Addition Chemistry of Rod-Shaped 1,6-Dicyanohexatriyne: Regioselectivity Control by the Remote Cyano Function

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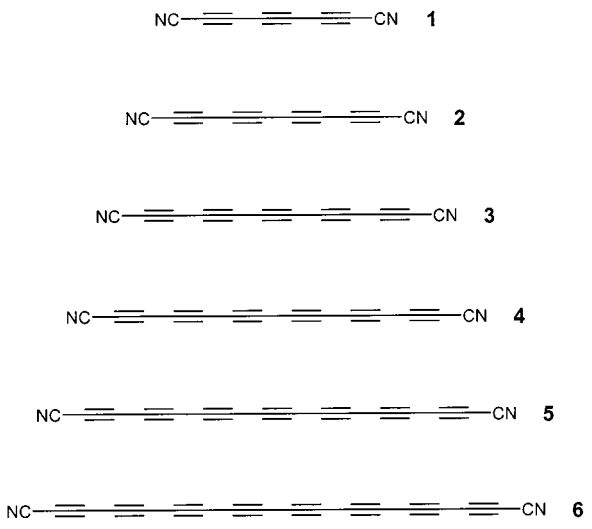
Keywords: Addition reactions / Cycloadditions / Dicyanohexatriyne / Enediyne / Regioselectivity

The addition of different alcohols, amines, thioalcohols, ethers, cycloalkanes, tin hydride, alkenes or alkadienes to 1,6-dicyano-1,3,5-hexatriyne **(1)** leads, with a pronounced regioselectivity, to a series of substituted 1-ene-3,5-diynes. The addition of alcohols, amines and thiols proceeds preferentially in a *syn* mode leading to diastereomers with an *E* configuration. The reaction with free radicals, on the other hand, proceeds in an *anti* addition mode. The [4+2] and [2+2] cycloadditions performed with **1** yielded unsaturated six- and four-membered ring adducts, respectively. The cyclobutene derivatives resulting from [2+2] cycloadditions underwent spontanous electrocyclic ring-opening reactions with the formation of butadiene derivatives. Nucleophilic additions to form **1** lead exclusively to products where the donor atom is bound at C-1. All the reactions, except the formation of **19**, showed an excellent regioselectivity with respect to the preferred addition to a terminal C≡C triple bond.

Introduction

Recently we reported on the first synthesis of conjugated α,ω-dicyanopolyynes with the general formula $N{\equiv}C-(C{\equiv}C)_n-C{\equiv}N$ (n = 3−8, **1−6**) in one step from the vaporization of graphite in the presence of cyanogen $(CN)_2$.[1][2] These rodlike molecules were investigated as model substances[2] for the linear sp-carbon allotrope "carbyne".[3] The cyano end groups confer a pronounced polarization at the termini and especially to the C≡C triple bond connecting C-1 and C-2.[2][4] This was demonstrated by the first examples of regioselective cycloaddition reactions[2] leading to dienynes, enediynes and enetriynes and clearly illustrates the synthetic potential of the dicyanopolyynes. Here, we report in a broader context on systematic investigations of the chemistry of 1,6-dicyano-1,3,5-hexatriyne **(1)** in order to investigate its synthetic potential further. We reveal a remarkable regioselectivity for nucleophiles and radicals, which is controlled by the remote cyano group.



Results and Discussion

Addition of Alcohols, Amines and Thiols

Since the reactivity of conjugated polyynes towards nucleophilic reagents increases with an increasing number of triple bonds,[5] the weak O-nucleophiles ethanol and *tert*-butyl alcohol were chosen for nucleophilic addition reactions. After the treatment of 1,6-dicyano-1,3,5-hexatriyne (**1**) with ethanol, an isomeric mixture of the (*E*)- and (*Z*)-enol ethers **7** and **8** was obtained in a ratio of 3:1. The analogous treatment of **1** with *tert*-butyl alcohol yielded an isomeric mixture of the (*E*)- and (*Z*)-enol ethers **9** and **10** in a ratio of 1.2:1. No subsequent isomerization of the diastereomers was observed. The addition of neat amines, representing strong N-nucleophiles, to **1** resulted in almost explosive and uncontrolled reactions. Hence, diisopropylamine and N-methylaniline were each allowed to react with **1** in toluene solution. After a few minutes, mixtures of the *E* and *Z* isomers of the N-diisopropyl enamines **11** and **12** or the N-methyl-N-phenyl enamines **13** and **14** were obtained almost quantitatively. In both cases the *E* isomers are the major diastereomeric components (ratio 5:1, NMR spectroscopy). Storing these mixtures for a longer period of time causes isomerization of the *Z* isomers **12** and **14** of both enamines to the corresponding *E* compounds **11** and **13**. The reaction of the S-nucleophile ethyl thiol with a solution of **1** in toluene at room temperature led to the formation of (*E*)-1-thioethyl-1-hexene-3,5-diyne **15** (60% yield) and the (*Z*) isomer **16**. The latter, which isomerized to the (*E*) isomer on storage, was formed in 19% yield only, corresponding to an (*E*)/(*Z*) ratio of the adducts of about 3:1.

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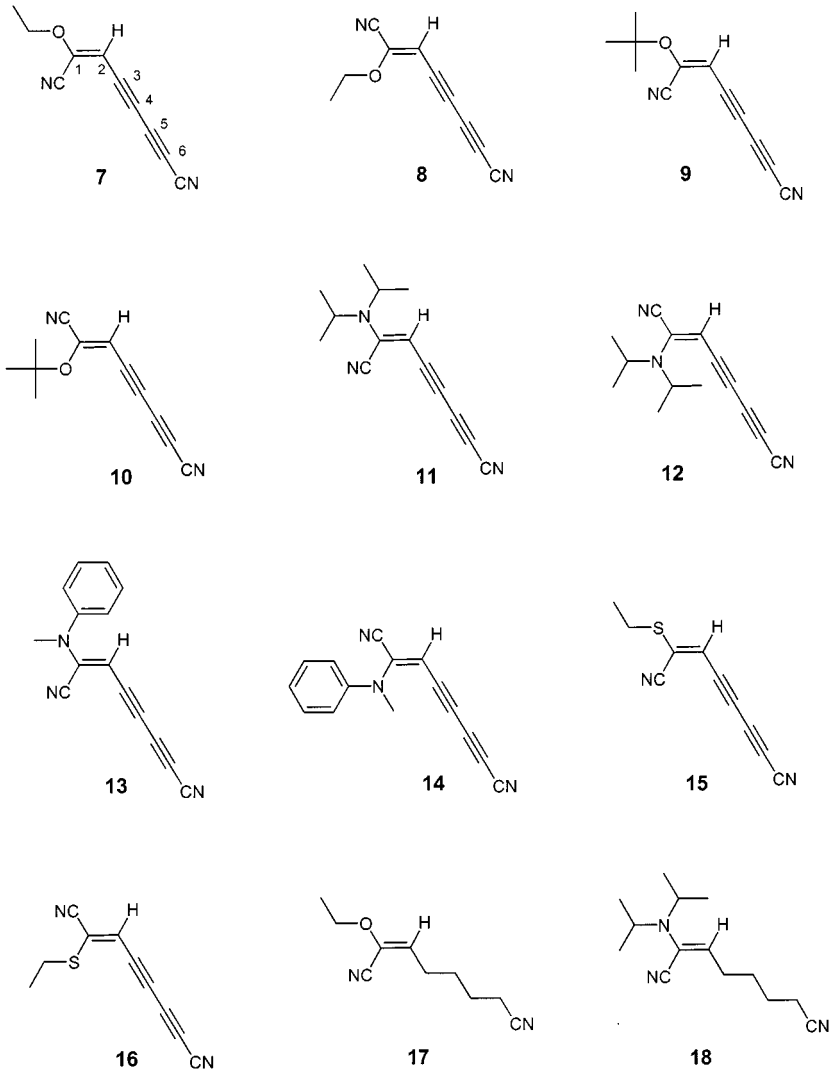


The isomeric mixtures of enol ethers **7/8** and **9/10** were separated by flash chromatography (silica gel, cyclohexane:ethyl acetate = 3:1 and 12:1, respectively) and the isolated components characterized completely by ^{1}H, ^{13}C, IR and UV/Vis spectroscopy and mass spectrometry. The enamine mixtures **11/12** and **13/14** could not be separated chromatographically and were characterized as mixtures. Only the (*E*)-enamine **13** was isolated by preparative TLC and completely analyzed. Cyclohexane/ethyl acetate (25:1) served as eluent for flash chromatographic separation of the diastereomeric enethiol ether mixture **15/16**. The assignment of the configuration of the double bonds was carried out by ^{1}H- and ^{13}C-NMR spectroscopy, including NOE measurements. Characteristic features of the ^{1}H-NMR spectra were the downfield shift of the signals of the olefinic C-2 proton of the (*E*)-enols and (*E*)-enamines relative to the chemical shift of the corresponding (*Z*)-enediyne protons (Table 1). For example, the olefinic protons at C-2 of both (*E*) isomers **7** (δ = 5.50) and **9** (δ = 5.70) revealed a downfield shift of 0.13 and 0.17 ppm, respectively, in contrast to those of the (*Z*) isomers **8** (δ = 5.37) and **10** (δ = 5.53). These values are in agreement with similar data from the literature.[6] Comparable chemical shift differences of 0.02 to 0.11 ppm are found for the corresponding signals in the proton NMR spectra of the isomeric enamines **11**, **12**, **13** and **14** (Table 1). With the enethiols **15** and **16**, however, the chemical shift sequence of olefinic protons was reversed, with a signal at lower field for the (*Z*) isomer **16**. Except for the enethiols, the signals in the ^{13}C-NMR spectra for the C-1 atoms of the (*E*) isomers always appear downfield relative to those of the (*Z*) isomers. The ^{13}C-NMR chemical shifts for C-2, however, vary from δ = 82.83 for the (*Z*)-diisopropyl amine adduct **12** to δ = 114.36 for **16** (Table 1). For an unambiguous assignment of the configuration of the double bonds, NOE measurements were carried out.

