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Model Studies on the Dimerization of 1,3-Diacetylenes

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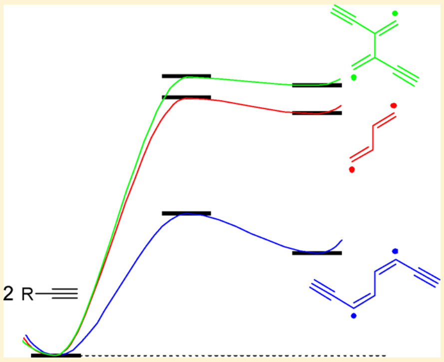
Supporting Information

ABSTRACT: By means of high-level quantum chemical calculations (B2PLYPD and CCSD(T)), the dimerization of 1,3-diacetylenes was studied and compared to the dimerization of acetylene. We found that substituted 1,3-diacetylenes are more reactive than the corresponding substituted acetylenes having an isolated triple bond. The most reactive centers for a dimerization are always the terminal carbon atoms. The introduction of a test reaction allows the calculation of the relative reactivity of individual carbon centers in phenylacetylene, phenylbutadiyne, and phenylhexatriyne. A comparison shows that the reactivity of the terminal carbon atoms increases with increasing numbers of alkyne units, whereas the reactivity of the internal carbon atoms remains very low independent of the number of alkyne units.



INTRODUCTION

During the last few decades the thermal reactions of two acetylenic units with formation of diradical species have been investigated by various authors.[1,2] In the 1970s Bergman et al.[3−5] studied the thermal cyclization of (*Z*)-hex-3-ene-1,5-diyne (**1**) to 1,4-didehydrobenzene (**2**) at temperatures over 470 K (Scheme 1a). The activation energy (E_a) for the cyclization of (*Z*)-hex-3-ene-1,5-diyne (**1**) has been experimentally determined to be 29.2 ± 0.5 kcal/mol in the gas phase at 470 K.[6] Sondheimer[7] and Gleiter[8] have shown that conjugated and nonconjugated cyclic diynes also undergo a transannular ring closure, if the two parallel oriented alkyne units are located in close proximity (Scheme 1b). For 1,6-cyclodecadiyne (**3**) an activation energy (E_a) of 29.7 ± 0.4 kcal/mol in the gas phase at 450 K was reported.[9]

Recently, we have investigated the dimerization of substituted acetylenes using high level ab initio methods and kinetic studies.[10] We were able to demonstrate that electron-withdrawing groups having oxygen or chlorine centers attached to the triple bond reduce the activation barrier of the dimerization considerably and stabilize the corresponding 1,3-butadiene-1,4-diyl intermediates.[10a] The higher the electronegativity of the substituent attached at the reacting carbon centers, the lower the activation energy. Accordingly, the activation barrier for the dimerization of **5a** (16.8 ± 1.0 kcal/mol) is lower than that obtained for **5b** (21.9 ± 1.1 kcal/mol) (Scheme 1c).[10b]

The strong dependence of the thermal dimerization on the substituents encouraged us to extend our studies to 1,3-diacetylenes which show a special behavior and stability. For example, Wegner found that parallel aligned 1,3-butadiyne units yielded, upon irradiation or heating, a 1,4-addition in a topochemical reaction (Scheme 2a).[11,12] Furthermore, the stability of conjugated oligoalkynes decreases with an increasing number of acetylenic units.[13] Conjugated oligoalkynes with terminal triple bonds are particularly unstable.[13b] For example, while phenylacetylene is stable, the corresponding di- and triacetylene compounds **8a**[14] and **9a**[15] are unstable in concentrated solution (Scheme 2b).[16] An increase of the stability can be achieved by the introduction of a trimethylsilyl group (**8b** and **9b**) as a protective group of the terminal triple bond.

In this paper we show by using model calculations that the activation energy and the reaction energy for the thermal dimerization of 1,3-diacetylenes strongly depend on the substituent and the position of the reacting carbon center within the alkyne chain. The most reactive centers are the terminal carbon atoms. Electronegative substituents decrease and electropositive substituents increase the reaction barrier.

RESULTS AND DISCUSSION

(a). Model Studies on the Dimerization of 1,3-Diacetylene.

