1,3-Heterocumulene-to-Alkyne [3 + 2] Cycloaddition Reactions: A Theoretical and Experimental Study

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Transition structures and energy barriers of the concerted prototypical cycloaddition reaction of 1,3-heterocumulenes (S═C═S, S═C═NR, RN═C═NR, and heteroanalogs) to acetylene resulting in nucleophilic carbenes were calculated by G2(MP2) and CBS-Q ab initio quantum chemical and by density functional theory (DFT) methods. According to the calculations the activation energies (activation enthalpies) of the homoheteroatomic cumulenes decrease in the order O > S > Se and NH > PH and the reaction energies in the order O > S ≈ Se and PH > NH. The reaction of carbon disulfide and acetylene has a lower reaction barrier than that of carbodiimide and acetylene although the first reaction is less exothermic than the second one. The stronger cyclic stabilization of the 1,3-dithiol-2-ylidene in the transition state is discussed in terms of deformation and stabilization energies and of bond indices. The known reactions of carbon disulfide with ring-strained cycloheptynes were examined by DFT and by DFT:PM3 two-layered hybrid ONIOM methods. In agreement with qualitative experimental findings the activation energy increases and the reaction energy decreases in the sequence S, SO_2, and $SiMe_2$ if CH_2 in the 5-position of 3,3,7,7-tetramethyl-1-cycloheptyne is replaced by a heteroatom or heteroatomic group, respectively. The results of these calculations were corroborated by experimental studies with carbon diselenide and isothiocyanates as 1,3-heterocumulenes. The cycloaddition of carbon diselenide to cyclooctyne proceeded faster than with carbon disulfide, the main product being the 1,3-diselenol-2-selone. Under more drastic conditions it was possible to add methyl and phenyl isothiocyanate, respectively, to 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne. The products are 1:3 adducts (cycloalkyne:isothiocyanate) whose formation is explained by a trapping reaction of the first formed 1,3-thiazol-2-ylidenes.

Introduction and Background

The Diels−Alder-type [4 + 2] and 1,3-dipolar [3 + 2] cycloaddition reactions have attracted much experimental[1] and theoretical interest.[2,3] The reaction proceeds generally in a concerted way resulting in stereospecific products. The concerted reaction is favored over the nonconcerted reaction.[4] The 1,3-dipolar cycloaddition reactions with acetylenes were also studied experimentally[1] and theoretically.[5] However, 1,3-heterocumulenes do not comply with the definition of 1,3-dipolar compounds. Nevertheless, they can undergo [3 + 2] cycloadditions with acetylenes[6] although preferably providing [2 + 2] adducts in various reactions.[7] In contrast to 1,3-dipolar compounds leading to saturated or unsaturated five-membered heterocycles in cycloaddition reactions with alkenes and alkynes, respectively, reactions of 1,3-heterocumulenes would provide nucleophilic carbenes (**1**) (Scheme 1, eq 1). In fact, alkynes having electron-withdrawing substituents added carbon disulfide under drastic conditions (high temperatures or high pressure) yielding tetrathiafulvalenes and more complex products.[6,8−11] At about the same time benzyne reactions with carbon disulfide were described in the literature;[12,13] in both publications the expected tetrathiafulvalene was not isolated[12] and observed in very low yield.[13] One of us reported the reaction of ring-strained seven-membered acetylenes and carbon disulfide at room or even lower temperatures resulting primarily in **2**[14] (Scheme 1, eq 2). The nucleophilic carbenes **2** were not stable and dimerized to tetrathiafulvalenes. The reaction failed, however,

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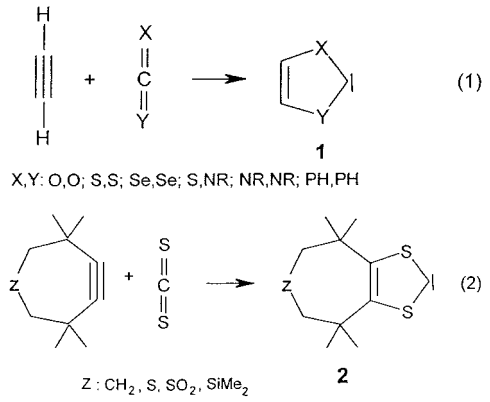
Scheme 1



with carbodiimides although nitrogen-containing nucleophilic carbenes are more stable. Structure, properties, and reactivity of 1,3-imidazol-2-ylidenes were extensively studied by first-order principles methods (cf. ref 15). Ab initio studies predicted aromatic stabilization of the 6π electron heterocylic carbenes with O, N, or S atoms.[16] As found by calculating isodesmic reactions, the stabilization is largest for 1,3-imidazol-2-ylidene. Substituted 1,3-imidazol-2-ylidene carbenes are available from the imidazolium ions[17] and are stable. The synthesis of a stable 1,3-thiazol-2-ylidene carbene has also been reported.[18]

To understand the factors governing these [3 + 2] cycloaddition reactions leading to stabilized carbenes we will address the following questions: First, how do the heteroatoms in the heterocumulenes influence the energetics of the [3 + 2] cycloaddition to alkynes? Second, how does ring strain in the alkynes influence the energetics of the [3 + 2] cycloaddition?

