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Synthesis and Properties of Medium-Sized (C_9–C_{12}) Carbocyclic Diacetylenes[†]

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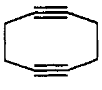
Abstract: The syntheses of 1,5-cyclononadiyne (**3**), 1,5-cyclodecadiyne (**4**), 1,5-cycloundecadiyne (**5**), 1,6-cycloundecadiyne (**6**), 1,6-cyclododecadiyne (**7**), and 1,7-cyclododecadiyne (**8**) have been carried out. Diacetylenes **3** and **4** are prepared from 5-cyclononynone and 5-cyclodecynone, respectively. Compounds **5–8** are synthesized from cyclic diones by thermolysis of the corresponding bisselenadiazoles. The obtained cyclic diacetylenes are further characterized by their bis(hexacarbonyldicobalt) complexes. The geometrical parameters of **3–8** were calculated with force field and semiempirical methods. From the structural data, a correlation between the ^{13}C resonance of the sp-hybridized carbon atoms adjacent to the ethano bridge in **3–5** and the corresponding resonance of the symmetric dialkynes 1,5-cyclooctadiyne (**1**), 1,6-cyclodecadiyne (**2**), and 1,7-cyclododecadiyne (**8**) with the bending angle at this center can be verified. The PE spectra of **3–8** have been recorded, and an interpretation of the bands in the low-energy region is presented. It is found that the splitting of the PE bands that are assigned to the in-plane π-MO's (π_i) strongly depends on the size of the methylene bridge. In the case of a propano bridge (e.g., in **3**, **6**, and **7**), the splitting between π_i^- and π_i^+ is relatively large. The splitting of the bands that are assigned to the out-of-plane π-MO's (π_o) decreases with increasing transannular distance.

Introduction

Monocyclic carbocyclic diacetylenes of medium-sized rings (C_9–C_{12}) are compounds that combine a number of interesting features. (1) They incorporate two linear C—C≡C—C moieties in a relatively small framework, thus leading to sizeable interaction of the p orbitals of the two π-units. As will be shown, this interaction depends strongly on ring size and can be explained in terms of a combination of through-space and through-bond effects.[1] (2) Monocyclic diacetylenes are bifunctional compounds and thus show interesting properties with respect to their use as ligands in transition metal chemistry.[2] (3) A ten-membered enediyne fragment has been identified as part of the reactive subunit in naturally occuring antitumor agents such as calicheamycin and esperamycin.[3a,b] Consequently, a number of research groups are currently working on the synthesis of such systems, and the applications of cyclic acetylenes in tumor therapy.[3c]

In this report, we will concentrate on the first-mentioned aspect; following a detailed description of the synthesis of this class of compounds, we will evaluate the consequences of electronic interaction of two closely spaced π-systems and discuss this effect in relation to the reactivity toward electrophilic attack on the triple bonds.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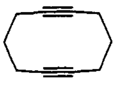
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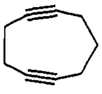
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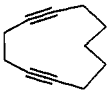
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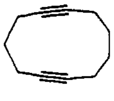
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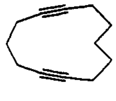
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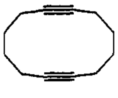
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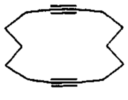
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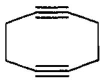
The ligand properties of cyclic diacetylenes of *large* ring size (>12) have been investigated by King et al.[2a,6] As anticipated, it was found that reactivity not only depends on the relevant ring size but also on the metal used. Since unsubstituted carbocyclic diacetylenes of *medium*-sized rings were unknown, we started to explore different approaches to their synthesis. The two routes described in this paper lead to the following six diacetylenes: 1,5-cyclononadiyne (**3**), 1,6-cyclodecadiyne (**2**),[5] 1,5-cyclodecadiyne (**4**), 1,5-cycloundecadiyne (**5**), 1,6-cycloundecadiyne (**6**), and 1,6-cyclododecadiyne (**7**).[7] For the sake of comparison, we have also prepared 1,7-cyclododecadiyne (**8**) and 1,8-cyclotetradecadiyne (**9**). The former was prepared according to the procedure given below (this compound has already been synthesized via a different route[8a]), while the latter was obtained by a modified cyclization method originally described by Dale et al.[8b]

Comparison of the photoelectron spectra of the medium-sized rings 1,5-cyclooctadiyne (**1**)[4] and 1,6-cyclodecadiyne (**2**)[5] revealed a strong π/σ interaction[5] for both of the linear combinations of the in-plane π-MO's. For **1** strong π/σ interaction is observed for $7a_g$, while for **2** the corresponding MO is $6a_u$. This difference leads to a different sequence of the highest occupied MO's and in turn has lead to the prediction[2c] that an electrophile should attack **1** perpendicular to the molecular plane, while **2** should be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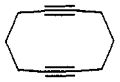
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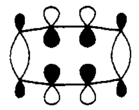
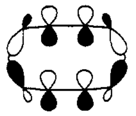

$7a_g$


$6a_u$

[†] Dedicated to Professor Horst Prinzbach on the occasion of his 60th birthday.