To determine the effect of an alkyne unit (attached to the reacting center) on the dimerization of alkynes, the 1,1′-, 2,2′-, and 1,2′-dimerizations of 1,3-diacetylene (**13**) were compared to the dimerization of acetylene (**10**; Scheme 3). The stationary points of these reactions were optimized using the double-hybrid method B2PLYPD by Grimme.[17] cc-pVTZ[18] was employed as the basis set. Additionally, the energies were calculated by means of the CCSD(T)[19] approximation. In earlier studies regarding the thermal cyclization of 1,6-cyclodecadiyne (**3**) to its corresponding diradical (**4**; Scheme 1b), we obtained values with this method

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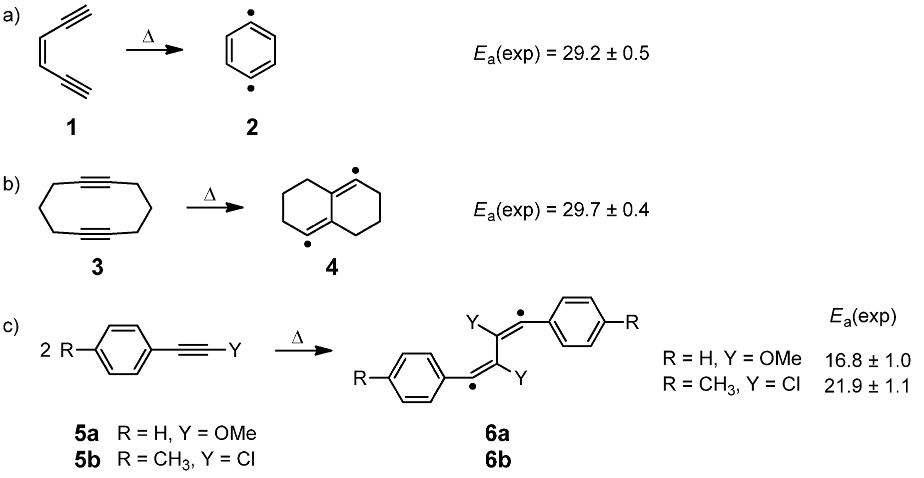
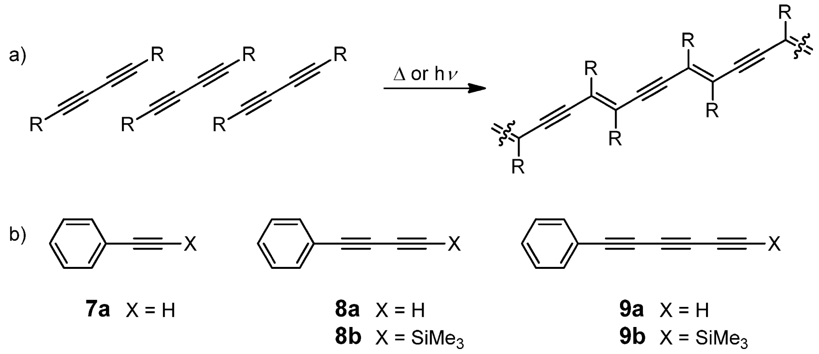
Scheme 1. Bergman Cyclization (a), Transannular Ring Closure of 1,6-Cyclodecadiyne (b), and Dimerization of the Substituted Phenylacetylenes 5a,b (c)[a]

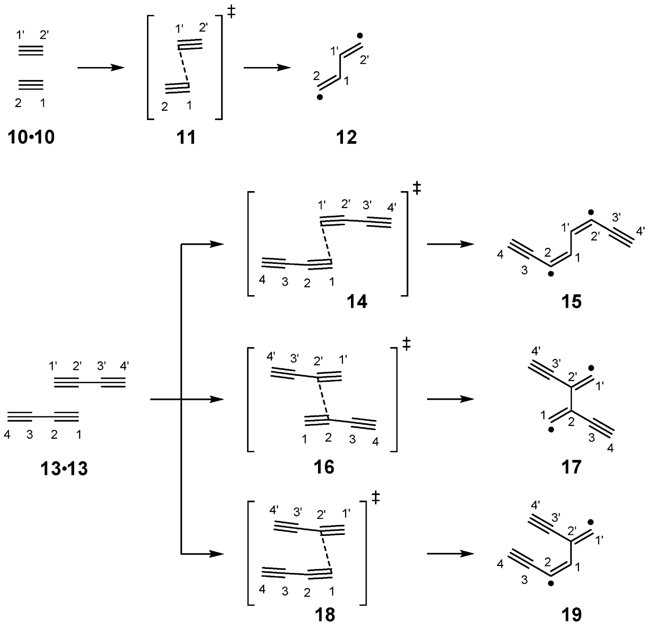


[a] The experimentally determined activation energies (E_a) are given in kcal/mol.