All these additions showed a preferred formation of the diastereomers with (*E*) configuration formed by a *syn* addition. The additions occurred exclusively at a terminal C≡C triple bond. The ^{13}C-NMR chemical shifts for the cyano groups bound to the double bonds are in the range of δ = 111−117 and those for the cyano groups bound to a triple bond are in the region between δ = 104 and 107 (Table 1). To prove at which position the donor atoms are bound, the remaining C≡C triple bonds between C-3 and

Table 1. ^{1}H-NMR chemical shifts of the olefinic protons, ^{13}C-NMR chemical shift of double bond carbon atoms C-1 and C-2 and the vinylic and acetylenic cyano groups of **7**−**16** (X = nucleophile)

Compound	^{1}H: C=C(2)-*H*	^{13}C: X-*C*(1)=C	C=*C*(2)-H	CsC-*C*N	C=C-*C*N
7	5.50	145.35	94.87	105.14	111.81
8	5.37	143.63	96.64	105.12	112.35
9	5.70	141.53	104.11	105.12	113.54
10	5.53	140.34	103.56	105.04	115.06
11	4.93	134.44	83.87	106.07	113.46
12	4.82	132.29	82.83	105.87	116.76
13	5.00	143.56	87.30	105.78	112.35
14	4.92				
15	6.10	131.30	114.16	104.95	112.43
16	6.17	132.16	114.36	104.96	113.28

C-4 and between C-5 and C-6 were completely hydrogenated and the products analyzed. The C≡C bonds of alkynes undergo catalytic hydrogenations much faster than the C=C bonds of alkenes; hence only the two C≡C triple bonds were reduced. For example, **7** was hydrogenated in toluene under Pd(C) catalysis and the (*Z*)-alkene **17** isolated and characterized by NMR spectroscopy. Since the ^{1}H-NMR signal at δ = 5.41 for the olefinic proton of **17** appears as a triplet, the hydrogen atom must be bound to C-2 and the ethoxy group at C-1. To locate the position of the amino group, the mixture **11/12** was hydrogenated. The analysis of the ^{1}H-NMR spectrum revealed a 1-amino-1-cyano structure (**18**) for the main component **11**. Winterfeldt et al. have shown that upon addition of methanol and isopropyl alcohol to dicyanoacetylene mainly the *syn* addition products (ratio 4:1 = *syn*/*anti*) are obtained.[4] Tani et al.[7] have reported that, when they allowed alcohols to react with dimethyl acetylenedicarboxylate in the presence of a silver(I) triflate catalyst, *anti* addition products are exclusively obtained. The addition of ethanol to **1** with silver(I) triflate as catalyst yielded a ratio of the (*E*) isomer **7** (*syn* addition) and the (*Z*) isomer **8** (*anti* addition) of 1:1. Additions of amines to activated triple bonds of acetylenic esters[4,8,9] and ketones[10] reported in the literature also proceed preferentially in a *syn* mode − the degree of stereoselectivity was dependent on the structures of the amine and the acetylene, the solvent and the reaction conditions.[4,6,9,11]

Addition products of alcohols with alkyl propynoates or alkyl 2-alkynoates reported in the literature are typical Michael products, since the nucleophilic attack always occurs at the β position of the C≡C triple bond.[7][12] Similarly, the site of nucleophilic attack is the β position when primary and secondary amines are added to cyanoacetylene,[13] propynoates[8,9,12] or acetylenic ketones.[10] Thus, all those nucleophilic attacks on electron-deficient acetylenes show the expected regioselectivity for Michael additions. In the investigation presented here, however, we surprisingly obtained products with the inverse orientation, formed by a nucleophilic attack at the α position, such as the formation of the α-alkoxy-substituted nitriles **7**, **8**, **9** and **10** or the α-substituted enamines **11**, **12**, **13** and **14**. Furthermore, we obtained the α adducts **15** and **16** upon addition of ethyl thiol to the hexatriyne **1**, whereas normally vinylogous β products are formed when thiols are added to diacetylenes,[14][15] diacetylenic ketones[14] or diacetylenecarboxylic acid.[16] This unexpected regioselectivity represents an inverse reactivity with respect to the nearby cyano group. Obviously, the regioselectivity is controlled by the remote cyano group in the 6 position.

This assumption is corroborated by semiempirical calculations (PM3, Spartan) on the two carbanionic model intermediates **A** and **B**, formed by a nucleophilic attack of hydride at C-1 and C-2, respectively (Figure1). The intermediate **A**, resulting from an attack at C-1, is about 10.5 kcal/mol more stable (H_f = 166.741 kcal/mol, Figure 1) than product **B** formed by an attack at C-2. In **B** the negative charge is predominantly localized at C-1 and the nearby cyano group (red area of the electrostatic potential surface, Figure 1), whereas in **A** it is delocalized over most of the enediynide backbone, including the remote cyano group. The charge delocalization in **A**, which exhibits significant cumulene character, is impressively reflected also in the 180° bond angle between C-1, C-2 and C-3 and the reduced bond-length alternation of the single and triple bonds relative to **B** and **1**. As a consequence, four plausible VB structures for the intermediate **A** can be depicted representing the mesomeric stabilization and distribution of charge along the carbon rod between C-2 and the remote cyano group. In **B**, however, only two VB structures can be drawn, including an unfavorable nonlinear cumulenic form. This is, to the best of our knowledge, the first demonstration of regioselectivity control by the remote functional group within conjugated α,ω-bifunctional compounds.

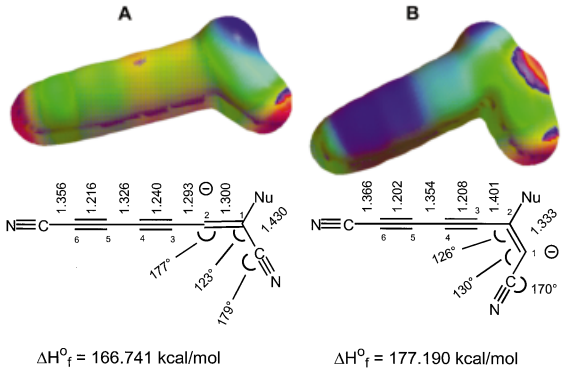
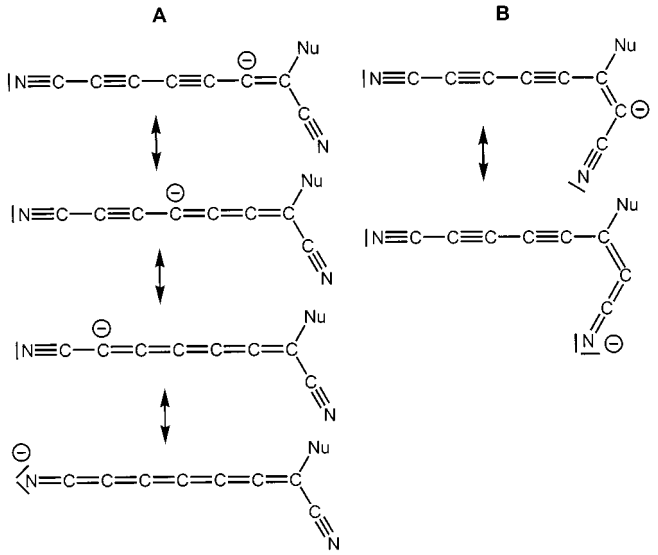


Figure 1. Semiempirical PM3 calculations of carbanionic intermediates formed by nucleophilic attack of hydride at C-1 (**A**) and C-2 (**B**); electrostatic potential density (red = negative, blue = positive), bond lengths, bond angles and heat of formation ΔH_f^0

Addition of Ethers, Cycloalkenes and Tributyltin Hydride

It is known that aliphatic ethers are able to undergo radical additions to C≡C triple bonds activated by adjacent acceptor substituents.[17][18] The first step in such reactions is the formation of an α-alkoxyalkyl radical by abstraction of a secondary hydrogen from the ether. The addition of

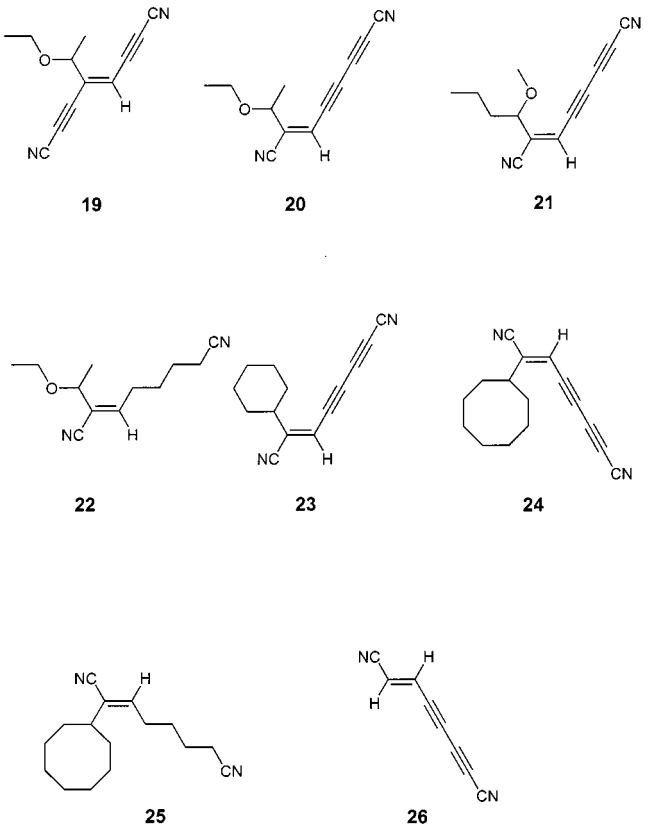


such a secondary radical to an alkyne leads to the formation of a π-type vinyl radical in which the unpaired electron resides in a p orbital.[19] This vinyl radical can subsequently be quenched by, for example, hydrogen abstraction from another ether molecule. To study the regiochemistry of such radical additions to dicyanopolyynes, 1,6-dicyanohexatriyne (**1**) was dissolved in diethyl ether and stirred at room temperature. After only 30 minutes two enediyne addition products **19** and **20** had already been formed. After separation by flash chromatography (cyclohexane/ethyl acetate = 15:1) they were isolated in 10% and 7% yield, respectively. Free radical addition also occurred when **1** was stirred at room temp. for 3 h in butyl methyl ether as the radical source, giving compound **21** in 7% yield.