Computational Details

The study is mainly based on the Hohenberg−Kohn−Sham density functional theory (DFT).[19] As shown in the literature, the results of this method are generally comparable in the performance with those obtained by low-order many-body perturbation methods of ab initio chemistry.[2b,20] The DFT calculations of this study were based on the generalized gradient approximation (GGA) that is the most established form of the application of this method. The functional used throughout this study is the hybrid HF/DF exchange functional defined by Becke's three-parameter-equation.[21] It is used in conjunction with the Lee−Yang−Parr correlation functional[22] (B3LYP). The valence triple-ζ standard basis set 6-311+G** was preferably employed in the density functional calculations. Stationary points such as minima and saddle points of the parent structures were characterized by the number of negative eigenvalues of the Hessian matrix (zero for minima and one for saddle points, respectively). Since the ring-strained acetylenes' transition structures become computationally very demanding with extended basis sets, the ONIOM hybrid method has also been employed.[23] Using this method the reactive site of molecules is calculated by DFT and the strained cycloalkyne rings are calculated as the outer shell semiempirically by PM3.[24] The prototypical reactions were also studied by refined ab initio methods denoted as G2(MP2)[25] and CBS-Q.[26] These methods take into account the effect of basis set extension and of correlation in an additive correction scheme. They were developed to reproduce experimental data of a series of small molecules to an accuracy of ±2 kcal/mol. Enthalpies and free enthalpies were calculated for room temperature. These energies include zero-point vibrational energies. The atomic charges are derived as defined by natural orbital analysis (NBO).[27,28] The Wiberg bond indices (WBI)[29] were calculated by means of natural atomic orbitals.[28] Nucleus-independent chemical shifts (NICS values) were calculated by GIAO B3LYP/6-31+G* as proposed in ref 30. NICS values are the negative of the isotropic magnetic shielding calculated at the center of the conjugated rings. The quantum chemical calculations were carried out using the 1995 and 1998 releases of the GAUSSIAN suite of programs.[31,32]

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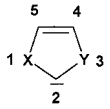
Table 1. Selected Bond Lengths of the Parent Carbenes 1 (B3LYP/6-311+G)**



bond (Å)[a]	O,O	S,S	Se,Se	S,NH	NH,NH	PH,PH
			Carbene[b]			
X_1–C_2	1.344	1.688	1.834	1.734	1.366	1.718
C_2–Y_3				1.348		
Y_3–C_4	1.389	1.766	1.914	1.398	1.392	1.819
C_4–C_5	1.327	1.344	1.339	1.347	1.354	1.349
X_1–C_5				1.754		
			Transition Structure			
X_1–C_2	1.277	1.578	1.715	1.593	1.256	1.655
C_2–Y_3				1.239		
Y_3–C_4	1.831	2.375	2.541	2.028	2.065	2.495
C_4–C_5	1.256	1.245	1.241	1.242	1.241	1.238
X_1–C_5				2.452		

[a] Calculated bond lengths of heterocumulenes in Å and bond angles δ and dihedral angles ω in deg (experimental values[46] in parentheses): O=C=O 1.161 (1.160, r_e); S=C=S 1.561 (1.559, r_g); Se=C=Se 1.701 (1.692, r_e); S=C=NH, 1.575, 1.202 (1.567, 1.207, r_s), δ_{SCN} 174.1 (173.8); HN=C=NH 1.221, δ_{NCN} 170.7; ω_{HNNH} 93.4; HP=C=PH 1.647, δ_{PCP}, ω_{HPPH}. [b] Planar compounds (C_{2v} symmetry) except for the phosphorus-containing carbene (C_2 symmetry).

Theoretical Results and Discussion

Molecular Structure. The molecular geometries of the reactants, transition structures, and products of the parent structures were calculated at the B3LYP/6-311-G** level of theory. Selected bond lengths are collected in Table 1. Apart from acetylene and a few 1,3-heterocumulenes experimental data are missing; the calculated bond lengths of the 1,3-imidazol-2-ylidene are in very good accordance with the experimental X-ray values of substituted analogues.[17a,c] As far as DFT and gas phase geometries are compared the agreement is remarkably good within twice the experimental uncertainty (cf. footnote *a* of Table 1). In general, DFT methods with the B3LYP functional overestimate bond lengths of second or higher row elements.[33] Experimental geometries are unknown for the parent carbenes. As detailed in Table 1, the parent carbenes considered show CC bond lengths between 1.33 and 1.35 Å. The lengths indicate the essential double bond character of the CC bond. The experimental NCN bond angle of the 1,3-imidazol-2-ylidene carbene is 101° in good agreement with the experimental bond angle of about 102° found in X-ray diffraction studies of substituted carbenes.[17a,c]

There are two particular features that should be mentioned: First, 1,3-heterocumulenes with terminal trivalent groups, such as nitrogen (**1**, X, Y = NH) or phosphorus (**1**, X, Y = PH), are nonplanar and exhibit C_2-symmetry; i.e., the two intersecting planes along the N=C=N axis are inclined to each other by nearly 90° (cf. footnote *a* of Table 1). The molecular dissymmetry of carbodiimide derivatives has been earlier discussed in the literature.[34] The nonplanar structure is clearly more stable than the planar one (by about 6 kcal/mol, in the case of the cis compound). The planar structures are the transition structures to inversion. It should also be mentioned that cumulenic bonds are not fully linear in the some cases (**1**, X, Y = NH, NH, PH, PH, and NH, S). Second, the geometries of the transition structures are similar to that of the reactants. Thus, the C_2-symmetry is retained in the transition structure of the carbodiimide-to-acetylene cycloaddition as shown in Figure 1. More general, according to the geometrical data collected in Table 1 the acetylenic fragment of the transition structures has CC bonds of about 1.24 Å. This bond length is closer to the length of the bond in acetylene (about 1.20 Å) as the reactant than to the bond length in the product (about 1.34 Å). Relatively small changes of about 0.2 Å in the CX(Y) bond lengths are also found in comparing the corresponding fragments of the transition structure with those of the free heterocumulenes as reactants. The bending of the linear or nearly linear heterocumulenes in the transition structure indicates the ring formation. These results are strong arguments in favor of an "early transition state" of the cycloaddition reaction.