Scheme 2. (a) Solid-State Polymerization of 1,3-Diynes To Yield a *trans*-Polybutadiyne and (b) Substituted Phenylacetylenes 7–9



Scheme 3. Dimerization of Acetylene (10) and 1,3-Diacetylene (13) to the Corresponding Diradicals 12, 15, 17, and 19



which show a very high consistency with experimental data.[10a] Therefore, we decided to use this method for the dimerization of 1,3-diacetylenes. Furthermore, single-point calculations were performed on the B2PLYPD-optimized structures using the (8/8)CASSCF and (8/8)CASPT2 approximations. Here again, the cc-pVTZ[18] basis set was used. The calculated data for the dimerizations are shown in Table 1.

A comparison of the CASSCF wave functions shows that the transition states and products are open-shell species. As a measure of the diradical character of the stationary points, the occupation numbers of the frontier orbitals n_1 (antibonding linear combination) and n_2 (bonding linear combination) can be used (Figure 1 and Table 1).[20] In a perfect diradical both frontier orbitals would be equally populated. All transition states and diradicals are far from being perfect, which is due to through-bond interactions[21] via the orbitals of the reacting centers. If the radical centers of the three diradicals **12**, **15**, and **17** are considered, the different hybridizations of the carbon atoms become evident. The diradicals **12** and **17** have sp^2-hybridized radical centers. In the case of **15** the C1–C2–C3 angle was calculated to be 152°, which means that the hybridization of the carbon centers C2 and C2′ lies between sp^2 and sp. The reason for this difference is an energetically favored conjugation of the terminal acetylenic units (C3≡C4 and C3′≡C4′) with the radical centers C2 and C2′ in **15** (Figure 1).

Table 1. Distances *R* of C1−C1′, C2−C2′, and C1−C2′, Respectively, Relative Energies (Δ*E*), and Occupation Numbers for the Linear Combinations of the Nonbonding Orbitals n_1 (Antibonding Linear Combination) and n_2 (Bonding Linear Combination) of 11, 12, and 14−19

	11	12	14	15	16	17	18	19
R (Å)[a]	1.670	1.541	1.849	1.483	1.695	1.554	1.748	1.541
ΔE^a (kcal/mol)	37.4	36.7	21.3	15.1	45.3	44.7	34.4	32.8
ΔE^b (kcal/mol)	34.4	30.5	25.0	17.4	39.9	36.6	33.6	4.31
ΔE^c (kcal/mol)	49.3	46.3	45.6	39.1	56.1	56.7	58.7	48.3
ΔE^d (kcal/mol)	27.3	24.0	18.3	8.2	31.9	31.2	25.5	22.7
$n_1{}^c$	1.549	1.373	1.794	1.275	1.542	1.344	1.545	1.309
$n_2{}^c$	0.455	0.629	0.210	0.727	0.459	0.656	0.455	0.691

[a] B2PLYPD/cc-pVTZ. [b] CCSD(T)/cc-pVTZ//B2PLYPD/cc-pVTZ. [c] (8/8)CASSCF/cc-pVTZ//B2PLYPD/cc-pVTZ. [d] (8/8)CASPT2/cc-pVTZ//B2PLYPD/cc-pVTZ.