All three adducts exhibit (*Z*) configuration. Since the two cyano groups of **19** are nearly magnetically equivalent only one signal for the cyano group is observed in the ^{13}C-NMR spectrum (Table 2). In the IR spectrum of the 3-ene-1,5-diyne **19**, the C≡C valence modes at 2156 cm^{-1} are considerably less intense than those of the 1-ene-3,5-diynes. In **19**, **20** and **21** the secondary carbon atoms of the ether moieties, adjacent to the oxygen atom, are attached to the double bonds. This can be deduced from the multiplicities of their signals in the ^{1}H-NMR spectra. This is a consequence of the preferred formation of stabilized α-alkoxyalkyl radicals. To further corroborate the correct structure assignment of compound **20**, a catalytic hydrogenation reaction was carried out. As shown for the examples above, only the C≡C triple bonds were reduced leading to the (*Z*)-1,6-dicyano-1-hexene **22**. The olefinic proton appears as a triplet in the ^{1}H NMR spectrum, demonstrating the presence of a methylene group at C-3.

Cycloaliphatic hydrocarbons can be thermally converted into cycloalkyl radicals available for addition to C≡C triple bonds.[20] To investigate this cycloalkane reactivity with dicyanopolyynes, compound **1** was heated for 24 h in cyclohexane giving the cyclohexyl hexenediyne **23** in 35% yield. Similarly, heating **1** for 12 h at 100°C in cyclooctane gives the corresponding 1-cyclooctylhexenediyne **24** in 62% yield. The configuration of the double bonds is (*E*), therefore **23** and **24** are presumably formed by *anti* addition, which exclusively occurs at a terminal C≡C triple bond. Their structures can unequivocally be assigned by NMR spectroscopy. The assignment of the configuration at the double bonds was possible by carrying out NOE experiments. Catalytic hydrogenation of **24** afforded the olefin **25**. The triplet of the olefinic proton in the ^{1}H-NMR spectrum proved the connectivity of the cycloalkyl moiety with C-1. All the addition products from ethers or cycloalkanes undergo *cis-trans* isomerization when stored in solution at room temp. for several weeks.

After the treatment of **1** with tributyltin hydride for 12 h at room temperature under N_2, followed by flash chromatography of the crude reaction mixture, (*E*)-1,6-dicyano-1-hexene-3,5-diyne (**26**) was isolated in 37% yield. No tributyltin group was found in the product. However, prior to the chromatographic purification, the tributyltin group was still present, as demonstrated by the ^{1}H-NMR spectrum of the crude mixture.



Characteristic features in the NMR spectra of **19**−**24** and **26** are the ^{1}H-NMR chemical shifts of the olefinic protons which, for the ether additions, vary between δ = 6.25 (**19**) and δ = 6.39 (**21**). For the cycloalkyl derivatives they are in the range between δ = 6.02 (**24**) and δ = 6.07 (**23**) (Table 2). The ^{1}H-NMR chemical shifts of the two olefinic hydrogens in the enediyne **26** are δ = 6.05 and δ = 6.47. The positions of the signals in the ^{13}C-NMR spectra of both cyano groups of **19**−**26** are similar to those of the nucleophilic addition products **7**−**18**. The signals in the ^{13}C-NMR

spectra for the methine carbon atoms C-2 of **19**, **20**, **21**, **23** and **24** are observed between δ = 116.59 and δ = 121.25 (Table 2). The signals for C-1 of **19**−**26** appear between δ = 137.24 and 145.44 (Table 2). NOE measurements on **19**−**24**, as well as the magnitude of the ^{1}H-^3J coupling constant (16.5 Hz) of the olefinic protons of enediyne **26**, enabled an unambiguous assignment of the configuration of the corresponding diastereomers.

Table 2. ^{1}H-NMR chemical shifts of the olefinic protons and ^{13}C-NMR chemical shifts of the cyano groups and the double bond of enediynes **19**−**21**, **32**, **24** and **26**, and the hydrogenation product **22**

Compound	^{1}H: C=C-*H*	^{13}C: C-*C*(1)=C	C=*C*(2)-H	CsC-*C*N	C=C-*C*N
19	6.25	145.44	118.62	104.39	
20	6.32	138.45	120.11	104.67	115.39
21	6.40	119.95	147.41		117.47
22	6.39	137.24	121.25	104.68	115.46
23	6.07	140.87	116.59	104.43	117.59
24	6.02	142.39	116.82	104.82	116.92
26	6.05		126.71	104.62	115.29
	6.47		116.52		

Thermally induced radical additions of ethers to 1,2-disubstituted acetylenes, such as the addition of diethyl ether to dicyanoacetylene[21] or dichloroacetylene,[22] or of tetrahydrofuran to dicyanoacetylene[21] or acetylene dicarboxylate,[23] are known. Di-*tert*-butyl peroxide initiated radical additions of cyclopentane or cyclohexane to acetylene have been reported by Cywinski and Hepp.[24] Similar additions, initiated by irradiation with UV light, have been described by Büchi and Feairheller.[25] Leusink et al.[26][27] have carried out similar investigations on the reaction of acetylenic compounds with organotin hydrides. Most of these experiments were performed with symmetrically substituted acetylenes and, consequently, did not show regioselectivity with respect to the addend connectivity. The other reactions led to mixtures of diastereomeric as well as constitutional isomers. In the experiments presented here, except for the formation of compound **19**, all additions occur at the terminal C≡C triple bond of **1** and *anti* additions are the preferred mode of attack. The reason for the preferred attack of a radical at C-1 is the same as that for an attack of a nucleophile at the same position.

Cycloadditions

A number of cycloadditions, ranging from the [4+2] and [3+2] to the [2+2] type, are known for α,ω-disubstituted electron-deficient acetylenes and polyynes. In [4+2] cycloadditions, dicyanoacetylene exhibits an exceptional reactivity as an acetylenic dienophile toward a number of substituted furan derivatives[28] and dienes.[29] Only moderate yields are obtained with acetylene dicarboxylic acid[30] or its methyl ester[31] as dienophiles. With 1,6-dicyanohexatriyne (**1**), the [4+2] cycloaddition of 9,10-dimethylanthracene or 2,3-dimethylbutadiene gives the corresponding monoaddition products (**27** in the case of 9,10-DMA) formed by addition at the terminal C≡C triple bond. At higher temperatures the formation of bisadducts with attack at both external triple bonds is observed.[2]

As another example of Diels−Alder type cycloadditions, **1** was treated with 1,3-cyclohexadiene in toluene at room temperature. After heating **1** with anthracene for 3 d in toluene at 120°C under nitrogen, the cycloadduct **28** was formed in 72% yield. By extending the heating period to 3 weeks at 120°C, the yellow bisadduct **29** was obtained from addition of anthracene to both terminal triple bonds. Since both cyano groups attached to the sp^2 carbon atom became equivalent, only one signal is observed in the ^{13}C-NMR spectrum at δ = 116.04.

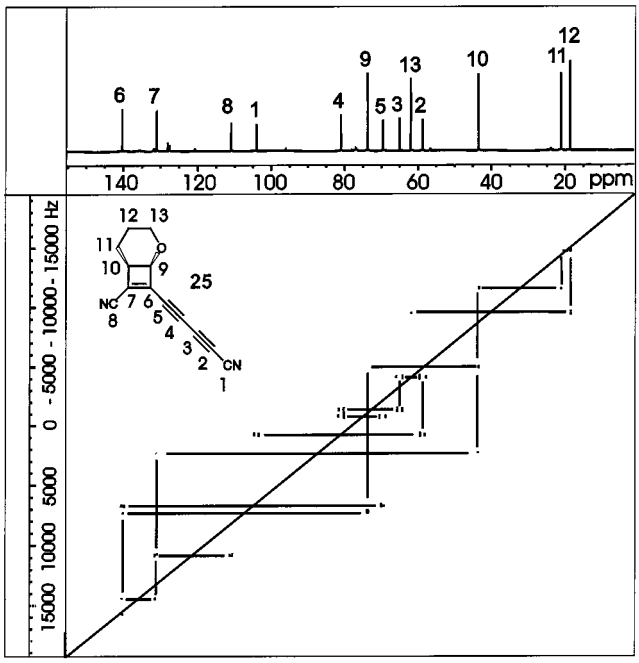
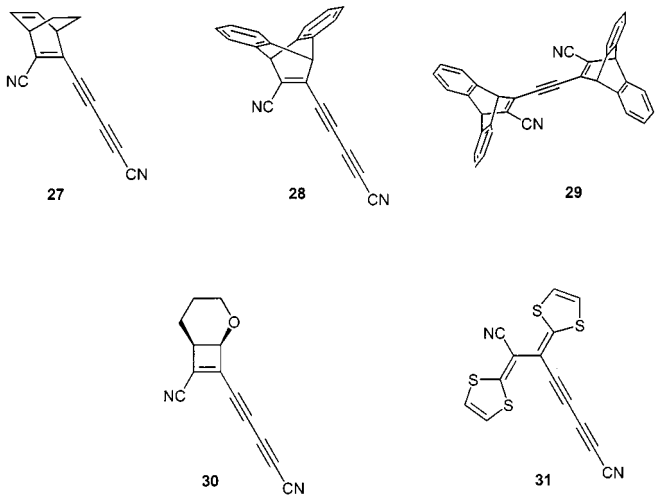


Figure 2. ^{13}C-2D inadequate NMR spectrum (125.65 MHz, 25°C, $CDCl_3$, J = 175 Hz) of 8-(4-cyano-1,3-butadiynyl)-2-oxabicyclo[4.2.0]oct-7-ene-7-carbonitrile (**30**)



Cyclobutenes can be formed from two C_2 building blocks by a [2+2] cycloaddition of electron-rich alkenes with electron-deficient acetylenes and vice versa.[32] A polar mechanism invoking the involvement of ionic intermediates has been suggested for these reactions. Reactions involving enamines and enolethers with acetylene dicarboxylates, propiolates or other acetylenic derivatives are well documented and have been comprehensively reviewed.[33] However, only a few of the cyclobutenes generated in this manner have been found to be sufficiently stable to allow their isolation. Many of them undergo a spontaneous electrocyclic ring opening which gives rise to the formation of other products.[33] The reaction of an unsubstituted 3,4-dihydro-2*H*-pyran with acetylenedicarboxylate leads to a stable oxabicyclo[4.2.0]octene, whereas similar reactions with substituted pyrans cannot be stopped at the cyclobutene stage.[34]

A thermally initiated [2+2] cycloaddition of 3,4-dihydropyran to **1** in toluene at 100°C afforded the stable adduct cyclobutapyran **30** in 62% yield. From a ^{13}C-2D inadequate NMR spectrum (J = 175, 70 and 40 Hz) of **30** the orientation of addition could be confirmed and the connectivity of C-1 of triyne **1** with C-5 of the 3,4-dihydro-2*H*-pyran, and C-2 of **1** with C-6 of the pyran moiety proven (Figure 2). This orientation is in line with the preferred attack of nucleophiles at C-1. The proton coupling of ^3J = 4.63 Hz, determined from the doublet of the cyclobutene hydrogen adjacent to the oxygen atom, indicates a *syn* addition, which was also confirmed by the NOE spectrum.