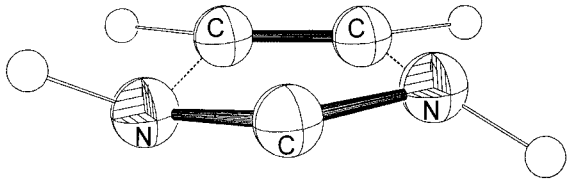


Figure 1. Perspective view of the dissymmetric transition structure of the concerted carbodiimide-to-acetylene cycloaddition.

Table 2. Activation and Reaction Energies $\Delta E^{\ddagger}$ and ΔE (kcal/mol)[a] of the Addition of X=C=Y to Acetylene (B3LYP/6-311+G)**

X	Y	$\Delta E^{\ddagger}$	$\Delta E_{strain}{}^{\ddagger}$	$\Delta E_{int}{}^{\ddagger}$	ΔE
O	O	61.9	75.8	−13.9	35.3
S	S	32.0	42.9	−10.9	1.8
Se	Se	27.1	37.4	−10.4	−1.6
S	NH[a]	33.4	40.6	−7.2	−16.2
S	NMe	33.9			−15.0
S	NPh	35.5			−10.4
NH	NH	36.3	42.0	−5.7	−32.1
NMe	NMe	33.5			−36.9
NCF_3	NCF_3	33.5			−28.1
PH	PH	25.6	29.5	−3.8	−13.0

[a] Deformation energy $\Delta E_{strain}{}^{\ddagger}$, transition state interaction energy $\Delta E_{int}{}^{\ddagger}$; $\Delta E^{\ddagger} = \Delta E_{strain}{}^{\ddagger} + \Delta E_{int}{}^{\ddagger}$— see text.

Energetics of the Parent Reactions. The energetic features were studied by density functional calculations, and the calculated reaction parameters are summarized in Table 2. The activation energy drops in the order O > S > Se and NH > PH. The activation energies are lower for heterocumulenes with elements of the higher row chalcogenes and pictogenes, such as sulfur and phosphorus. On the other hand, nitrogen containing compounds exhibit a more exothermic reaction. The stability of the resulting carbene in the latter case is well-known. An intermediate case is the compound containing one nitrogen and one sulfur atom in the ring. As to be expected, isothiocyanates are less reactive than carbon disulfide and more reactive than carbodiimides. Replacement of NH by NMe and NCF_3 has a noticeable effect on the

Cossi, J. M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, C.; Gonzalez, M.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN 98, Revision A.5*; Gaussian, Inc.: Pittsburgh, PA, 1998.

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Table 3. Thermodynamic Reaction Parameters of Prototype 1,3-Heterocumulene-to-Acetylene Cycloaddition Reactions (kcal/mol)[a]

method	X	Y	$\Delta E^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	ΔE	ΔH	ΔG
G2(MP2)								
	S	S	25.8	24.7	33.8	−7.5	−9.0	1.2
	S	NH	30.0	28.7	39.2	−18.8	−21.0	−8.9
	NH	NH	34.0	32.8	42.8	−30.4	−33.0	−21.3
CBS-Q								
	S	S	23.0	20.6	30.7	−9.1	−11.9	−0.7
	S	NH	28.3	29.2	37.1	−18.9	−18.8	−9.4
	NH	NH	32.6	30.1	41.2	−31.0	−34.4	−21.7

[a] Zero-point vibrational energies considered.

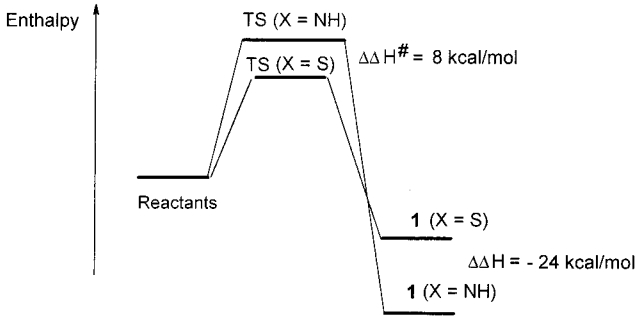

Figure 2. Qualitative reaction path diagram illustrating different stabilization effects for the transition and product structures. Energies were calculated by G2(MP2).

reaction energy (cf. Table 2). To the best of our knowledge, none of the parent reactions was studied experimentally so far.

Results of the calculations by the ab initio quantum chemical methods G2(MP2) and CBS-Q are presented in Table 3. The energies differ more widely than by DFT. The activation energy of the carbon disulfide-to-acetylene cycloaddition is clearly lower than that of the carbodiimide-to-acetylene addition. Again the lower barrier of the sulfur containing compounds is accompanied by a lower heat of reaction. This contradicts the Bell−Evans−Polanyi principle[35] suggesting a lower barrier in the case of the more exothermic reaction. The distinct reaction paths are illustrated in Figure 2 along with the calculated differences in the activation and reaction energies. The sulfur-containing transition structure is favored by about 8 kcal/mol relative to the nitrogen-containing one. On the other hand, the sulfur-containing carbene is disfavored with respect to the nitrogen containing compound by an reaction energy three times as large. Qualitatively the same conclusion is drawn from calculated energies, enthalpies, and free enthalpies. In the latter case the energies are enhanced by the entropic terms. The increase in energy amounts to about 10 kcal/mol.