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(1) (a) Gleiter, R.; Schäfer, W.; Flatow, A. *J. Org. Chem.* **1984**, *49*, 372. (b) Gleiter, R. *Pure Appl. Chem.* **1987**, *59*, 1585. (c) Gleiter, R.; Schäfer, W. *Acc. Chem. Res.* **1990**, *23*, 369.

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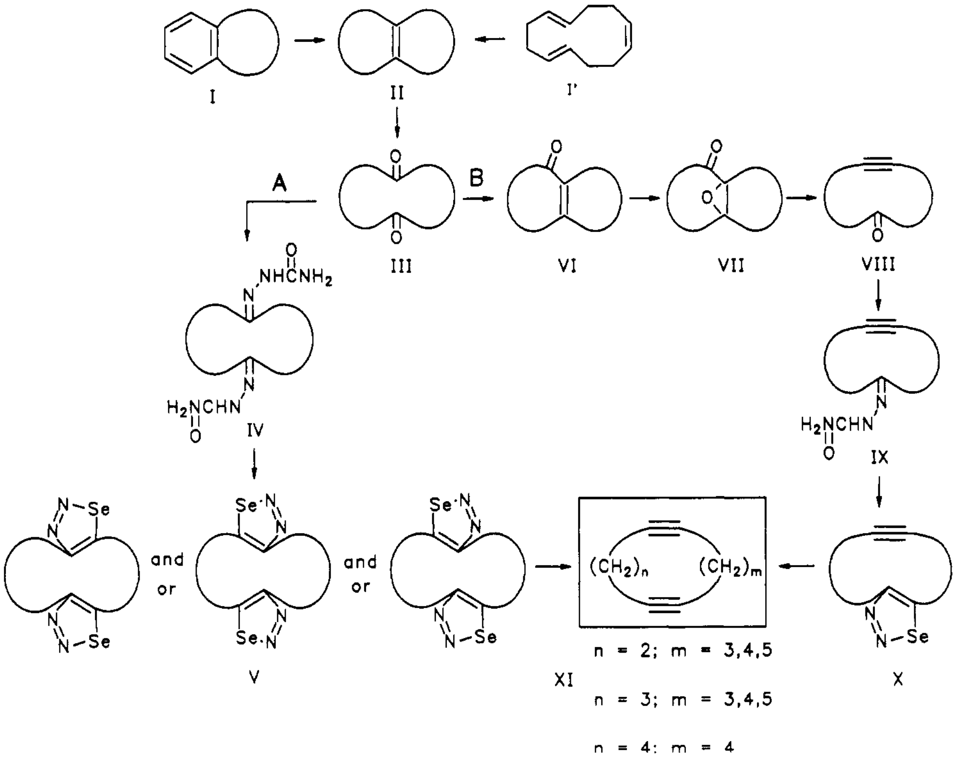
Scheme I. Synthetic Strategy to Obtain the Diacetylenes **2–8**



approached in the molecular plane. Several experiments with **2** and silver triflate or $CpCo(CO)_2$ have been found to be in line with these predictions.[2c]

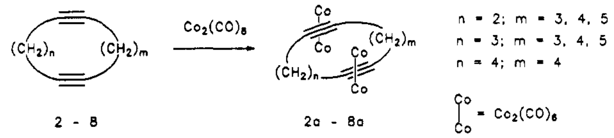
Synthesis

Since ring-closing reactions to medium-sized rings are difficult to execute, we decided to start from commercially available medium-sized bicyclic systems that already contained the required number of carbon atoms. Scheme I demonstrates two possible approaches to **3–8**. The key reaction in both alternatives is the decomposition of a selenadiazole ring to yield the corresponding triple bond, a reaction first used by Lalezari[9] and later applied by Meier et al. to construct cyclic enynes.[10] Starting from either a bicyclic benzene derivative I or *cis,trans,trans*-1,5,9-cyclododecatriene I′ (see Scheme I) both of which can be partially hydrogenated to the bicyclic tetrasubstituted ethylene derivative II, we obtain the diketone III on ozonolysis. Transformation can yield either the bicyclic enone VI (path B) or the bissemicarbazone IV (path A). The enone can be rearranged to the cyclic alkynone VIII in a one-pot reaction.[12] The last steps of both routes involve the preparation of the aforementioned selenadiazoles V or X, according to a procedure reported by Lalezari et al.[9] Thermolysis yields the desired cyclic bisacetylenes XI.