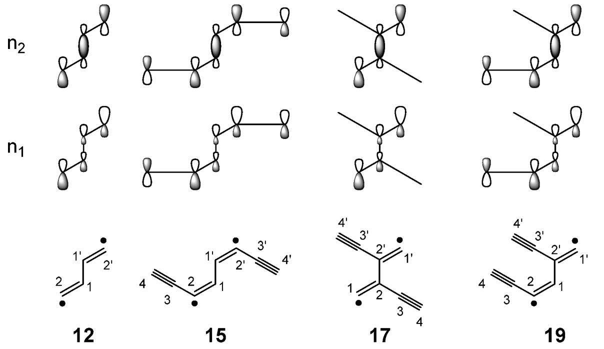
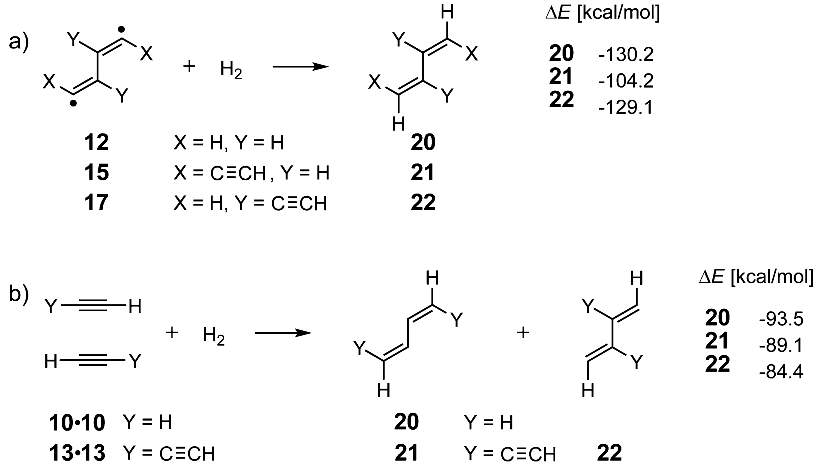


Figure 1. Schematic representation of the linear combinations of the nonbonding orbitals of the diradicals **12**, **15**, **17**, and **19**. The orbital n_1 represents the antibonding linear combination, whereas the orbital n_2 is the bonding linear combination.

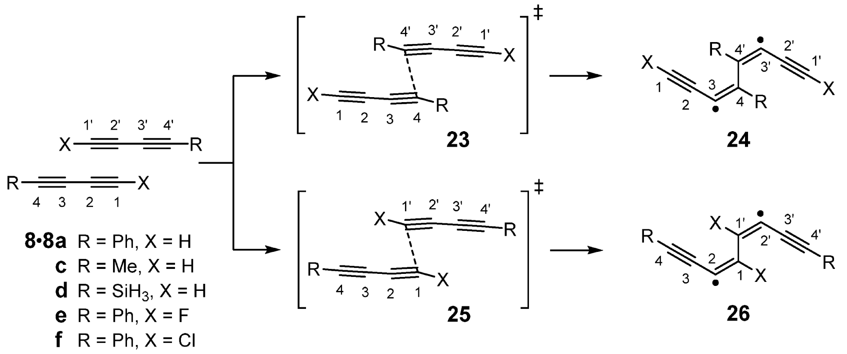
A comparison of the calculated energies for the 1,1′- and 2,2′-dimerization of **13** reveals a quite good agreement between the B2PLYPD values and the data obtained using the CCSD(T) approximation. In the case of the 1,1′ dimerization of **13** the CCSD(T) energies are slightly higher and in the case of the 2,2′-dimerization of **13** they are lower than the corresponding B2PLYPD energies. As expected, the energies calculated by means of CASSCF theory are too high. This can be explained by the fact that CASSCF calculations do not take dynamic correlation into account. The CASPT2 energies for the diradicals are lower than those calculated using B2PLYPD and CCSD(T). This is due to the fact that the CASPT2 approximation tends to overestimate the stabilizing energies of diradical states in comparison to closed shell systems.[22,8b,10]

However, the relative reactivity (difference in the activation energies) is independent of the method used: the lowest activation energy by far is predicted for the 1,1′-dimerization of 1,3-diacetylene, followed by the 1,2′-dimerization of 1,3-diacetylene and the dimerization of acetylene, which show similar activation barriers. The highest activation energy is found for the 2,2′-dimerization of 1,3-diacetylene (Table 1). This series can easily be explained if additionally the energies for the hydrogenation of the diradicals **12**, **15**, and **17** and the dimers **10·10** and **13·13** to the alkenes **20**−**22** are considered (Scheme 4). The energies for the hydrogenation of the diradicals **12** (−130.2 kcal/mol; B2PLYPD/cc-pVTZ) and **17** (−129.1 kcal/mol) are very similar, which means that the radical centers in **17** are neither stabilized nor destabilized in comparison to those in the diradical **12**. The higher reaction energy for the formation of **17** (44.7 kcal/mol; B2PLYPD/cc-pVTZ) in comparison to that for **12** (36.7 kcal/mol) is caused instead by loss of conjugation energy. The conjugation energy between the four π bonds in 1,3-butadiyne yields—depending on the used model—up to 45 kcal/mol.[23] For 1,3-butenyne the π conjugation was calculated to be only −21 kcal/mol.[23b] Thus, during the dimerization reaction of **13** a part of its stabilizing conjugation energy is lost. The energy of hydrogenation of the dimers **10·10** and **13·13** to the alkenes **20**−**22** underlines this (Scheme 4b). The energy of hydrogenation for the diradical **15**