A [2+2] cycloaddition with subsequent opening of cyclobutene ring was observed when tetrathiafulvene was treated with 1,6-dicyano-1,3,5-hexatriyne (**1**). The first step is a [2+2] cycloaddition of one of the terminal triple bonds with the central double bond of tetrathiafulvalene leading to the formation of a 3,3,4,4-tetrathiasubstituted cyclobutene intermediate. This intermediate is stabilized by subsequent electrocyclic ring opening forming a butadiene derivative **31**. Similar cycloadditions have been reported by Hopf et al.[35]

Conclusions

Additions of nucleophiles or radicals, or cycloadditions, to 1,6-dicyano-1,3,5-hexatriyne (**1**) occur almost exclusively at one of the terminal triple bonds with the formation of 1,6-dicyano-1-hexene-3,5-diynes. The prefered site of attack of the nucleophiles or radicals is C-1. This is, to the best of our knowledge, the first demonstration of regioselectivity control by a remote functional group within conjugated α,ω-bifunctional compounds, and can be explained by resonance stabilization of the corresponding anionic or radical intermediates. Due to this unexpected regioselectivity, corresponding to building blocks formed by an umpolung, α,ω-dicyanopolyynes have great synthetic potential for the development of new functionalized enynes.

Experimental Section

General: ^{1}H and ^{13}C NMR: Jeol Alpha 500, Bruker AMX 400, Jeol JNM EX 400 and Jeol JNM GX 400. − MS: Varian MAT 711 (FD), Micromass Zabspec (EI). − IR: Bruker FT-IR IFS 48 and Bruker FT-IR Vector 22. − UV/Vis: Shimadzu UV 3102 PC. − The semiempirical PM3 calculations were carried out with the PC software package SPARTAN. − 1,6-Dicyano-1,3,5-hexatriyne (**1**) was prepared by vaporization of graphite in the presence of cyanogen $(CN)_2$ and separated by HPLC according to ref.[2] Reagents were prepared according to common procedures. Materials and solvents were obtained from commercial suppliers and were dried and purified following literature techniques.[36] Products were isolated, wherever possible, by flash column chromatography (silica gel 60, particle size 0.04−0.063 nm, Merck) or preparative TLC (silica gel, particle size 0.04−0.063 nm, Merck).

(*E*)-1,6-Dicyano-1-ethoxy-1-hexene-3,5-diyne (7) and (*Z*)-1,6-Dicyano-1-ethoxy-1-hexene-3,5-diyne (8): 1,6-Dicyano-1,3,5-hexatriyne (**1**) (97 mg, 0.78 mmol) was dissolved in 50 mL of ethanol and stirred for 4 h at 60°C. The products **7** and **8** were purified by column chromatography with a mixture of cyclohexane/ethyl acetate (3:1) as eluent (yield: **7** 67 mg, 50%; **8** 24 mg, 18%, both dark oils).

7: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 1.38 (t, 3 H, CH_3), 4.00 (q, 2 H, CH_2), 5.50 (s, 1 H, C*H*). − ^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ = 14.02 (1 C, *C*H$_3$), 56.62 (1 C, Cs*C*−*C*N), 66.86 (1 C, Cs*C*), 68.15 (1 C, *C*H$_2$), 74.47 (1 C, Cs*C*), 78.15 (1 C, Cs*C*), 94.87 (1 C, C=*C*−*H*), 105.14 (1 C, CsC−*C*N), 111.81 (1 C, C=C−*C*N), 145.35 (1 C, C=*C*−OC$_2$H$_5$). − IR (KBr): $\tilde{\nu}$ = 3053 (C=C−H), 2992, 2943, 2925 (CH$_2$, CH$_3$), 2231 (CN), 2192 (CsC), 2150 (CsC), 2100 (CsC), 1582, 1307, 1230, 1017, 801 cm^{-1}. − UV/Vis (cyclohexane): l_{max} (e) = 246 (13000), 254 (16500), 298 (6800), 317 (9800), 337 (8000), 379 nm (350). − MS (EI); *m*/*z* (%): 170 (44) [M$^+$], 142 (53), 115 (78), 87 (100), 29 (92), 27 (45). − $C_{10}H_6N_2O$: calcd. 170.0480; found 170.0481 (HRMS).

8: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 1.39 (t, 3 H, CH_3), 4.29 (q, 2 H, CH_2), 5.37 (s, 1 H, C*H*). − ^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ = 14.88 (1 C, *C*H$_3$), 58.04 (1 C, Cs*C*−CN), 66.60 (1 C, Cs*C*), 69.86 (1 C, *C*H$_2$), 73.33 (1 C, Cs*C*), 81.92 (1 C, Cs*C*), 96.64 (1 C, C=*C*−H), 105.12 (1 C, CsC−*C*N), 112.35 (1 C, C=C−*C*N), 143.63 (1 C, C=*C*−OC$_2$H$_5$). − IR (KBr): $\tilde{\nu}$ = 3043 (C=C−H), 2995, 2961, 2927, 2907, 2856 (CH$_2$, CH$_3$), 2247 (CN), 2224 (CN), 2188 (CsC), 2147 (CsC), 2100 (CsC), 1595, 1377, 1344, 1294, 1177, 1107, 1045, 804, 468 cm^{-1}. − UV/Vis (cyclohexane): l_{max} (e) = 246 (22000), 259 (33000), 301 (14000), 319 (21000), 340 (18000), 380 nm (1200). − MS (EI); *m*/*z* (%): 170 (48) [M$^+$], 142 (66), 115 (74), 87 (100), 29 (95), 27 (48). − $C_{10}H_6N_2O$: calcd. 170.0480; found 170.0482 (HRMS).

(*E*)-1,6-Dicyano-1-ethoxy-1-hexene (17): (*E*)-1,6-Dicyano-1-ethoxy-1-hexene-3,5-diyne (**7**) (11 mg, 0.055 mmol) was hydrogenated in the presence of Pd(C) in toluene at room temperature for 2 h. The product was isolated by flash column chromatography with cyclohexane/ethyl acetate (4:1) as eluent (yield: 5 mg, 44%, a colorless liquid). − **17**: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 1.25 (t, 3 H, CH_3), 1.51 (m, 2 H, CH_2), 1.61 (m, 2 H, CH_2), 2.21 (m, 2 H, CH_2), 2.30 (m, 2 H, CH_2), 3.93 (m, 2 H, CH_2), 5.41 (t, 1 H, C=C*H*). − $C_{10}H_{14}N_2O$: calcd. 178.1105; found 178.1102 (HRMS).

(*E*)-1,6-Dicyano-1-(1,1-dimethylethoxy)-1-hexene-3,5-diyne (9) and (*Z*)-1,6-Dicyano-1-(1,1-dimethylethoxy)-1-hexene-3,5-diyne (10): 1,6-Dicyano-1,3,5-hexatriyne (**1**) (133 mg, 1.07 mmol) was dissolved in 50 mL of *tert*-butyl alcohol and stirred for 36 h at 50°C. The products **9** and **10** were separated by flash chromatography with cyclohexane/ethyl acetate (12:1) as eluent (yield: 9 52 mg, 25%; 10 42 mg, 20%, both dark oils).

9: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 1.42 (t, 9 H, CH_3), 5.70 (s, 1 H, C*H*). − ^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ = 28.26

(3 C, *C*H_3), 57.09 (1 C, Cs*C*−CN), 66.75 (1 C, Cs*C*), 74.55 (1 C, Cs*C*), 79.14 (1 C, Cs*C*), 86.12 (1 C, *C*$(CH_3)_3$), 104.11 (1 C, C=*C*−H), 105.12 (1 C, CsC−*C*N), 113.54 (1 C, C=C−*C*N), 141.53 (1 C, C=*C*−OC$(CH_3)_3$). − IR (KBr): $\tilde{\nu}$ = 3030 (C=C−H), 2988, 2940, 2877 (CH_3), 2223 (CN), 2187 (CsC), 2096 (CsC), 1575, 1372, 1312, 1260, 1224, 1146, 858, 817, 728, 491 cm^{-1}. − UV/Vis (cyclohexane): l_{max} (e) = 248 (32600), 259 (38900), 294 (16500), 314 (24700), 333 nm (21900). − MS (EI); *m*/*z* (%): 194 (6) [M^+], 183 (13) [$M^+ - CH_3$], 87 (26), 57 (100), 41 (79), 29 (58). − $C_{12}H_{10}N_2O$: calcd. 198.0793; found 198.0800 (HRMS).