The different stabilizing effects of heteroatoms on the reaction parameters seem not to be found in 1,3-dipolar cycloaddition reactions. In general, the Bell−Evans−Polanyi principle holds for 1.3-dipolar cycloaddition reactions,[3b] i.e., that increasing exothermicity of the reaction is accompanied by a reduced barrier height. To rationalize the exceptional behavior of the title reaction the DFT activation energies of 1 (X, Y = S, NH) were decomposed in two components as described formerly.[36] One contribution stands for the geometric deformation of the two reactant molecules in passing from the reactant geometry to the geometry of the transition structure. The second contribution is the net stabilizing interaction energy when the deformed reactant molecules are bound in the calculated structure of the transition state. Following a recent paper[36b] the two component energies are called activation strain energy (ΔE_{strain}) and transition state interaction energy (ΔE_{int}). The energies of deformation are obtained by single-point calculations of the fragments with geometries of the transition structure. This activation strain energy is higher than the activation energy of the reaction. The difference between the last mentioned energies is the stabilization of the transition structure including the various attractive and repulsive interaction energies between the components. According to the data listed in Table 2 the strain activation energy is nearly equal for the nitrogen- and sulfur-containing transition structure (about 42 kcal/mol) but the stabilization energy of the transition structure is larger by about 5 kcal/mol for the carbon disulfide-to-acetylene reaction. The sulfur containing 1,3-heterocumulenes are obviously more capable to form the long intermolecular bonds between the linear reactants in the "early transition state". In sharp contrast, oxygen-containing compounds with a large activation energy show an extremely large deformation energy and the gain in energy by interaction is relatively low. Moreover, the reaction is predicted to be strongly endothermic.

Table 4. Wiberg Bond Indices WBI of the Forming Bonds, Charge Transfer Q_{CT} from 1,3-Heterocumulene to the Acetylene Moiety, and Nucleus-Independent Chemical Shifts NICS in the Transition Structure

X	Y	WBI_{CX}	Q_{CT}	σ_{NICS} (ppm)
S	S	0.41	0.17	−25.9
S	NH	0.36	0.05	−26.4
NH	NH	0.35	0.02	−27.0

This different bonding in the transition structure of the cycloaddition reaction is supported by Wibergs bond indices (WBI). These values decrease in the order S, S > S, NH > NH, NH when sulfur is successively replaced by nitrogen (see Table 4). Concomitantly, the heterocumulene-to-acetylene charge transfer also decreases. The NICS values, however, proved to be less sensitive to heteroatomic substitution. The high negative values of NICSs only confirm the aromatic stabilization in the transition structures considered (see ref 37). This type of stabilization was early discussed by Evans in the case of the Diels−Alder reaction.

The different nature of the above-mentioned transition structures can also be discussed in terms of resonance structures derived by the natural resonance theory (NRT) of Weinhold and co-workers.[27] Although this concept is mainly developed for analyzing ground-state structures, it may be useful, in proper cases, for transition structures as well.[27] The analysis of the transition structures of the carbodiimide-to-acetylene and carbon disulfide-to-acetylene cycloaddition revealed characteristically different features. In the first case the NRT calculation decribes the transition structure in terms of localized structures that closely resemble the reacting components. These structures are acetylene and carbodiimide with a cumu-

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(36) (a) Sbai, A.; Branchadell, V.; Ortuña, R. M.; Oliva, A. *J. Org. Chem.* **1997**, *62*, 3049. (b) Bickelhaupt, F. M. *J. Comput. Chem.* **1999**, *20*, 114.

(37) (a) Morao, I.; Lecea, B.; Cossío, F. P. *J. Org. Chem.* **1997**, *62*, 7033. (b) Jiao, H.; Schleyer, P. v. R. *J. Phys. Org. Chem.* **1998**, *11*, 655.

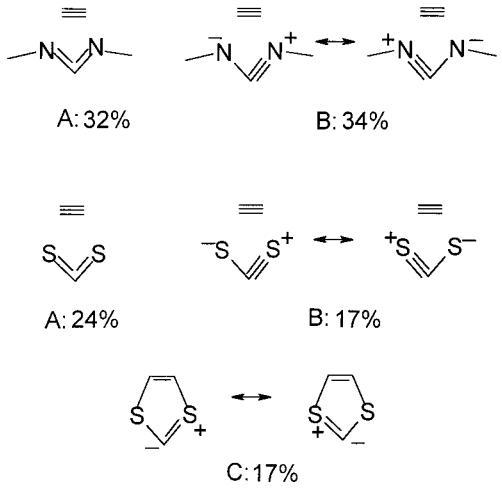


Figure 3. Weights of the main resonance contributors of the transition structures of the carbodiimide-to-acetylene and carbon disulfide-to-acetylene cycloaddition reactions derived by the natural resonance theory (DFT B3LYP/6-311+G**).

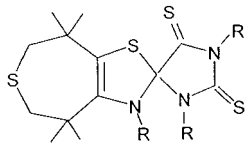
lenic bond in a single resonance structure and two equivalent charge-separated resonance structures. These structures are depicted in Figure 3. They are the leading structures in the NRT analysis. The remaining structures contribute to less than 5%. The bonding in the transition structure is obviously weak. In the case of the sulfur-containing transition structure calculated at the same footings[28b] the above-mentioned structures are also present but with lower weights. However, in addition two more delocalized structures appear as leading structures. They indicate bond formation between the reactants. The weights of these two structures increase in passing from the transition structure to the reaction product carbene. The charge-separated resonance structures actually dominate in the description of the carbene structure (73%). These structures are the typical and dominant resonance contributors of nucleophilic carbenes. The contribution of the resonance structure free of charge generally used in carbene formulas is negligibly low. Thus, the NRT analysis confirms the particular feature of the sulfur-containing compounds. The early bond formation makes evidently carbon disulfide more reactive than carbodiimide.