Scheme 4. Energies for the Hydrogenation of the Diradicals 12, 15, and 17 (a) and the Dimers 10·10 and 13·13 (b) to the Alkenes 20−22 Calculated using B2PLYPD/cc-pVTZ



Scheme 5. Dimerization of the Substituted 1,3-Diacetylenes 8·8 to the Diradicals 24 and 26



(−104.2 kcal/mol; B2PLYPD/cc-pVTZ) is significantly lower than those for **12** (−130.2 kcal/mol) and **17** (−129.1 kcal/mol). This is a result of the aforementioned stabilization of the radical centers in **15** by the adjacent alkyne units. This stabilization also overcompensates the loss of the conjugation energy between the two alkyne units in **13** during the dimerization reaction. Thus, the 1,1′-dimerization of 1,3-diacetylene is more favorable than the dimerization of acetylene and the 2,2′-dimerization of 1,3-diacetylene.

(b). Model Studies on Substituent Effects in the Dimerization of 1,3-Diacetylenes and Relative Reactivity of the Carbon Centers of Phenyloligoacetylenes. In order to investigate the substituent effect on the dimerization of 1,3-diacetylenes, the 1,1′- and 4,4′-dimerization reactions of the diynes **8** were calculated (Scheme 5). Methyl, phenyl, and silyl groups were used as substituents R. Hydrogen as well as the electronegative elements fluorine and chlorine were employed as the substituents X. The latter are known to decrease the activation energies of the dimerization of isolated triple bonds when they are attached to the reacting centers.[10b] The geometry optimization was performed by means of B2PLYPD. In all cases the 6-31G* basis set was employed. As no convergence was reached with 6-31G* for the diradicals **24e,f**, the SVP basis was used for the geometry optimization of **24e,f**. The energies of the stationary points were calculated using B2PLYPD/def2-TZVP. In case of the 1,3-diacetylenes with small substituents (**8c,d**) the energies were additionally computed with the CCSD(T)/def2-TZVP and DLPNO-CCSD(T)[24]/def2-TZVP methods. In order to test if the use of these basis sets causes a change in the energies, the dimerizations of **10** and **13** were also computed by this method. The calculated data are summarized in Table 2 and Figure 2.

Table 2. Energies (Δ*E* in kcal/mol) of the Transition States (11, 14, 23, and 25) and Products (12, 15, 24, and 26) Relative to the Corresponding Starting Materials (8·8, 10·10, and 13·13)[a]

	R	X	*R* (Å)[b]	Δ*E*[c]	Δ*E*[d]	Δ*E*[e]
11			1.706	37.8	34.5	38.5
12			1.518	37.7	29.2	36.3
14			1.878	21.7	24.5	27.7
15			1.479	15.7	15.7	25.5
23a	Ph	H	1.858	22.8		
24a	Ph	H	1.514	19.2		
23c	Me	H	1.857	23.3	25.0	30.1
24c	Me	H	1.499	18.9	19.5	29.6
23d	SiH_3	H	1.718	29.8	32.2	37.6
24d	SiH_3	H	1.571	29.8	31.6	40.0
23e	Ph	F	1.849	23.6		
24e	Ph	F	1.519[f]	21.6[g]		
23f	Ph	Cl	1.885	21.2		
24f	Ph	Cl	1.506[f]	17.6[g]		
25a	Ph	H	1.946	17.3		
26a	Ph	H	1.468	7.7		
25c	Me	H	1.890	21.2	24.0	27.7
26c	Me	H	1.479	14.7	15.8	26.0
25d	SiH_3	H	1.908	19.7	23.1	26.3
26d	SiH_3	H	1.456	11.6	15.9	26.7
25e	Ph	F	2.173	5.1		
26e	Ph	F	1.444	−24.7		
25f	Ph	Cl	2.070	14.4		
26f	Ph	Cl	1.457	−5.9		

[a] The distances *R* of C1−C1′, C2−C2′, and C4−C4′, respectively, are also given. [b] B2PLYPD/6-31G*. [c] B2PLYPD/def2-TZVP//B2PLYPD/6-31G*. [d] CCSD(T)/def2-TZVP//B2PLYPD/6-31G*. [e] DLPNO-CCSD(T)/def2-TZVP//B2PLYPD/6-31G*. [f] B2PLYPD/SVP. [g] B2PLYPD/def2-TZVP//B2PLYPD/SVP.