10: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 1.46 (t, 9 H, C*H*$_3$), 5.53 (s, 1 H, C*H*). − ^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ = 28.38 (3 C, *C*H_3), 57.89 (1 C, Cs*C*−CN), 60.50 (1 C, Cs*C*), 73.82 (1 C, Cs*C*), 81.57 (1 C, Cs*C*), 86.43 (1 C, *C*$(CH_3)_3$), 103.56 (1 C, C=*C*−H), 105.04 (1 C, CsC−*C*N), 115.06 (1 C, C=C−*C*N), 140.49 (1 C, C=*C*−OC$(CH_3)_3$). − IR (KBr): $\tilde{\nu}$ = 3046 (C=C−H), 2985, 2938, 2874 (CH_3), 2222 (CN), 2185 (CsC), 2148 (CsC), 2101 (CsC), 1578, 1398, 1373, 1134, 964, 810, 626, 497 cm^{-1}. − UV/Vis (cyclohexane): l_{max} (e) = 249 (29400), 259 (34700), 294 (16000), 313 (22800), 333 nm (19700). − MS (EI); *m*/*z* (%): 194 (4) [M^+], 183 (13) [$M^+ - CH_3$], 87 (24), 57 (100), 41 (86), 29 (64). − $C_{12}H_{10}N_2O$: calcd. 198.0793; found 198.0800 (HRMS).

(*E*)-1,6-Dicyano-1-diisopropylamino-1-hexene-3,5-diyne (11) and (*Z*)-1,6-Dicyano-1-diisopropylamino-1-hexene-3,5-diyne (12): 1,6-Dicyano-1,3,5-hexatriyne **(1)** (100 mg, 0.81 mmol) was dissolved in 50 mL of toluene, diisopropylamine (114µl, 0.81 mmol) was added and the solution stirred for 15 min at room temperature. The reaction was nearly quantitative, but it was not possible to separate the isomers by chromatography. The mixture was a dark oil.

11: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 1.28 (d, 6 H, C*H*$_3$), 3.87 (m, 1 H, C*H*), 4.93 (s, 1 H, C=C−*H*). − ^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ = 20.15 (2 C, *C*H_3), 50.66 (1 C, *C*−H), 58.80 (1 C, Cs*C*−CN), 69.21 (1 C, Cs*C*), 76.92 (1 C, Cs*C*), 81.34 (1 C, Cs*C*), 83.87 (1 C, C=*C*−H), 106.07 (1 C, CsC−*C*N), 113.46 (1 C, C=C−*C*N), 134.44 (1 C, C=*C*−N).

12: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 1.35 (d, 6 H, C*H*$_3$), 4.10 (m, 1 H, C*H*), 4.82 (s, 1 H, C=C−*H*). − ^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ = 21.59 (2 C, *C*H_3), 50.66 (1 C, *C*−H), 57.31 (1 C, Cs*C*−CN), 68.38 (1 C, Cs*C*), 79.59 (1 C, Cs*C*), 81.18 (1 C, Cs*C*), 82.83 (1 C, C=*C*−H), 105.87 (1 C, CsC−*C*N), 116.76 (1 C, C=C−*C*N), 132.29 (1 C, C=*C*−N). − $C_{14}H_{15}N_3$: calcd. 225.1266; found 225.1274 (HRMS).

(*E*)-1,6-Dicyano-1-diisopropylamino-1-hexene (18): (*E*)-1,6-Dicyano-1-diisopropylamino-1-hexene-3,5-diyne (**7**) (22.5 mg, 0.10 mol) was hydrogenated in the presence of Pd(C) in toluene at room temperature for 3 h. The product was isolated by flash chromatography (cyclohexane/ethyl acetate, 3:1) as a colorless liquid (yield: 8.9 mg, 39%).

18: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 1.28 (d, 3 H, C*H*$_3$), 1.51 (m, 2 H, C*H*$_2$), 1.61 (m, 2 H, C*H*$_2$), 1.95 (m, 2 H, C*H*$_2$), 2.28 (m, 2 H, C*H*$_2$), 3.96 (q, H, C*H*), 4.24 (t, 1 H, C=C*H*). − $C_{14}H_{23}N_3$: calcd. 233.1893; found 233.1898 (HRMS).

(*E*)-1,6-Dicyano-1-[methyl(phenyl)amino]-1-hexene-3,5-diyne (13) and (*Z*)-1,6-dicyano-1-[methyl(phenyl)amino]-1-hexene-3,5-diyne (14): The triyne **1** (78 mg, 0.65 mmol) was dissolved in 50 mL of toluene and then *N*-methylaniline (70µl, 0.65 mmol) was added and the mixture stirred for 15 min at room temperature. Pure **13** was obtained by preparative TLC with cyclohexane/ethyl acetate (9:1) as eluent (yield: 50 mg, 31%, as a dark oil). Compound **14** was characterized in solution only.

13: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 3.32 (s, 3 H, CH_3), 5.00 (s, 1 H, C=C*H*), 7.18 (m, 2 H, Ar−H), 7.33 (m, 1 H, Ar−H), 7.43 (m, 2 H, Ar−H), − ^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ = 41.50 (1C, CH_3), 57.12 (1 C, Cs*C*−CN), 68.47 (1 C, *C*sC−CN), 77.44 (1 C, C=C−*C*sC), 79.34 (1 C, C=C−Cs*C*), 87.30 (1C, C=*C*−H), 105.78 (1 C, CsC−*C*N), 112.35 (1 C, C=C−*C*N), 125.43 (2C, Ar−C), 128.17 (1C, Ar−C), 130.02 (2C, Ar−C), 136.02 (1C, Ar−C), 143.56 (1 C, C=*C*−CN). − IR (KBr): $\tilde{\nu}$ = 3059 (Ar−H, C=C−H), 3007 (Ar−H, C=C−H), 2923 (CH_3), 2853 (CH_3), 2222 (CN), 2169 (CN), 2118 (CsC), 2090 (CsC), 1560, 1493, 1383, 1245, 1136, 767, 698 cm^{-1}. − UV/Vis (cyclohexane): l_{max} (e) = 261 (9000), 279 (10500), 373 nm (24200). − MS (EI); *m*/*z* (%): 231 (66) [M^+], 216 (100) [$M^+ - CH_3$], 189 (39), 77 (43) [$C_6H_5^+$], 51 (28) [$C_4H_3^+$]. − $C_{15}H_9N_3$: calcd. 231.0796; found 231.0794 (HRMS).

14: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 3.52 (s, 3 H, CH_3), 4.92 (s, 1 H, C=C*H*), 7.14 (m, 2 H, Ar−H), 7.28 (m, 1 H, Ar−H), 7.36 (m, 2 H, Ar−H).

(*E*)-1,6-Dicyano-1-thioethyl-1-hexene-3,5-diyne (15) and (*Z*)-1,6-Dicyano-1-thioethyl-1-hexene-3,5-diyne (16): To a solution of 1,6-dicyano-1,3,5-hexatriyne (**1**) (134 mg, 1.08 mmol) in 50 mL of toluene was added ethanthiol (3 mL, 2.52 g, 40.5 mmol) and this solution stirred for 48 h at room temperature. The products were separated from the polymer by filtration through silica gel with toluene as solvent. Compounds **15** and **16** were isolated by flash column chromatography with a mixture of cyclohexane/ethyl acetate (25:1) as eluent (yield: **15** 121 mg, 60%; **16** 39 mg, 19%, both dark oils).

15: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 1.35 (t, 3 H, C*H*$_3$), 2.99 (q, 2 H, C*H*$_2$), 6.10 (s, 1 H, C=C−*H*). − ^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ = 14.08 (1 C, CH_3), 28.15 (1 C, CH_2), 58.49 (1 C, Cs*C*−CN), 66.40 (1 C, Cs*C*), 75.37 (1 C, Cs*C*), 79.91 (1 C, Cs*C*), 104.95 (1 C, CsC−*C*N), 112.43 (1 C, C=C−*C*N), 114.16 (1 C, C=*C*−H), 131.30 (1 C, C=*C*−SCH_2CH_3). − IR (KBr): $\tilde{\nu}$ = 3070 (C=C−H), 2975 (CH_2, CH_3), 2932 (CH_2, CH_3), 2873 (CH_2, CH_3), 2232 (CN), 2182 (CN), 2098 (CsC), 1528, 1452 (CH_2, CH_3), 1380 (CH_2, CH_3), 1266, 1071, 1007, 973, 935, 823, 593, 495. − UV/Vis (cyclohexane): l_{max} (e) = 229 (13900), 262 (2900), 278 (3500), 360 (14700), 370 nm (15300). − MS (EI); *m*/*z* (%): 186 (39) [M^+], 171 (20) [$M^+ - CH_3$], 158 (17), 131 (43), 124 (9) [$C_8N_2^+$], 113 (11), 97 (7), 87 (17), 61 (6) [$SCH_2CH_3^+$], 45 (7), 28 (100). − $C_{10}H_6N_2S$: calcd. 186.0252; found 186.0254 (HRMS).

16: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 1.39 (t, 3 H, C*H*$_3$), 3.10 (q, 2 H, C*H*$_2$), 6.17 (s, 1 H, C=C−*H*). − ^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ = 15.07 (1 C, CH_3), 28.47 (1 C, CH_2), 60.76 (1 C, Cs*C*−CN), 65.92 (1 C, Cs*C*), 74.25 (1 C, Cs*C*), 87.05 (1 C, Cs*C*), 104.96 (1 C, CsC−*C*N), 113.28 (1 C, C=C−*C*N), 114.36 (1 C, C=*C*−H), 132.16 (1 C, C=*C*−SCH_2CH_3). − IR (KBr): $\tilde{\nu}$ = 3064 (C=C−H), 2989 (CH_2, CH_3), 2962 (CH_2, CH_3), 2926 (CH_2, CH_3), 2853 (CH_2, CH_3), 2230 (CN), 2181 (CN), 2140 (CsC), 2097 (CsC), 1529, 1446 (CH_2, CH_3), 1380 (CH_2, CH_3), 1261, 1108, 1051, 981, 816, 544, 497. − UV/Vis (cyclohexane): l_{max} (e) = 220 (13300), 228 (153000), 236 (150000), 262 (44500), 277 (34500), 296 (22500), 318 (35500), 360 (105000), 374 (113000), 398 nm (22500). − MS (EI); *m*/*z* (%): 186 (93) [M^+], 171 (52) [$M^+ - CH_3$], 158 (40), 131 (100), 124 (18) [$C_8N_2^+$], 113 (22), 107 (9), 99 (15), 87 (29), 70 (26), 61 (11) [$SCH_2CH_3^+$], 45 (12), 29 (49). − $C_{10}H_6N_2S$: calcd. 186.0252; found 186.0256 (HRMS).

