne 12 in Solvents with Different Dielectric Constants

chemical shifts (ppm)	C_6D_6 $\epsilon = 2$	D_6 − acetone $\epsilon = 18$	CD_3CN $\epsilon = 37$
C_1	14.5	14.8	14.9
C_2	29.0	29.6	29.9
C_3	74.4	74.4	74.8
C_4	82.8	84.3	84.1

TABLE 4: Relative ^{13}C Chemical Shifts for Ethylthioethynyl Azide (10a) for the Investigated Methods and Basis Sets for the MP2/cc-pVTZ Geometry[a]

^{13}C chemical shifts (ppm)	C_1	C_2	C_3	C_4
MP2/tz2p	14.3	36.2	60.3	83.6
MP2/qz2p	14.3	36.3	60.5	83.4
CCSD(T)/qz2p	14.3	35.3	62.7	83.9
experiment [16]	14.3	28.1	86.0	116.2

[a] Relative shifts were obtained by converting the computed shielding constants σ via $\delta = \sigma_{C_1} - \sigma + \delta_{C_1,\mathrm{exp}}$ to relative shifts with C_1 as the internal standard.[70] The experimental shifts have been published in ref 16.

it is often very difficult and time-consuming to achieve highly accurate results using theoretical approaches like polarizable cavity [53−63] methods or solvent-shell cluster models [64−66] for larger systems. Thus, we have chosen to obtain an estimate for solvent effects by a more empirical approach using experimental results.[67]

Table 3 summarizes the experimental ^{13}C chemical shifts of **12** measured in solvents with different dielectric constants. This experimental investigation indicates that the chemical shifts do not change very much if solvents with different dielectric constants are used. This effect can be estimated to be on the order of 1−2 ppm.

Although both of these effects cannot be determined quantitatively, an estimate yields that the sum of zero-point vibrational and solvent effects is on the order of at most 5−6 ppm, so these are most likely the largest contributions to the deviations from the experiment.

C. Comparison of the Calculated NMR Chemical Shifts of Ethylthioethynyl Azide 10a to the Experiment. On the basis of the results obtained for the benchmark compound **12**, it is possible to estimate the accuracy for the calculation of ^{13}C chemical shifts of 1-azidoalkynes. Until now, only one publication of the synthesis of 1-azidoalkynes exist, namely, compound **10**.[16]

In this section, the chemical shifts of **10a** are investigated. For this purpose, the ^{13}C NMR chemical shifts have been calculated at the CCSD(T)/qz2p level of theory using the molecular geometry obtained at the MP2/cc-pVTZ level of theory (see Table 4). Figure 2 shows the calculated NMR chemical shifts[68] in comparison to the published values. For this compound, the deviations to the experiment are on the order of 23 ppm for C_3 and 32 ppm for C_4 in comparison to the deviations of the benchmark compound **12** of about 5 ppm for C_3 and 3 ppm for C_4. Thus, the deviations for the compound in question are far greater than can be expected from the results of the benchmark molecule and the only conclusion the authors can draw from this drastic discrepancy is that this synthesis has not been successful and remains a challenge to experimentalists.[69]

Nevertheless, the authors are convinced that the results of the high-level ab initio study presented here will be of help in the challenging task of synthesizing 1-azidoalkynes and characterizing them via NMR spectroscopy.

As we conclude that the ^{13}C NMR chemical shifts given in ref 16 are very likely not the ones of **10a**, and the chemical shift of the internal standard C_1[70] given in Table 4 might not be correct. However, comparison of the ^{13}C chemical shifts of similar compounds have indicated that the shift for C_1 is on the order of about 14−15 ppm (**9a**, ref 71: 14.8 ppm, **12**: 14.5 ppm, Et_2S, ref 72: 14.8 ppm). Thus, the authors are confident that the experimental values of the real compound will be within 6 ppm deviation to the theoretical results given here.