Cycladdition Reactions of Ring-Strained Cycloheptynes. When the triple bond is part of a seven- or eight-membered ring, the acetylenic bond is deformed and the ring is strained. In the consequence the acetylene is more reactive. The experimentally known reactions with carbon disulfide[14] enable some comparison with theoretical results to be made. The results of DFT calculations are assembled in Table 5. In the case of the reaction of 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne (4) with carbon disulfide the DFT energies were calculated at the same level of theory as those of the parent compounds listed in Table 2 (B3LYP/6-311+G**). The calculated lowering of the activation energy of about 10 kcal/mol for the sulfur-containing compound is in the same order of magnitude as the decrease of energy when reducing the CCH bond angle of acetylene from 180 to 150°. The counteracting effect of substitution due to the carbocyclic ring is less than expected from methyl substitution of acetylene (about 6 kcal/mol at the same DFT level).

Because of the lengthy computer time, the whole series 2 was calculated with the smaller 6-31+G* basis set. According to these calculations the barrier height increases in the order S < SO_2 < $SiMe_2$. This is the order of increasing angle deformation (cf. Table 5). To maintain the level of theory used in the calculation of the parent reaction (DFT B3LYP/6-311+G**) the more complex molecules were also calculated by the ONIOM method. The DFT method was used for the five-membered ring fragment with link atoms in the overlapping region of the remaining fragment of the molecule (HL; see Table 5). The atoms denoted by L are only considered by the simultaneously performed semiempirical PM3 calculation of the whole compound. The reaction energies are obviously overestimated by the ONIOM calculations. Only in the case of the carbon disulfide-to-3,3,6,6-tetramethyl-1-thia-4-cycloheptyne cycloaddition reaction the data are complete to compare both activation and reaction parameters. The activation energy of the ONIOM calculation differs only by about 1 kcal/mol from that of the more expensive full DFT calculation. The ONIOM calculation also reproduces very well the geometric parameters calculated by the full DFT calculation. As shown in Table 6 the bond lengths of the five-membered ring are very similarly predicted. The bond lengths differ no more than 0.005 Å. The conclusions drawn from the results of calculations obtained by the different theoretical models are consistent: The barrier increases with substitution of Z in **2** in the order S < SO_2 < $SiMe_2$. As mentioned above the reaction times of 5-substituted 3,3,7,7-tetramethyl-1-cycloheptynes with carbon disulfide actually increase in the same order.

Experimental Results

The results of these calculations stimulated new experiments with 1,3-heterocumulenes and angle-strained cycloalkynes. Particularly isothiocyanates, although less reactive than carbon disulfide, should be promising candidates for a [3 + 2] cycloaddition to reactive alkynes. However, hexafluoro-2-butyne was found to be totally inert toward phenyl isothiocyanate at 100 °C.[38] In contrast, the strained cycloalkyne 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne (**4**) reacts with excess methyl-isothiocyanate at 120 °C (3.5 h) to give a 1:3 (cycloalkyne: $H_3CN{=}C{=}S$) adduct in 60% yield. On the basis of the ^1H and ^{13}C NMR data, structure **3a** is assigned to this compound:



3a: R=Me
3b: R=Ph

The formation of the product **3a** can most plausibly be explained via a concerted [3 + 2] cycloaddition of the two reaction partners to yield the corresponding 1,3-thiazol-2-ylidene **5**, which adds two further molecules of methyl isothiocyanate to yield the spiroheterocycle **3a** (cf. Scheme 2).

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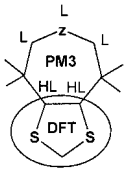
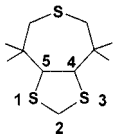
Table 5. Calculated Reaction Parameters (kcal/mol) of the Addition of Carbon Disulfide to Ring-Strained Acetylenes Calculated by DFT and ONIOM2 (kcal/mol) and Angle of Deformation δ of the Acetylene)



	DFT			DFT			ONIOM2[a]		
	B3LYP/6-31G*			B3LYP/6-311+G**			(B3LYP/6-311+ G**: PM3)		
Z	$\Delta E^{\ddagger}$	ΔE	δ^b	$\Delta E^{\ddagger}$	ΔE	δ^b	$\Delta E^{\ddagger}$	ΔE	δ^b
CH_2	16.8	−9.0	147.6		−5.4	147.7	18.1	−13.4	147.2
S	19.8	−2.5	150.4	21.8	0.8	150.0	20.7	−8.5	151.7
SO_2	21.8	−0.9	151.8		4.0	152.0	20.8	−8.2	152.1
$SiMe_2$	23.0	3.5	155.0		6.7	154.9	24.1	−4.0	156.7

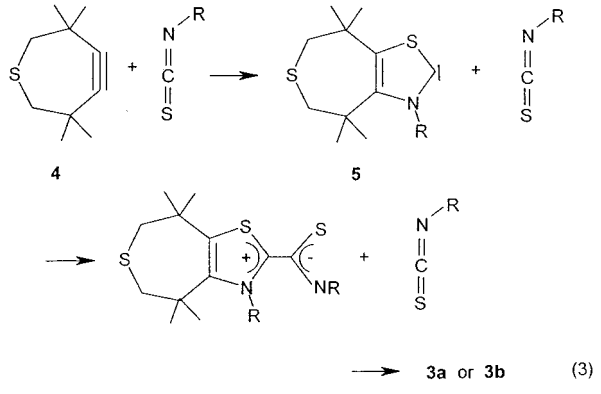
[a] ONIOM2 (B3LYP/6-311+G**: AM1) calculation X = CH_2: $\Delta E^{\ddagger}$ = 16.4 kcal/mol, ΔE = −13.8 kcal/mol, δ = 146.8°. [b] CCC bond angle of ring-strained acetylenes in deg.