(*Z*)-1,6-Dicyano-3-(1-ethoxyethyl)-3-hexene-1,5-diyne (19) and (*Z*)-1,6-Dicyano-1-(1-ethoxyethyl)-1-hexene-3,5-diyne (20): 1,6-Dicyano-1,3,5-hexatriyne (**1**) (102 mg, 0.82 mmol) was dissolved in 50 mL of diethyl ether and stirred for 24 h at room temperature. The products **19** and **20** were purified by flash column chromatog-

raphy with cyclohexane/ ethyl acetate (15:1) as eluent (yield: **19** 17 mg, 10%; **20** 12 mg, 7%, both dark oils).

19: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 1.22 (t, 3 H, CH_3), 1.37 (d, 3 H, CH_3), 3.41 (m, 1 H, CH_2), 3.44 (m, 1 H, CH_2), 4.42 (m, 1 H, CH), 6.25 (s, 1 H, C*H*). − ^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ = 15.14 (1 C, *C*H_3), 20.31 (1 C, *C*H_3), 65.23 (1 C, CH_2) 71.34 (1 C, Cs*C*), 74.66 (1 C, *C*H), 75.36 (1 C, Cs*C*), 75.96 (1 C, Cs*C*), 78.48 (1 C, Cs*C*), 104.39 (2 C, CsC−*C*N), 118.62 (1 C, C=*C*−H), 145.44 (1 C, C=*C*−C). − IR (KBr): ṽ = 2964, 2259 (CN), 2156 (CsC), 1635, 1375, 1261, 1102, 1022, 803 cm^{-1}. − UV/Vis (cyclohexane): l_{max} (e) = 220 (27000), 232 (1400), 244 (1800), 273 (4600), 285 (5000), 303(5500), 342 nm (600). − MS (EI); *m*/*z* (%): 198 (4) [M$^+$], 183 (8) [M$^+$ − CH_3], 170 (25), 155 (43), 127 (43), 73 (55), 45 (100), 29 (39). − $C_{12}H_{10}N_2O$: calcd. 198.0793; found 198.0793 (HRMS).

20: ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 1.22 (t, 3 H, CH_3), 1.40 (d, 3 H, CH_3), 3.43 (m, 1 H, CH_2), 3.47 (m, 1 H, CH_2), 4.42 (m, 1 H, CH), 6.32 (s, 1 H, C*H*). − ^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ = 15.07 (1 C, *C*H_3), 20.06 (1 C, *C*H_3), 59.70 (1 C, Cs*C*−CN), 65.18 (1 C, CH_2) 65.27 (1 C, *C*sC−CN), 72.90 (1 C, C=C−*C*sC), 73.46 (1 C, *C*H), 84.51 (1 C, C=C−Cs*C*),), 104.67 (1 C, CsC−*C*N), 115.39 (1 C, C=C−*C*N), 120.11 (1 C, C=*C*−H), 138.45 (1 C, C=*C*−C). − IR (KBr): ṽ = 3028 (C=C−H) 2981, 2933, 2895 (CH, CH_2, CH_3),2258 (CN), 2240 (CN), 2223 (CsC), 2193 (Cs*C*), 1443, 1375, 1261, 1159, 1106, 1062, 802 cm^{-1}. − UV/Vis (cyclohexane): l_{max} (e) = 233 (27500), 244 (41300), 271 (8000), 286 (14100), 304 (19500), 325 nm (12200). − MS (EI); *m*/*z* (%): 198 (4) [M$^+$], 183 (7) [M$^+$ − CH_3], 170 (23), 155 (77), 142 (42) 127 (56), 115 (31), 100 (30), 73 (49), 45 (100), 29 (59). − $C_{12}H_{10}N_2O$: calcd. 198.0793; found 198.0797 (HRMS).

(*Z*)-3,8-Dicyano-2-ethoxy-3-octene (22): (*Z*)-1,6-dicyano-1-(1-ethoxyethyl)-1-hexene-3,5-diyne (**20**) (11 mg, 0.055 mmol) was hydrogenated in the presence of Pd(C) in toluene at room temperature for 2 h. The product was isolated by flash column chromatography with cyclohexane/ethyl acetate (4:1) as eluent (yield: 5 mg, 44%, a colorless liquid). − ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 1.20 (t, 3 H, CH_3), 1.35 (d, 3 H, CH_3), 1.64 (m, 4 H, 2 CH_2), 2.29 (m, 2 H, CH_2), 2.37 (m, 2 H, CH_2), 3.34 (m, 1 H, CH_2), 3.46 (m, 1 H, CH_2), 4.23 (q, 1 H, CH), 6.40 (t, 1 H, C=C−H). − ^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ = 15.21 (1 C, CH_3), 17.04 (1 C, CH_2), 20.33 (1 C, CH_3), 24.86 (1 C, CH_2), 27.58 (1 C, CH_2), 27.73 (1 C, CH_2), 64.16 (1 C, CH_2), 70.13 (1 C, CH), 117.47 (1 C, C=C−*C*N), 119.02 (1 C, CH_2*C*N), 119.95 (1 C, C=*C*−CN), 147.41 (1 C, C=*C*H). − IR (KBr): ṽ = 2979 (CH_3, CH_2, CH), 2933 (CH_3, CH_2, CH), 2917 (CH_3, CH_2, CH), 2870 (CH_3, CH_2, CH), 2849 (CH_3, CH_2, CH), 2243 (CN), 2218 (CN), 1462 (CH_3, CH_2, CH), 1425, 1381, 1261, 1136, 1103 (C−O), 1020, 802 (C=C−H) cm^{-1}. − UV/Vis (cyclohexane): l_{max} (e) = 206 (2200), 275 (55), 371 (75), 385 nm (75). − $C_{12}H_{18}N_2O$: calcd. 206.1420; found 206.1425 (HRMS).

(*Z*)-1,6-Dicyano-1-(1-methoxybutyl)-1-hexene-3,5-diyne (21): 1,6-Dicyano-1,3,5-hexatriyne (**1**) (247 mg, 2.00 mmol) was dissolved in 50 mL of butyl methyl ether and this solution stirred for 3 h. The polymer was filtered off through silica gel using an eluent gradient from toluene/cyclohexane (1:1 to pure toluene). The product was then isolated by flash column chromatography with cyclohexane/ethyl acetate (15:1) as eluent (yield: 27 mg, 7%, a dark oil). − ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 0.94 (t, 3 H, CH_3), 1.39 (m, 2 H, CH_2), 1.57 (m, 1 H, CH_2), 1.80 (m, 1 H, CH_2), 3.33 (s, 3 H, OCH_3), 4.15 (t, 1 H, OC*H*), 6.39 (s, 1 H, C=C−*H*). − ^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ = 13.73 (1 C, *C*H_3), 18.28 (1 C, *C*H_2), 36.06 (1 C, *C*H_2), 54.47 (1 C, O*C*H_3), 59.77 (1 C, Cs*C*−CN), 65.23 (1 C, Cs*C*), 71.59 (1 C, Cs*C*), 79.39 (1 C, O*C*H), 84.44 (1 C, Cs*C*), 104.68 (1 C, CsC−*C*N), 115.46 (1 C, C=C−*C*N), 121.25 (1 C, C=*C*−H), 137.24 (1 C, C=*C*−C). − IR (KBr): ṽ = 3028 (C=C−H), 2962 (CH, CH_2, CH_3), 2934 (CH, CH_2, CH_3), 2874 (CH, CH_2, CH_3), 2240 (CN), 2225 (CN), 2194 (CsC), 1636, 1458 (CH, CH_2, CH_3), 1375 (CH, CH_2, CH_3), 1261 (C−O), 1196 (C−O), 1089 (C−O), 958, 866, 496 cm^{-1}. − UV/Vis (cyclohexane): l_{max} (e) = 235 (24300), 245 (32700), 271 (7400), 287 (12400), 305 (16800), 326 nm (12500). − MS (EI); *m*/*z* (%): 212 (4) [M$^+$], 197 (7) [M$^+$ − CH_3], 183 (21), 169 (100), 155 (32), 88 (23), 57 (22), 45 (40), 27 (28). − $C_{13}H_{12}N_2O$: calcd. 212.0950; found 212.0949 (HRMS).

(*E*)-1,6-Dicyano-1-cyclohexyl-1-hexene-3,5-diyne (23): A solution of 1,6-dicyano-1,3,5-hexatriyne (**1**) (96 mg, 0.77 mmol) in cyclohexane was heated for 24 h under reflux. The product was purified by flash column chromatography with cyclohexane/ethyl acetate (25:1) as eluent (yield: 57 mg, 35%, a brown-white solid). − ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 1.25 (m, 6 H, CH_2), 1.67 (m, 2 H, CH_2), 1.78 (m, 2 H, CH_2), 2.67 (m, 1 H, C*H*), 6.07 (s, 1 H, C=C−*H*). − ^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ = 24.97 (1 C, CH_2), 25.30 (2 C, CH_2), 30.89 (2 C, CH_2), 41.85 (1 C, CH), 58.95 (1 C, Cs*C*−CN), 65.78 (1 C, *C*sC−CN), 74.04 (1 C, C=C−*C*sC), 83.13 (1 C, C=C−Cs*C*), 104.43 (1 C, CsC−*C*N), 116.59 (1 C, C=C−*C*N), 117.59 (1 C, C=*C*−H), 140.87 (1 C, C=*C*−CN). − IR (KBr): ṽ = 3021 (C=C−H), 2934 (CH_2, CH), 2854 (CH_2, CH), 2242 (CN), 2219 (CN), 2192 (CsC), 2155 (CsC), 1450 (CH_2, CH), 1346, 1261, 990, 891, 870, 625, 488 cm^{-1}. − UV/Vis (cyclohexane): l_{max} (e) = 236 (21700), 242 (24300), 250(29600), 274 (8700), 289 (15500), 307 (22400), 327 (15600), 344 (1200), 371 nm (500). − MS (EI); *m*/*z* (%): 208 (33) [M$^+$], 193 (8), 180 (16), 166 (28), 152 (42), 140 (23), 125 (22), 82 (74), 67 (100), 54 (23), 41 (62), 27 (35). − $C_{14}H_{12}N_2$: calcd. 208.1000; found 208.0999 (HRMS).