A comparison of the energy values for the dimerization of **10** and **13** shows that the use of the smaller basis sets leads to no significant change for the B2PLYPD and CCSD(T) approximations (Tables 1 and 2). Furthermore, the dimerization energies for **8** obtained using B2PLYPD/def2-TZVP match well, within 3−4 kcal/mol, with the values calculated by means of CCSD(T)/def2-TZVP. This shows that the method B2PLYPD/def2-TZVP//B2PLYPD/6-31G* is in principle appropriate for describing the dimerization of substituted diynes.

It is interesting that the deviation between the CCSD(T) and DLPNO-CCSD(T) values can be up to 10 kcal/mol. In general, local pair natural orbital coupled-electron pair and coupled-cluster methods reproduce their canonical counterparts with excellent accuracy (typically below 1 kcal/mol) while leading to orders of magnitude computational savings.[25] In our case the deviation between the methods seems to depend strongly on the diradical character of the calculated species. For example, the activation energies obtained by DLPNO-CCSD(T) are 3−5 kcal/mol higher than those calculated using CCSD(T). In the case of the diradicals the difference amounts to 7−10 kcal/mol.

A glance at the values for the 1,3-diacetylenes **8a,c−f** shows that the 1,1′-dimerization is always preferred in comparison to the corresponding 4,4′-dimerization. The difference and the reason for this behavior is, however, strongly dependent on the substituents R and X (Table 2 and Figure 2). If the activation energy of the 1,1′-dimerization of the nonsubstituted 1,3-diacetylene (**13**; 21.7 kcal/mol; B2PLYPD/def2-TZVP//

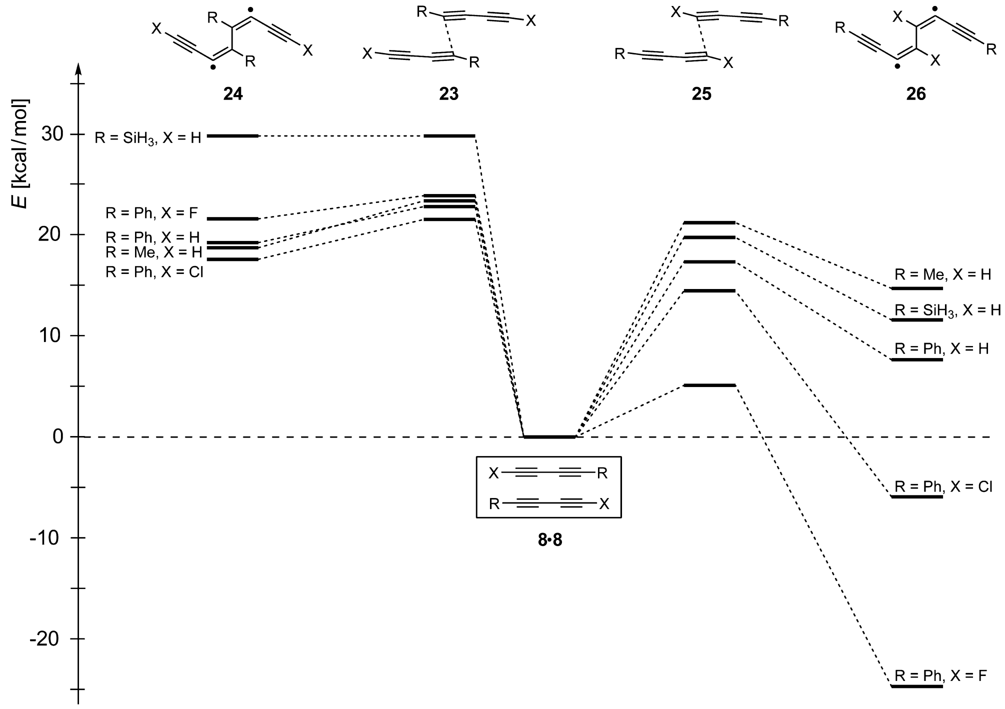


Figure 2. Energy profiles of the dimerization of substituted 1,3-diacetylenes **8·8** to diradicals **26** and **28** calculated using B2PLYPD/def2-TZVP.