Table 6. Comparison of Selected Bond Lengths in Å and Angles of the 3,3,6,6-Tetramethyl-1-thia-4-cyloheptyne/ Carbon Disulfide Transition Structures of the Concerted Cycloaddition and of the Resulting Carbene Calculated by Full DFT and ONIOM2 (DFT: PM3) Hybrid Method



struct	B3LYP/ 6-311+G**	ONIOM2 (B3LYP/ 6-311+G**: PM3)
	Transition Structure	
C_4C_5	1.254	1.259
S_1C_2	1.577	1.574
S_1C_5	2.432	2.427
$S_1C_5C_4$	110.1	110.3
$S_1C_2S_3$	136.3	138.0
	Product Structure	
C_4C_5	1.360	1.364
S_1C_2	1.669	1.667
S_1C_5	1.813	1.819
$S_1C_5C_4$	112.2	112.4
$S_1C_2S_3$	109.7	111.0

Scheme 2



Whereas there is no precedence for the first step of this reaction sequence in the literature, the addition of isothiocyanates to 1,3-thiazol-2-ylidenes to yield compounds analogous to **3** via a dipolar intermediate has been observed before.[39,40] Phenyl isothiocyanate gave an analogous addition product **3b**, but as predicted by the calculations, the reaction proceeds slower and the yield was significantly lower (17%). The lower yield may be due to a reduced reactivity of phenyl isothiocyanate in relation to methyl isothiocyanate toward the carbene. The same trend is also observed in reactions where the 1,3-thiazol-2-ylidene was generated from other precursors.[39,40]

Attempts to carry out an analogous [3 + 2] cycloaddition with dicyclohexylcarbodiimide and dibenzo[*d,h*]1,3-diazacyclonona-1,2,4,8-tetraene,[41] respectively, and **4** failed. As suggested by the calculations the free enthalphy of activation for the addition of carbodiimides is much higher than for the addition of carbon disulfide or isothiocyanates. The temperature cannot be increased beyond 120 °C since then decomposition of **4** occurs.

In high-pressure (4500−5000 atm) experiments carbon diselenide was more reactive toward acetylenic compounds bearing electron-withdrawing substituents or trimethylsilyl groups. Acetylenes disubstituted with methyl, phenyl, and chloromethyl groups did not react with carbon diselenide even under high-pressure conditions.[42,43]

The calculations show that the energy of activation for the addition of carbon diselenide is about 5 kcal/mol lower than that of carbon disulfide. Since the addition of carbon disulfide to **4** is already fast at room temperature under normal pressure, the less reactive cyclooctyne (**6**) was used in the experiments with carbon diselenide. The reaction of **6** with carbon diselenide was faster than with carbon disulfide. However, the main product was not the expected tetraselenafulvalene **7** (0.6%), but the 1,3-diselenol-2-selone **8** (19.2%); a third product, to which structure **9** is assigned on the basis of the mass spectrum, is obtained in 3.3% yield (cf. Scheme 3). The formation of 8 can be rationalized by addition of carbon diselenide to **6** yielding the 1,3-diselenol-2-ylidene **10**, which then picks up a selenium atom from carbon diselenide or another selenium intermediate. Obviously this reaction competes successfully with the dimerization of the carbene, which leads to **7**. The structure of **7** is proved by

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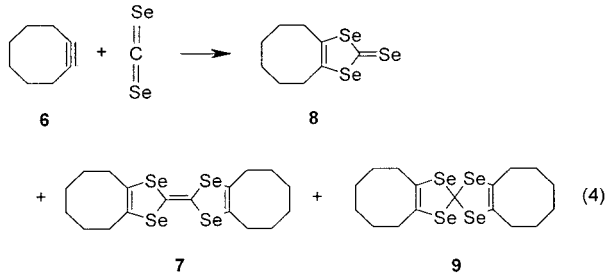
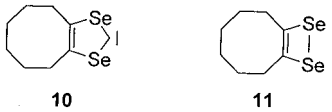
(40) Hoffmann, R. W.; Hagenbruch, B.; Smith, D. M. *Chem. Ber.* **1977**, *110*, 23.
(41) Molina, P.; Alajarin, M.; Sánchez-Andrada, P.; Elguero, J.; Jimeno, M. L. *J. Org. Chem.* **1994**, 59.
(42) Rice, J. E.; Wojciechowski, P.; Okamoto, Y. *Heterocycles* **1982**, *18*, 191.
(43) Okamoto, Y.; Lee, H. S.; Attarwala, S. T. *J. Org. Chem.* **1985**, *50*, 2788.

Scheme 3



the spectral data and an X-ray crystal structure analysis. If the reaction of **6** and carbon diselenide is carried out in the presence of red selenium, the yield of **8** is highly increased (59%); this supports the proposed mechanism of formation of **8** from **10**. Compound **9** may be formed by reaction of an intermediate 1,2-diselenete **11** with **10**, but other ways of formation are also possible.