(*E*)-1,6-Dicyano-1-cyclooctyl-1-hexene-3,5-diyne (24): 1,6-Dicyano-1,3,5-hexatriyne (**1**) (97 mg, 0.78 mmol) was dissolved in 50 mL cyclooctane and heated overnight at 100°C. The product was isolated by flash column chromatography with cyclohexane/ethyl acetate (49:1) as eluent (yield: 60 mg, 62%, a brown-white solid). − ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 1.61 (m, 14 H, cyclooctane), 2.93 (m, 1 H, C*H*), 6.02 (s, 1 H, C=C−*H*). − ^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ = 25.16 (2 C, CH_2), 26.09 (1 C, CH_2), 26.36 (2 C, CH_2), 31.40 (2 C, CH_2), 41.39 (1 C, CH), 58.88 (1 C, Cs*C*−CN), 65.68 (1 C, *C*sC−CN), 74.15 (1 C, C=C−*C*sC), 83.01 (1 C, C=C−Cs*C*), 104.82 (1 C, CsC−*C*N), 116.82 (1 C, C=*C*−H), 116.92(1 C, C=C−*C*N), 142.39 (1 C, C=*C*−CN). − IR (KBr): ṽ = 3017 (C=C−H), 2967 (CH_2, CH), 2932 (CH_2, CH), 2903 (CH_2, CH), 2852 (CH_2, CH), 2240 (CN), 2216 (CN), 2190 (CsC), 2152 (CsC), 1702 (C=C), 1475 (CH_2, CH), 1145 (CH_2, CH), 1346, 1031, 878, 627, 492 cm^{-1}. − UV/Vis (cyclohexane): l_{max} (e) = 236 (23900), 241 (25800), 249(31900), 273 (8400), 289 (15200), 307 (22500), 328 (17500), 344 (1300), 370 nm (650). − MS (EI); *m*/*z* (%): 236 (22) [M$^+$], 221 (8), 207 (17), 193 (18), 180 (19), 166 (29), 152 (84), 139 (23), 125 (28), 110 (28), 95 (28), 82 (54), 69 (65), 55 (86), 41 (100), 29 (38).

(*E*)-Dicyano-1-cyclooctyl-1-hexene (25): (*E*)-1,6-Dicyano-1-cyclooctyl-1-hexene-3,5-diyne (**24**) (23 mg, 0.10 mmol) was hydrogenated as described above (yield: 11.6 mg, 50% **25**, colorless liquid). − ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ = 1.60 (m, 15 H, CH_2), 2.56 (m, 1 H, CH), 6.06 (t, 1 H, C=C*H*). − $C_{16}H_{24}N_2$: calcd. 244.1941; found 244.1936 (HRMS).

(*E*)-1,6-Dicyano-1-hexene-3,5-diyne (26): 1,6-Dicyano-1,3,5-hexatriyne (**1**) (166 mg, 1.34 mmol) was dissolved in 50 mL of toluene, then tributyltin hydride (360 µl, 389 mg, 1.34 mmol) was added to the solution. The reaction was stirred overnight at room tempera-

ture under nitrogen. The product was obtained by flash column chromatography with cyclohexane/ethyl acetate (15:1) as eluent (yield: 63 mg, 37%, a brown-white solid). − ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 6.05 (d, *J* = 16.5 Hz, 1 H, C=C−*H*), 6.47 (d, *J* = 16.5 Hz, 1 H, C=C−*H*). − ^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ = 58.55 (1 C, Cs*C*−CN), 65.34 (1 C, Cs*C*), 74.97 (1 C, Cs*C*), 80.73 (1 C, Cs*C*), 104.62 (1 C, CsC−*C*N), 115.29 (1 C, C=C−*C*N), 116.52 (1 C, C=*C*−CN), 126.71 (1 C, *C*=C−CN). − IR (KBr): ṽ = 3051 (C=C−H), 3016 (C=C−H), 2225 (CN), 2193 (CN), 1636, 1253, 945 (C=C−H), 492, 455 cm^{-1}. − UV/Vis (cyclohexane): l_{max} (e) = 230 (41500), 241 (64500), 252 (5500), 267 (9900), 283 (19600), 301 (28500), 321 nm (21300). − MS (EI); *m*/*z* (%): 126 (100) [M$^+$], 99 (41) [M$^+$ − HCN], 86 (8), 75 (93), 62 (8), 50 (5), 28 (5). − $C_8H_2N_2$: calcd. 126.0218; found 126.0221 (HRMS).

3-(4-Cyano-1,3-butadiynyl)bicyclo[2.2.2]oct-2,5-diene-2-carbonitrile (27): 1,6-Dicyano-1,3,5-hexatriyne (**1**) (162 mg, 1.31 mmol) was dissolved in toluene and 1,3-cyclohexadiene (125 µl, 1.31 mmol) was added. This solution was stirred for 3 d at room temperature. The product was obtained by flash column chromatography with toluene/cyclohexane (1:1) as eluent (yield: 163 mg, 61%, a brown-white solid). − ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 1.48 (m, 4 H, CH_2), 3.90 (m, 2 H, CH), 6.34 (t,2 H, CH). − ^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ = 24.05 (1 C, *C*H$_2$), 24.49 (1 C, *C*H$_2$), 40.94 (1 C, *C*H), 42.93 (1 C, *C*H), 59.15 (1C, Cs*C*−CN), 66.09 (1 C, Cs*C*), 74.42 (1 C, Cs*C*), 81.48 (1 C, Cs*C*), 104.97 (1 C, CsC−*C*N), 115.29 (1 C, C=C−*C*N), 130.28 (1 C, C=*C*), 132.38 (1 C, C=*C*−H), 132.52 (1 C, C=*C*−H), 139.63 (1 C, C=*C*). − IR (KBr): ṽ = 3062 (C=C−H), 2997, 2977, 2948, 2875 (CH, CH_2), 2237 (CN), 2212 (CN), 2182 (CsC), 2098 (CsC), 1567, 1341, 1218, 1150, 848, 747, 492 cm^{-1}. − UV/Vis (cyclohexane): l_{max} (e) = 239 (12700), 250 (20500), 275 (3300), 292 (4700), 311 (7800), 333 (7200), 375 nm (300). − MS (EI); *m*/*z* (%): 204 (12) [M$^+$], 176 (100), 149 (14), 123 (9), 99 (16), 80 (20). − $C_{14}H_8N_2$: calcd. 204.0687; found 204.0692 (HRMS).

2-Cyano-3(4′-cyano-buta-1,3-diynyl)-5,6;7,8-dibenzobicyclo-[2.2.2]oct-2-ene (28): 1,6-Dicyano-1,3-5-hexatriyne (**1**) (125 mg, 1.00 mmol) was dissolved in 50 mL of toluene, anthracene (358 mg, 2.00 mmol) was added and the mixture stirred for 3 d at 120°C under nitrogen. The product was isolated by flash column chromatography with toluene/cyclohexane (1:1) as eluent (yield: 218 mg, 72%, a yellow-brown solid). − ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 5.30 (s, 1 H, CH), 5.34 (s, 1 H, CH), 7.08 (m, 4 H, Ar−H), 7.38 (m, 4 H, Ar−H). − ^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ = 53.69 (1 C, bridgehead-*C*), 55.93 (1 C, bridgehead-*C*), 61.14 (1 C, Cs*C*−CN), 65.62 (1 C, Cs*C*), 73.54 (1 C, Cs*C*), 86.15 (1 C, Cs*C*), 104.85 (1 C, CsC−*C*N), 115.04 (1 C, C=C−*C*N), 124.12 (4 C, Ar−*C*), 126.29 (2 C, Ar−*C*), 126.44 (2 C, Ar−*C*), 135.08 (1 C, C=*C*), 141.27 (2 C, Ar−*C*), 141.47 (2 C, Ar−*C*), 144.47 (1 C, C=*C*). − IR (KBr): ṽ = 3076 (Ar−H), 3045 (Ar−H), 2960 (CH), 2235 (CN), 2215 (CN), 2187 (CsC), 2147 (CsC), 1734, 1473, 1458, 1259, 1188, 1157, 1139, 1019, 942, 906, 866, 802, 742, 697, 632, 588 cm^{-1}. − UV/Vis (cyclohexane): l_{max} (e) = 243 (29600), 252 (42300), 290 (7000), 305 (6000), 316 (7300),348 (7900), 362 nm (8700). − MS (EI); *m*/*z* (%): 302 (100) [M$^+$], 275 (13) [M$^+$ − HCN], 178 (53) [$C_{14}H_{10}$]. − $C_{22}H_{10}N_2$: calcd. 302.0844; found 302.0836 (HRMS).

1,2-Bis{2-cyano-5,6;7,8-dibenzobicyclo[2.2.2]oct-2-enyl}acetylene (29): 2-Cyano-3(4′-cyano-buta-1,3-diynyl)-5,6;7,8-dibenzobicyclo[-2.2.2]oct-2ene (**28**) (100 mg, 0.33 mmol) was dissolved in 50 mL of toluene, anthracene (295 mg, 1.66 mmol) was added and the mixture heated at reflux for 2 weeks under nitrogen. The product was purified by flash column chromatography with toluene as eluent (yield: 50 mg, 32%, a yellow solid). − ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 5.21 (s, 2 H, CH), 5.24 (s, 2 H, CH), 6.98 (m, 8 H, Ar−H), 7.29 (m, 8 H, Ar−H). − ^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ = 53.34 (2 C, bridgehead-*C*), 56.61 (2 C, bridgehead-*C*), 98.47 (2 C, Cs*C*), 116.04 (2 C, C=C−*C*N), 123.81 (8 C, Ar−*C*), 124.19 (4 C, Ar−*C*), 126.07 (4 C, Ar−*C*), 128.65 (2 C, C=*C*), 142.02 (4 C, Ar−*C*), 142.06 (4 C, Ar−*C*), 147.16 (2 C, C=*C*). − IR (KBr): ṽ = 3070 (Ar−H), 3022 (Ar−H), 2980 (CH), 2954 (CH), 2208 (CN), 1599, 1474, 1458, 1353, 1261, 1190, 1151, 1106, 1019, 805, 781, 736, 696, 631 cm^{-1}. − UV/Vis (cyclohexane): l_{max} (e) = 251 (4600), 268 (4025), 296 (3175), 356 (3350), 373 nm (3775). − MS (EI); *m*/*z* (%): 480 (24) [M$^+$], 453 (5) [M$^+$ − HCN], 256 (13), 213 (9), 178 (83) [$C_{14}H_{10}^+$], 167 (15), 149 (59), 134 (35), 119 (100), 111 (37). − $C_{36}H_{20}N_2$: calcd. 480.1626; found 480.1639 (HRMS).