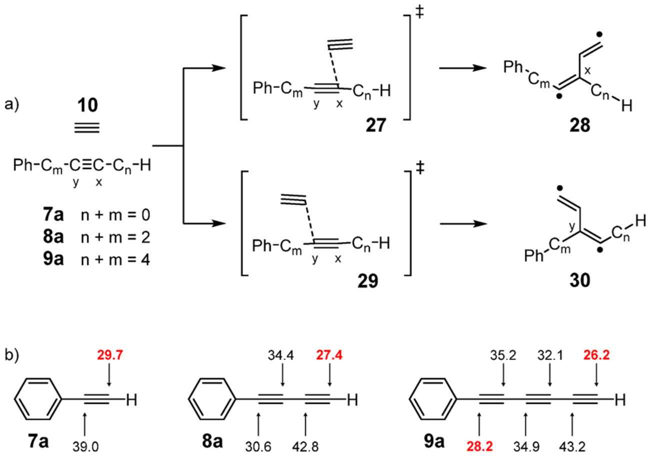
B2PLYPD/6-31G*) is used as reference, it can be seen that a methyl group (**23c**; 23.3 kcal/mol) or a phenyl group (**23a**; 22.8 kcal/mol) attached to the reacting centers slightly increases the reaction barrier. For the silyl group (**23d**; 29.8 kcal/mol) a drastic increase of the activation energy is found. On the other hand, if the substituent R is attached to the alkyne units which are not involved in the dimerization process, in all cases a decrease in the activation barrier is calculated. The most pronounced effect is found for the phenyl group (**25a**; 17.3 kcal/mol).

A further increase in the reactivity can be achieved if the terminal hydrogen atoms are replaced by the electron-withdrawing elements fluorine and chlorine. Here, the diradicals **26e,f** are even more stable than the corresponding dimers **8e·8e** and **8f·8f** (Table 2 and Figure 2). This decrease in the activation barriers and reaction energies can be explained by Bent's rule, which states that atoms direct hybrid orbitals with more p character toward more electronegative elements.[26] Accordingly, chloro- and fluoroalkynes are very reactive due to their unfavorable hybridization in the C–Cl bond and C–F bonds, respectively. A rehybridization of these bonds from sp to sp^2 facilitates the dimerizations of **8e,f**.[26]

These results explain why terminal conjugated diynes are rather unstable in comparison to their substituted congeners and why silyl groups are quite good protective groups for terminal alkynes. Furthermore, the calculations deliver an explanation for the higher reactivity of conjugated diynes in comparison to alkynes with isolated triple bonds. For example, the calculated (B2PLYPD/def2-TZVP//B2PLYPD/6-31G*) activation barrier for the dimerization of phenylacetylene (**7a**) amounts to 21.8 kcal/mol,[10b] whereas a value of 17.3 kcal/mol is obtained for phenylbutadiyne (**8a**) using the same level of theory.

In the above chapter we have shown that the 1,1′-dimerization of 1,3-diacetylene (**13**) is much more favorable than the 2,2′-dimerization (Table 1). The same is probably valid for the dimerization of substituted diynes. However, it would be of interest to know the amount of this difference and if this trend continues for higher conjugated alkynes. In order to investigate the relative reactivity of the carbon centers within the carbon chain of conjugated alkynes, a test reaction was introduced (Scheme 6a). In this test reaction the individual carbon centers of **7a–9a** were reacted with acetylene as the second alkyne unit. Depending on the reacting center, the diradicals **28** and **30** were formed (Scheme 6a). In this test reaction the alkyne units are subdivided into C$_m$–alkyne–C$_n$. In **7a** C$_m$ and C$_n$ is 0, in **8a** C$_m$ + C$_n$ = 2 and in **9a** C$_m$ + C$_n$ = 4. The use of acetylene as a probe has the advantage that the