D. Energy Barrier of the Decomposition of 1-Azidoalkynes. From the previous, section the following question arises: Are such thioazidoalkynes suitable compounds to isolate 1-azidoalkynes at all, or are there other 1-azidoalkynes that are more stable and thus could be isolated. Decisive for the stability is the height of the energy barrier of the unimolecular decomposition. Thus, a comparison of the energy barriers of the decomposition of 1-azidoalkynes with different functional groups has been carried out in order to investigate if substituents like donor or acceptor groups can be found, that are able to stabilize these azidoalkynes.

Because of the high stability of N_2, the first step of the decomposition can be assumed to be the separation of nitrogen. The transition states for the compounds illustrated in Figure 3 have been calculated at the MP2/cc-pVTZ level of theory by stretching the N_1N_2 bond slightly and applying a simple eigenvector-following scheme for the location of the transition state. To obtain an accurate estimate of the barrier height, we carried out energy calculations at the CCSD(T) level using the MP2/cc-pVTZ geometries. The results are summarized in Table 5. It is remarkable that the energy barrier of the parent compound **13** is highest. Thus, the results imply that the stability of 1-azidoalkynes cannot be increased by typical donor or acceptor groups.

To find other possibilities to stabilize 1-azidoalkynes, like extensive π-systems, one has to investigate larger molecules. If a screening for promising candidates is to be carried out for a larger set of molecules, then calculations at the MP2 or CCSD(T) level become very time-consuming and often unpractical. Thus, it is necessary to look for alternative approaches like DFT methods. Here, the results from the calculations at the MP2 and CCSD(T) level of theory can be used as benchmark examples. A comparison of the energy barriers obtained at the B3-LYP/DZP level to the values from the post-HF calculations is given in Table 5. The results indicate that the energies obtained at the B3-LYP level of theory are within 17 kJ/mol of the results obtained at the CCSD(T)/cc-pVQZ level of theory. Although the exact height of the barriers are not reproduced very well, the DFT methods appear to be reliable for the prediction of qualitative trends like the ordering from most stable to unstable. This way, the calculation of the energy barrier of the decomposition at the B3-LYP/DZP level of theory allows for a time-efficient screening of various kinds of 1-azidoalkynes.

Further calculations of the barrier heights of 1-azido-2-phenylethyne and 1-azido-2-silylethyne indicate that these compounds are more stable than the compounds with the different kinds of donor and acceptor groups and might be potential candidates for an isolation. The calculation of the barrier height at the B3-LYP level for ethylthioethynyl azide (**10a**) yields a comparably low energy barrier. This is in line with the results of the previous section that a successful synthesis of **10a** is very questionable. In light of these results, it might

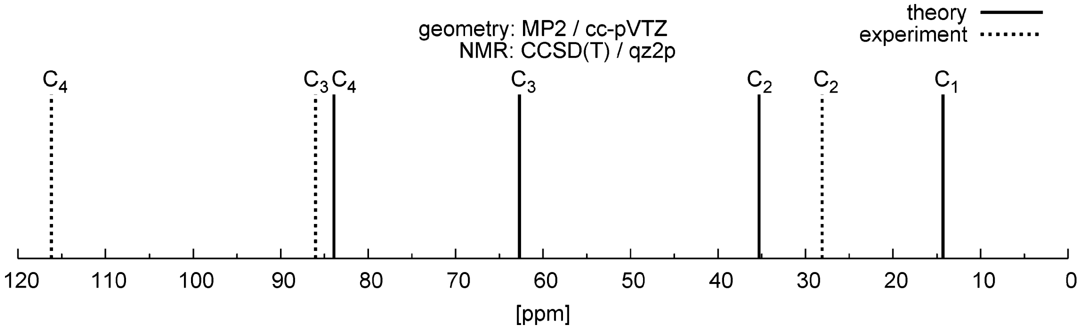


Figure 2. Calculated ^{13}C chemical shifts for ethylthioethynyl azide **10a** in comparison to the published NMR spectrum.[16]