7-Cyano-8-(4-cyano-1,3-butadiynyl)-2-oxabicyclo[4.2.0]oct-7-ene (30): 1,6-Dicyano-1,3,5-hexatriyne (**1**) (596 mg, 4.81 mmol) was dissolved in 100 mL of toluene, 3,4-dihydro-2*H*-pyran (3 mL, 33 mmol) was added and the mixture stirred for 48 h at 100°C. The product was purified by flash column chromatography with toluene/cyclohexane (1:1) as eluent (yield: 620 mg, 62%). − ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 1.67 (m, 2 H, CH_2), 1.96 (m, 1 H, CH_2), 2.08 (m,1 H, CH_2), 3.33 (m 1 H, CH), 3.83 (m, 2 H, CH_2), 4.73 (d, 1 H, CH). − ^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ = 19.16 (1 C, *C*H$_2$), 21.79 (1 C, *C*H$_2$), 44.08 (1 C, *C*H), 59.61 (1C, Cs*C*−CN), 62.66 (1 C, O*C*H$_2$), 65.49 (1 C, Cs*C*), 69.62 (1 C, Cs*C*), 74.35 (1 C, *C*H), 82.24 (1 C, Cs*C*), 104.68 (1 C, CsC−*C*N), 111.55 (1 C, C=C−*C*N), 131.04 (1 C, C=*C*), 141.26 (1 C, C=*C*). − IR (KBr): ṽ = 2949, 2874 (CH, CH_2), 2236 (CN), 2220 (CN), 2185 (CsC), 2147 (CsC), 1352, 1234, 1120, 896, 494 cm^{-1}. − UV/Vis (cyclohexane): l_{max} (e) = 238 (67000), 251 (102500), 261 (25000), 276 (18000), 293 (25500), 312 (37600), 333 (28300), 348 (1900), 360 (500), 376 nm (700). − MS (EI); *m*/*z* (%): 208 (15) [M$^+$], 179 (12), 152 (10), 124 (11) [$C_8N_2^+$], 99 (14), 84 (100) [$C_5H_8O^+$]. − $C_{13}H_8N_2O$: calcd. 208.0637; found 208.0637 (HRMS).

2,3-Bis(2,5-dithiacyclopent-3-enylidene-1)-octa-4,6-diynedinitrile (31): Tetrathiafulvalene (168 mg, 0.82 mmol) was added to a solution of 1,6-dicyano-1,3,5-hexatriyne (**1**) (102 mg, 0.82 mmol) in 50 mL of toluene and stirred for 48 h at room temp. in the dark under nitrogen. The product was obtained by flash column chromatography with toluene as eluent (yield: 109 mg, 40%, a dark solid). − ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 6.69 (d, *J* = 6.35 Hz 1 H, C=C−H), 6.74 (d, *J* = 6.35 Hz 1 H, C=C−H), 6.75 (d, *J* = 6.35 Hz 1 H, C=C−H), 6.80 (d, *J* = 6.35 Hz 1 H, C=C−H). − ^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ = 61.54 (1 C, Cs*C*−CN), 68.45 (1 C, Cs*C*), 77.84 (1 C, Cs*C*), 83.14 (1 C, Cs*C*), 85.60 (1 C, S_2C=*C*), 91.63 (1 C, CsC), 105.98 (1 C, CsC−*C*N), 115.59 (1 C, C=C−*C*N), 121.03 (1 C, S−*C*=C−S), 121.63 (1 C, S−*C*=C−S), 121.71 (1 C, S−*C*=C−S), 122.49 (1 C, S−*C*=C−S), 165.03 (1 C, C=*C*−S_2), 167.03 (1 C, C=*C*−S_2). − IR (KBr): ṽ = 3101 (C=C−H); 3071 (C=C−H), 2220 (CN), 2185 (CN), 2158 (CsC), 2079 (CsC), 1636, 1443, 1262, 1091, 814, 660 cm^{-1}. − UV/Vis (cyclohexane): l_{max} (e) = 232 (5075), 282 (1700), 351 (2675), 371 (2825), 424 nm (4275). − MS (EI); *m*/*z* (%): 328 (10) [M$^+$], 204 (100) [TTF$^+$], 146 (36), 102 (72), 91 (47), 76 (38), 58 (23), 44 (100), 28 (94). − $C_{14}H_4N_2S_4$: calcd. 327.9257; found 327.9256 (HRMS).

[1] T. Grösser, A. Hirsch, *Angew. Chem.* **1993**, *105*, 1390−1392; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1340.
[2] G. Schermann, T. Grösser, F. Hampel, A. Hirsch, *Chem. Eur. J.* **1997**, *3*, 1105−1112.
[3] F. Diederich, Y. Rubin, *Angew. Chem.* **1992**, *104*, 1123−1146; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1101.
[4] E. Winterfeldt, *Angew. Chem.* **1967**, *79*, 389−400; *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 423.

[5] F. Bohlmann, H-G. Viehe, *Chem. Ber.* **1955**, *88*, 1017−1027.
[6] E. Winterfeldt, W. Krohn, H. Preuss, *Chem. Ber.* **1966**, *99*, 2572−2578.
[7] Y. Katoka, O. Matsumoto, K. Tani, *Chem. Lett.* **1996**, 727−728.
[8] W. E. Truce, D. G. Brady, *J. Org. Chem.* **1966**, *31*, 3543−3550.
[9] R. Huisgen, K. Herbig, A. Siegel, H. Huber, *Chem. Ber.* **1966**, *99*, 2526−2545.
[10] R. Mestres, *J. Chem. Soc. Perkin I* **1972**, 805−809.
[11] K. Herbig, R. Huisgen, H. Huber, *Chem. Ber.* **1966**, *99*, 2546−2555.
[12] E. Winterfeldt, H. Preuss, *Chem. Ber.* **1966**, *99*, 450−458.
[13] T. Sasaki, T. Yoshioka, K. Shoji, *J. Chem. Soc. C* **1969**, 1086−1088; H.·Hopf, B. Witulski, in *Modern Acetylene Chemistry* (Eds.: P. J. Stang, F. Diederich), VCH, Weinheim−New York−Basel−Cambridge−Tokyo, p. 33−66.
[14] F. Bohlmann, H. Bornowski, D. Kramer, *Chem. Ber.* **1963**, *96*, 584−587.
[15] W. Schroth, F. Billig, A. Zschunke, *Z. Anorg. Allg. Chem.* **1969**, *9*, 184.
[16] F. Bohlmann, W. v. Kap-Herr, C. Ryback, J. Repplinger, *Chem. Ber.* **1965**, *98*, 1736.
[17] V. Jäger, H. G. Viehe, *Methoden Org. Chem. (in Houben-Weyl)*, 4th ed., **1977**, vol. V/2a, p. 790−795.
[18] Y. Amiel, in *The Chemistry of Functional Groups*, supplement C (Eds.: S. Patai, Z. Rappoport), John Wiley and Sons, Ltd., **1983**, p. 341−382; C. Chatgilialoglu, in *The Chemistry of Functional Groups*, supplement C2, John Wiley and Sons, Ltd., **1994**, p. 917−944.
[19] L. Singer, in *Selective Organic Transformations* (Ed.: B. S. Thyagarajan), Wiley, New York, **1972**, vol. 2, p. 239−268.
[20] B. Giese, J. A. Gonzales-Gomez, S. Lachhein, J. O. Metzger, *Angew. Chem.* **1987**, *99*, 475−476; *Angew. Chem. Int. Ed. Engl.*, **1987**.
[21] R. J. Bushby, *J. Chem. Soc., Perkin Trans. 1* **1974**, 274−275.
[22] J. H. Wotiz, F. Huba, R. Vendley, *J. Org. Chem.* **1961**, *26*, 1626−1627.
[23] G. Ahlgren, *J. Org. Chem.* **1973**, *38*, 1369−1374.
[24] N.F. Cywinski, H. J. Hepp, *J. Org. Chem.* **1965**, *30*, 3814−3817.
[25] G. Büchi, S. H. Feairheller, *J. Org. Chem.* **1969**, 609−612.
[26] A. J. Leusink, H. A. Budding, J. W. Marsman, *J. Organomet. Chem.* **1967**, *9*, 285−294·
[27] A. J. Leusink, H. A. Budding, W. Drenth, *J. Organomet. Chem.* **1967**, *9*, 295−306.
[28] C. D. Weis, *J. Org. Chem*. **1962**, *27*, 3520−3524.
[29] C. D. Weis, *J. Org. Chem*. **1963**, *28*, 74−78.
[30] H. Stockmann, *J. Org. Chem*. **1961**, *26*, 2025−2029.
[31] O. Diels, S. Olsen, *J. Prakt. Chem*. **1940**, *156*, 289.
[32] K. Gollnick, S. Fries, *Angew. Chem.*, **1980**, *92*, 848−849; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 823.
[33] T.-L. Chan, *Methods Org. Chem. (Houben-Weyl)*, 4th ed., additional and supplementary vol., **1997**, vol. E17f, p. 641−650.
[34] K. C. Nicolaou, C. K. Hwang, M. E. Duggan, K. Bal Reddy, *Tetrahedron Lett.* **1987**, *28*, 1501−1502.
[35] H. Hopf, M. Kreutzer, P. G. Jones, *Angew. Chem.* **1991**, *103*, 1148−1149; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1127.
[36] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed., Pergamon Press, Oxford, **1988**.

Received March 23, 1999
[O99175]