Scheme 6. Relative Reactivity of the Carbon Centers within the Carbon Chain of 7a–9a: (a) Test Reaction of 7a–9a with Acetylene (10) to the Diradicals 28 and 30 To Find out the Relative Reactivity; (b) Activation Energies Calculated using B2PLYPD/def2-TZVP//B2PLYPD/6-31G* (in kcal/mol) for the Test Reaction of 7a–9a with Acetylene (10)



reactivities of the individual centers within the carbon chain of conjugated alkynes can be compared with each other more easily. Furthermore, the computing time is less, as the number of atoms and the number of possible products are lower. For example, if all possible products of the dimerization of **8a** are considered, eight reaction paths had to be calculated. Using the test reaction, the number of reaction paths is reduced to four. The data for the test reactions of **7a**−**9a** are summarized in Table 3. Moreover, the calculated activation energies of the test reaction for the individual carbon centers are given in Scheme 6b.

Table 3. Energies (Δ*E* in kcal/mol) of the Transition States (27 and 29) and Diradicals (28 and 30) Relative to the Corresponding Starting Materials (7a−9a and 10) Calculated using B2PLYPD/def2-TZVP//B2PLYPD/6-31G*

	n	*m*	27	28	29	30
7a	0	0	29.7	28.7	39.0	38.8
8a	0	2	27.4	24.0	42.8	42.4
	2	0	34.4	33.8	30.6	28.9
9a	0	4	26.2	21.1	43.2	42.9
	2	2	32.1	29.3	34.9	33.0
	4	0	35.2	34.7	28.2	24.9

From the data obtained three conclusions can be drawn regarding the relative reactivity of the centers within the carbon chain of conjugated alkynes. First, the carbon centers at the nonsubstituted terminus are the most reactive ones. Their reactivity increases with an increasing number of alkyne units. Second, the carbon centers at the substituted terminus are the second most reactive ones. The difference in activation energies between the two terminal centers decreases with an increasing number of alkyne units. Third, the internal carbon centers—even in long acetylene chains—are rather inert regarding the reaction with a second alkyne unit.

CONCLUSION

In summary, we were able to show by means of high-level quantum chemical calculations that substituted 1,3-diacetylenes are more reactive with regard to dimerization than the corresponding substituted acetylenes having isolated triple bonds. The formed diradicals are stabilized by conjugation of the radical centers with the adjacent acetylene units. The reactive centers of the dimerizations are always the terminal carbon atoms of the diacetylenic units. The activation barrier and the reaction energy are strongly dependent on the substituents attached at the terminal carbon centers. Silyl groups reduce whereas fluorine and chlorine increase the reactivity of the 1,3-diacetylenes. The introduction of a test reaction made it possible to compare the relative reactivities of individual carbon centers in phenylacetylene, phenylbutadiyne, and phenylhexatriyne. Here it becomes apparent that the relative reactivity of the nonsubstituted terminal carbon atoms is always higher than that of the internal carbon centers and increases with an increasing number of alkyne units. The calculated results are in good agreement with the experimentally obtained data concerning the stability of conjugated di- and oligoacetylenes.

COMPUTATIONAL DETAILS

All calculations were performed by using the program packages Gaussian 09,[27] MOLPRO,[28] and ORCA.[29] The geometrical parameters of the stationary points were optimized by means of B2PLYPD. 6-31G*,[30] SVP,[31] and cc-pVTZ[18] were used as basis sets. For all stationary points no symmetry restriction was applied. Frequency calculations were carried out at each of the structures to verify the nature of the stationary point. It turned out that all transition states have exactly one imaginary frequency, whereas the alkynes and diradicals have none. The energies of the stationary points were calculated using CCSD(T),[19] DLPNO-CCSD(T),[24] (8/8)CASSCF,[32] and (8/8)CASPT2.[33] The 6-31G*,[30] def2-TZVP,[31,34] and cc-pVTZ[18] basis sets were employed. For the (8/8)CASSCF and (8/8)CASPT2 calculations of the dimers **10·10** and **13·13**, the distance between the reacting centers was fixed at a value of 7 Å and all other geometric variables were taken from the optimized structures of **10** and **13**, respectively.

ASSOCIATED CONTENT

Supporting Information

Tables and text giving Cartesian coordinates and absolute energies for all calculated compounds and complete refs 27 and 28. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00461.

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Notes

The authors declare no competing financial interest.

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