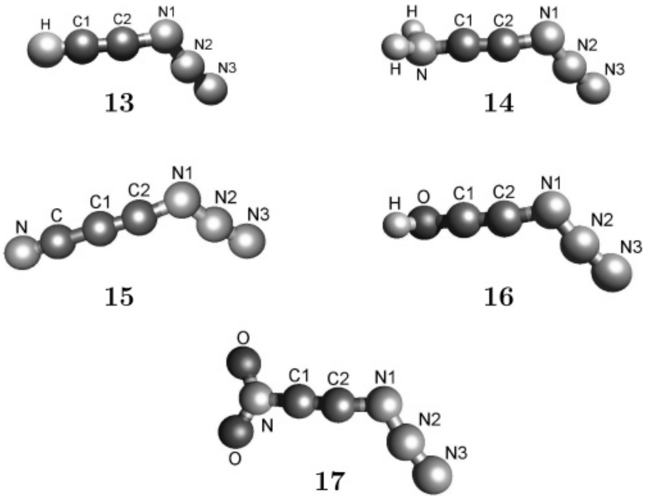


Figure 3. Equilibrium geometries for the five investigated compounds for which the energy barrier of the unimolecular decomposition was studied.

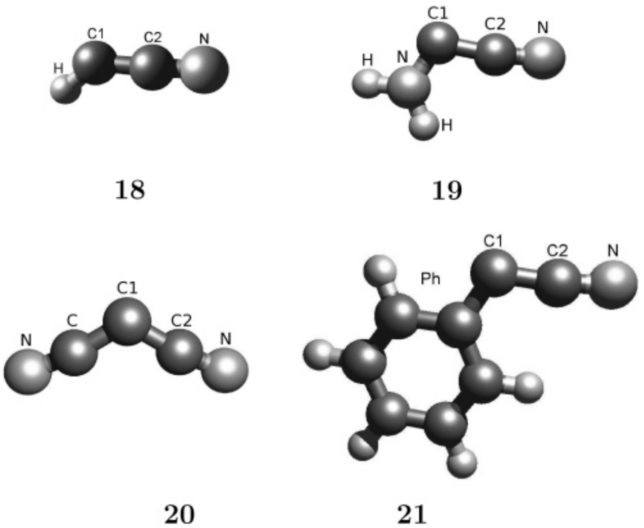


Figure 4. Equilibrium structures of the four investigated molecules that were studied as potential decomposition products of the species *R*$-$*C*$\equiv$*C*$-$*N*$_3$.

even be misleading to follow the thioethynyl azide route in further experimental investigations.

Table 6 summarizes the equilibrium geometries and the transition-state geometries of the investigated set of molecules. It should be noted that for all compounds the bond angle RC_1C_2 is smaller and the C_2N_1 bond is shorter for the transition state in comparison to the equilibrium structure. These transition-state structures already indicate that the compounds resulting from the decomposition probably have a carbene structure.

TABLE 5: Energy Barriers of the Decomposition under N_2 Separation in kJ/mol[a]

compound	ZPV*	MP2/ cc-pVTZ	CCSD(T)/ cc-pVTZ	CCSD(T)/ cc-pVQZ	ZPV**	B3-LYP/ DZP
13	15.8	137.8	90.4	90.0	11.8	87.9
14	16.6	83.5	54.6	54.2	9.1	37.7
15	14.4	131.0	78.4	77.9	11.1	73.1
16	13.1	109.5	70.8	70.1	7.4	59.4
17	15.3	114.0	64.2	61.6	9.9	57.6
$PhCCN_3$					10.4	76.0
H_3SiCCN_3					11.1	82.0
10a					9.2	41.6

[a] The barriers of columns 3−5 have been calculated using the MP2/cc-pVTZ geometries from Table 6. The zero-point vibrational effects (ZPV*) within the harmonic approximation, calculated at the MP2/cc-pVTZ level of theory, have been taken into account. For molecules **13**−**17** and three additional compounds, the barrier has also been calculated using the B3-LYP/DZP geometries, whereas the harmonic part of the zero-point vibrational effects (ZPV**), calculated at the B3-LYP/DZP level of theory, are included already.