Conclusions

The density functional methodology (DFT/B3LYP) has been used in conjunction with split-valence double or triple-ζ basis sets to study the reactivity of 1,3-heterocumulenes with acetylene and strained seven-membered ring acetylenes. The DFT calculations of the prototypical reactions led to the same conclusions as G2(MP2) and CBQ-S calculations. Some features of the present knowledge of such reactions are now better understood. Thus, sulfur-containing compounds are more reactive than the nitrogen-containing compounds although nitrogen stabilizes the carbene more than sulfur. The formation of 1,3-imidazol-2-ylidenes has not been observed by in carbodiimide-to-acetylene cycloaddition reactions. As shown experimentally, methyl and phenyl isothiocyanate are sufficiently reactive to undergo this reaction. As predicted by the calculations, carbon diselenide is found to be more reactive than carbon disulfide. In the calculations of ring-strained acetylenes the hybrid ONIOM methodology has been used. The heterocyclic five-membered ring was calculated by DFT, and the seven-membered ring, by the semiempical PM3 method in a more recently developed hybrid-type procedure. In accordance with experimental findings the reactivity of carbon disulfide toward 3,3,7,7-tetramethyl-1-cycloheptyne is reduced if the methylene group of the seven-membered ring is replaced at 5-position by sulfur or by the heteroatomic groups SO_2 or $SiMe_2$.

Experimental Section

Materials and Methods. The cycloalkynes **4**[14b] and **6**[44] and also carbon diselenide[45] were prepared according to literature procedures. Methyl isothiocyanate was purchased from Merck, Darmstadt, Germany. For preparative chromatography silica gel, mesh 70−230 (Merck), was used.

3,5,5,9,9,1′,3′-Heptamethylspiro(bicyclo[5.3.0]-3-aza-1,7-dithia-4(10)-decenyl-2,4′-imidazolidine)-2′,5′-dithione (3a). A mixture of **4** (270 mg, 1.60 mmol) and methyl isothiocyanate (2) (700 mg, 9.57 mmol) was kept at 120 °C for 3.5 h in an autoclave (Büchi Tinyclave). The resulting red oil was dissolved in *n*-hexane and purified by chromatography on silica gel (petroleum ether (50−70 °C):ethyl acetate 15:1); dark red crystals (370 mg, 0.96 mmol, 59.6%) of melting point 100−105 °C were obtained: ^{1}H NMR (400 MHz, C_6D_6) δ 1.04, 1.14, 1.16, 1.25 (4s, 3H each, CCH_3), 2.25 and 2.50 (AB, 2H, J_{AB} = 14.7 Hz, CH_2), 2.35 and 2.55 (AB, 2H, J_{AB} = 14.0 Hz, CH_2), 2.36, 3.08, 3.40 (3s, 3H each, NCH_3); ^{13}C NMR (100.62 MHz, C_6D_6) δ 27.95, 30.12, 30.43, 31.22 (CCH_3), 30.55, 33.33, 35.50 (NCH_3), 40.36, 40.54 (CCH_3), 45.44, 48.82 (SCH_2), 101.33 (spiro C), 115.51, 137.28 (C=C), 177.32 (NC(S)N), 197.63 (C*C*(S)N); EIMS (70 eV) *m*/*z* 387 (M^+, 100), 372 ($M^+ - CH_3$, 10), 285 ($M^+ - (H_3CN)_2$ C=S, 18). Anal. Calcd for $C_{16}H_{25}N_3S_4$: C, 49.55; H, 6.50; N, 10.88; S, 33.07. Found: C, 49.53; H, 6.57; N, 10.59; S, 32.90.

5,5,9,9-Tetramethyl-3,1′,3′-triphenylspiro(bicyclo[5.3.0]-3-aza-1,7-dithia-4(10)-decenyl-2,4′-imidazolidine)-2′,5′-dithione (3b). A mixture of **4** (530 mg, 3.15 mmol) and phenyl isothiocyanate (2.57 g, 19 mmol) was kept at 120 °C for 3.5 h in an autoclave. A red oil was obtained, which was dissolved in *n*-hexane and purified by chromatography on silica gel (petroleum ether (50−70 °C):ethyl acetate 15:1); orange crystals (310 mg, 0.54 mmol, 17.1%) of melting point 180−185 °C were isolated: ^{1}H NMR (400 MHz, THF-d_8) δ 0.73, 1.15, 1.30, 1.35 (4s, 3H each, C*C*H$_3$), 1.82, 2.23 (2d, 1H each, J = 13.7 Hz, CH_2), 2.25, 3.12 (2d, 1H each, J = 14.2 Hz, CH_2), 7.1−7.9 (m, 15H, arom. H); ^{13}C NMR (100.62 MHz, THF-d_8) δ 24.87, 26.89, 29.52, 30.31 (CH_3), 37.77, 38.47 ($C(CH_3)$), 39.42, 42.90 (CH_2), 100.49 (C spiro), 125.82, 142.87 (C=C), 123.19−129.36 (tert C_{arom}, 15C), 134.01, 135.31, 135.71 (quart. C_{arom}, 3C), 176.40 (NC(S)N), 192.00 (C*C*(S)N); FAB-MS *m*/*z* 574 (M^+, 25), 439 ($M^+ - C_6H_5N$=C=S, 56), 3.29 ($C_{15}H_{11}N_3S_3^+$, 56), 197 ($C_{13}H_{13}N_2^+$, 88), 169 ($C_{10}H_{17}S^+$, 100). Anal. Calcd for $C_{31}H_{31}N_3S_4$: C, 64.88; H, 5.45; N, 7.32; Found: C, 64.61; H, 5.94; N, 6.91.