E. Decomposition Products of 1-Azidoalkynes. The short lifetime and high reactivity of the 1-azidoalkynes are the reason that these compounds are difficult to isolate. If the compound cannot be isolated, then it is necessary to perform trapping reactions in order to detect these molecules. On this account, the nature of the molecules resulting from decomposition reactions is of central interest. Because of the high stability of N_2, compounds as shown in Figure 4 will presumably occur. In former publications,[73,74] model systems **18**−**20** have been investigated. It has been observed that these molecules have a carbene structure. However, Tanaka et al. have investigated 1-azido-2-phenylethyne (**2**) and postulated that this compound forms a nitrene structure.[9−11]

To be able to predict whether the intermediate species can be characterized as carbenes or nitrenes and under which circumstances a specific intermediate is stabilized, we carried out an investigation of the decomposition products of 1-azidoalkynes for a set of molecules with different functional groups.

The structural parameters of the investigated decomposition products optimized at the MP2/cc-pVTZ level of theory are summarized in Table 7. In comparison with typical C−N double (1.21 Å)[75] and triple bonds (1.16 Å),[75] the C_2 N bond seems to be a triple bond. For all cases, the angle RC_1C_2 is significantly smaller than 180°. Hence, these bent molecules have a carbene character. In ref 73, a carbene structure has been found for these compounds using several levels of theory like B3-LYP, MP2, or MP3. From a NBO investigation[73] and the analysis of the electron density obtained in the calculations presented in this work, the same conclusion can been drawn.[67] Interesting to note is that for none of the compounds under investigation a local minimum corresponding to a nitrene has been found in the geometry optimizations. Thus, all theoretical evidence seem to

TABLE 6: Important Bond Lengths and Angles for the Equilibrium Geometry (eg) and the Transition State (ts) of the Investigated Set of Molecules $R-C\equiv C-N_3$[a]

			bond length (Å)					bond angle (deg)			
compound	R		RC_1	C_1C_2	C_2N_1	N_1N_2	N_2N_3	RC_1C_2	$C_1C_2N_1$	$C_2N_1N_2$	$N_1N_2N_3$
13	H	eg	1.06	1.21	1.35	1.24	1.14	178.58	178.05	118.52	170.97
		ts	1.06	1.24	1.27	1.71	1.12	155.01	170.65	110.77	144.86
14	NH_2	eg	1.35	1.21	1.35	1.24	1.14	174.22	170.33	119.10	170.26
		ts	1.31	1.24	1.27	1.55	1.14	167.39	173.54	117.85	140.15
15	CN	eg	1.36	1.22	1.33	1.24	1.14	178.44	173.08	119.39	170.75
		ts	1.35	1.24	1.26	1.72	1.12	176.78	172.54	110.52	143.91
16	OH	eg	1.31	1.21	1.35	1.24	1.14	174.40	171.41	118.53	170.61
		ts	1.31	1.25	1.27	1.58	1.13	146.44	166.49	115.82	142.04
17	NO_2	eg	1.39	1.21	1.33	1.24	1.14	178.50	173.51	118.52	170.59
		ts	1.39	1.25	1.25	1.64	1.12	141.93	168.95	112.33	146.05

[a] The geometry optimizations as well as the transition-state searches have been carried out at the MP2/cc-pVTZ level of theory.

TABLE 7: Important Bond Lengths and Angles for the Equilibrium Structures of the Investigated Set of Species *RCCN* Including Different Functional Groups, R, and Multiplicity, M[a]

			bond length (Å)			bond angle (deg)	
compound	R	M	RC_1	C_1C_2	C_2N	RC_1C_2	C_1C_2N
18	H	3	1.07	1.36	1.14	136.88	177.91
19	NH_2	1	1.30	1.43	1.17	111.98	172.73
20	CN	1	1.38	1.38	1.18	118.09	172.05
21	Ph	1	1.42	1.40	1.18	115.51	173.03

[a] The geometry optimizations have been carried out at the MP2/cc-pVTZ level of theory.

confirm that the decomposition products of 1-azidoalkynes have a carbene character.

To investigate whether the ground state is a singlet or triplet state, we carried out geometry optimizations for both cases. For compound **18**, the preferred state is the triplet state with an energy difference of about 7 kJ/mol to the singlet state calculated at the MP2/cc-pVTZ level of theory taking into account the zero-point vibrational effects within the harmonic approximation. For the other molecules (**19**, **20**, and **21**), the singlet state is about 174, 59, and 128 kJ/mol, respectively, more stable than the triplet state.

It should be noted that the results for cyanophenylcarbene are in discrepancy to previous experimental investigations by Tanaka et al.[9−11] The authors of the work presented here are confident about the quality of the theoretical results and hope that this contribution motivates experimentalists to revisit this interesting case in order to arrive at a consistent characterization of the structural and electronic properties of these molecules also on an experimental basis.

V. Conclusions

Using modern electronic structure methods, the molecular properties of 1-azidoalkynes have been investigated. The study presented here aims at aiding experimental work by using highly accurate as well as efficient electronic structure methods in order to gain insight into the stability, molecular properties, and decomposition products of 1-azidoalkynes. We hope that our results initiate further work in the field and can be of help to obtain a proof of the existence of 1-azidoalkynes.

It has been shown that it is possible to predict the ^{13}C NMR chemical shifts at the CCSD(T)/qz2p level using the MP2/cc-pVTZ geometry of compounds like ethylthioethyne (**12**) with deviations of about 5−6 ppm to the experiment in solution. The remaining error is most likely due to zero-point vibrational and solvent effects, which are estimated to amount to 3−4 and 1−2 ppm, respectively.

The calculated NMR chemical shifts of ethylthioethynyl azide (**10a**) have been compared to the published experimental values.[16] Deviations of over 30 ppm occur, which lead the authors to conclude that the synthesis of **10a** claimed in ref 16 has not been successful.

In order to facilitate experimental progress on the synthesis of this interesting class of compounds, the energy barriers of the decomposition under N_2 separation have been investigated. The height of the energy barriers of different 1-azidoalkynes lead to the assumption that the stability of this class of molecules is decreased by typical donor or acceptor groups in comparison to the reference compound **13**. Furthermore, DFT calculations prove to be an efficient tool for the analysis of energy barriers. While the thio compounds are far from being promising candidates for stable 1-azidoalkynes, the results indicate that phenyl- and silyl-substituted species might be the preferred choice if one seeks to obtain a stable compound of this class of molecules.

To identify possible products of trapping reactions, we carried out an investigation of the decomposition products that result from 1-azidoalkynes under formation of nitrogen. It has been shown that these compounds can be characterized as carbenes. Furthermore, no local minimum corresponding to a nitrene structure has been found for these molecules.

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(49) It should be noted that because of the importance of a high-level description of correlation effects, this class of compounds is an interesting benchmark example for CCSD(T) calculations. Further studies on sulfur-substituted species are being carried out currently.

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(68) Absolute ^{13}C chemical shifts in ppm calculated at the CCSD(T)/qz2p level of theory: $C_1 = 181.638$, $C_2 = 160.637$, $C_3 = 133.256$, $C_4 = 111.991$.

(69) It should be noted that ref 16 also contains data from infrared spectroscopy. However, only a rather incomplete characterization of the molecular vibrations that the authors claim to originate from compound **10a** are given, which is not sufficient for a comparison with the calculated vibration spectra.

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