Reaction of Cyclooctyne (6) with Carbon Diselenide. A solution of carbon diselenide (1.0 g, 5.88 mmol) in 4 mL of dichloromethane was slowly added within 30 min to a boiling solution of **6** (634 mg, 5.88 mmol) in 4 mL of dichloromethane in an argon atmosphere. The solution turned red within 10 min and was refluxed for 14 h. The solvent was removed and the resulting red material chromatographed on 100 g of silica gel (petroleum ether (60−70 °C):diethyl ether 19:1). At first a mixture of **7** and **9** was eluted, which could be separated by fractional crystallization from *n*-hexane. Subsequently, the main product **8** was collected.

Bis(cycloocteno[1,2-*d*]1,3-diselenol-2-ylidene) (7): dark red crystals (9 mg, 0.016 mmol, 0.6%), mp 216 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.49−1.70 (m, 16H, β- and γ-CH_2), 2.31−2.44 (m, 8H, α-CH_2); EIMS (70 eV) *m*/*z* 560 (M^+ with four ^{80}Se, 72), 558 (M^+, 98), 450 ($M^+ - C_8H_{12}$, 9), 370 ($M^+ - C_8H_{12}$Se, 24). Anal. Calcd for $C_{18}H_{24}Se_4$: C, 38.87; H, 4.35; Se, 56.78. Found: C, 38.98; H, 4.35; Se, 56.53.

Spirobis(cycloocteno[1,2-*d*]1,3-diselenol-2-ylidene (9): yellow crystals (52 mg, 0.096 mmol, 3,3%), mp 135−136 °C (dec); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 26.29, 29.14, 29.85 (CH_2), 133.33 (C=C); EIMS (70 eV) *m*/*z* 548 (M^+ with four ^{80}Se, 7), 546 (M^+, 10), 438 ($M^+ - C_8H_{12}$, 31). Anal. Calcd for $C_{17}H_{24}Se_4$: C, 37.52; H, 4.45. Found: C, 37.43; H, 4.43.

Cycloocteno[1,2-*d*]1,3-diselenol-2-selone (**8**): red crystals (268 mg, 0.75 mmol, 19.2%), mp 102−103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.55−1.78 (m, 8H, β- and γ-CH_2), 2.71−2.79 (m, 4H, α-CH_2); EIMS (70 eV) *m*/*z* 360 (M^+ with three ^{80}Se, 38), 358 (M^+, 43), 268 (M^+ − CSe, 3), 188 ($M^+ - CSe_2$, 7). Anal. Calcd for $C_9H_{12}Se_3$: C, 30.27; H, 3.39; Se, 66.34. Found: C, 30.51; H, 3.37; Se, 66.34.

Reaction of Cyclooctyne with Carbon Diselenide in the Presence of Red Selenium Cycloocteno[1,2-*d*]1,3-diselenol-2-selone (8). A solution of **6** (955 mg, 8.83 mmol)

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(45) Ives, D. J.; Pittman, R. W.; Wardlaw, W. *J. Chem. Soc.* **1947**, 1080.
(46) . *Structure Data of Free Polyatomic Molecules*; Landolt-Börnstein, New Series, Vol. II/25; Kuchitsu, K., Ed.; Springer-Verlag: Berlin, 1999.

in 10 mL of dichloromethane was slowly added within 30 min to a refluxing mixture of carbon diselenide (3.0 g, 17.65 mmol) and red selenium (5.57 g, 70.6 mmol) in 25 mL of dichloromethane under an argon atmosphere. The reaction mixture was refluxed for 14 h, the excess selenium filtered off, and the solvent removed by rotary evaporation. The residue was recrystallized from *n*-hexane. Dark red crystals (1.85 g, 5.18 mmol, 58.7%) of melting point 100−102 °C were obtained. The compound was identical with **8** (mmp, IR spectrum).

Bis(cycloocteno[1,2.d]1,3-diselenol-2-ylidene) (7) from 8 and Trimethyl Phosphite. To a benzene solution (5 mL) of **8** (2.0 g, 5.6 mmol) was added a benzene solution (5 mL) of trimethyl phosphite (1.32 mL, 11.2 mmol). The reaction mixture was refluxed for 45 min; after cooling of the mixture to room temperature, 10 mL of *n*-pentane was added and the violet precipitate was filtered out, washed with 10 mL of *n*-pentane, and recrystallized from *n*-hexane. Yield: 1.47 g (2.64 mmol, 94.3%), mp 216 °C. The product was identical with **7** (mmp, IR spectrum).

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Supporting Information Available: Tables giving the Cartesian coordinates of the carbenes 1 (X, Y: O, O; S, S; Se, Se; S, NH; S, NMe; S, NPh; NH, NH; NMe, NMe; NCF_3, NCF_3; PH, PH) and carbenes **2,** as well as of transition structures of the concerted heterocumulene-to-acetylene cyloaddition reactions at the B3LYP/6-311+G** and BLYP/6-31+G* level, respectively, and Cartesian coordinates of B3LYP/6-311+G** and ONIOM B3LYP/6-311+G**: PM3) calculations of **2** (Y= S) and energies of G2(MP2) and CBS-Q calculations of **1** (X, Y: S, S; NH, S; NH, NH). This material is available free of charge via Internet at htt://pubs.acs.org.

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