The starting material for **3** is 5-cyclononynone (**10**),[11] which can be transformed to the semicarbazone **11** and the selenadiazole **12** (see Scheme II). Upon heating the latter leads to **3**, which is highly strained and decomposes rapidly at room temperature. The route to **4** also follows path B of Scheme I. In this case we begin with 5-cyclodecynone (**13**),[12] which is transformed to the semicarbazone **14** and the selenadiazole **16**. The other possible selenadiazole, **15**, is detected only in traces.

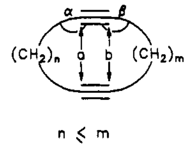
Route A of Scheme I has been used to prepare **5–8** (see Scheme II). To prepare a mixture of **5** and **6**, the starting point is 1,6-cycloundecadione (**17**).[13] On reaction with SeO_2 the corresponding bissemicarbazone **18** is transformed to a mixture of three bisselenadiazoles, **19–21**. Pyrolysis of **19–21** yields a 1:1 mixture of **5** and **6**. Both diynes can be separated by column chromatography in 20–30% yield. From 1,7-cyclododecadione (**22**)[14] and its bissemicarbazone **23**, a mixture of the two bisselenadiazoles **24** and **25** results. By heating this mixture with copper powder, the two diynes **7** and **8** are obtained in 4% and 27% yield, respectively.

To characterize **2–8** further we have treated them with excess amounts of octacarbonyldicobalt to obtain the bis(hexacarbonyldicobalt) products **2a–8a**. For **2a**, **3a**, **4a**, and **5a** we were able to confirm the bistetrahedral arrangement by X-ray investigations on single crystals obtained from pentane solutions.[15]



Properties of 3–8

The most interesting properties of cyclic diacetylenes are related to their structure. Since we have not been able to grow crystals of **3–7** so far, we have to rely on model calculations to elucidate the geometrical parameters of these molecules. In Table I we have listed the most important parameters, the intramolecular distances *a* and *b*, as well as the bending angles *α* and *β* as defined below.



These data were derived from force field and semiempirical calculations. The methods used were the MMP2,[16] the MINDO/3,[17a] and the MNDO[17b] methods. The data in Table I are

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[9] Lalezari, I.; Shafiee, A.; Yalpani, M. *Tetrahedron Lett.* **1969**, 5105. *Angew. Chem.* **1970**, *82*, 484. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 464.

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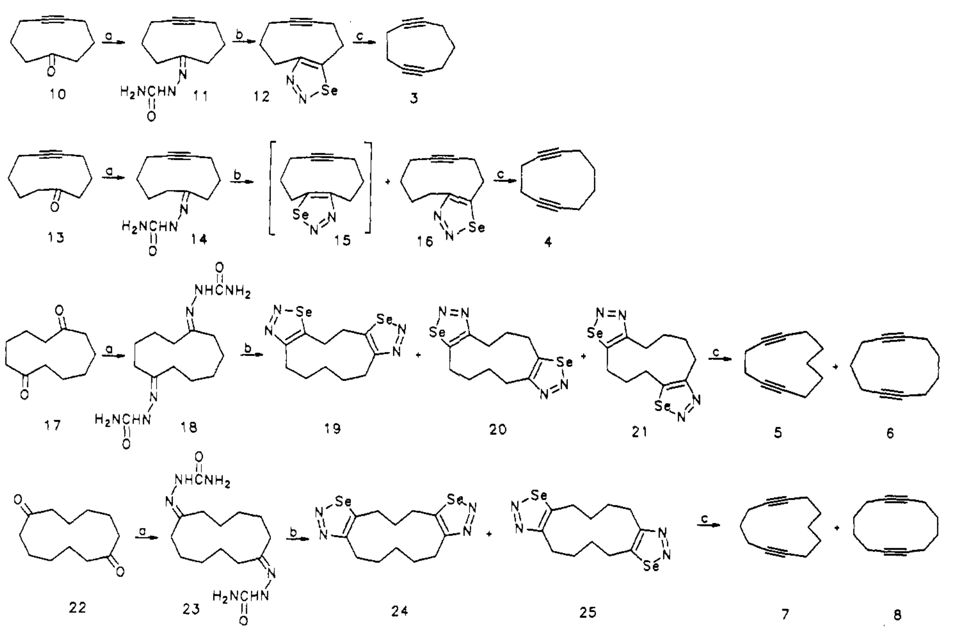
Scheme II. Synthesis of **3**, **4**, **5**, and **6** or **7** and **8** from Readily Available Cyclic Ketones[a]



[a] (a) Semicarbazide–acetate/ethanol. (b) SeO_2/dioxane. (c) Copper powder, 200 °C.

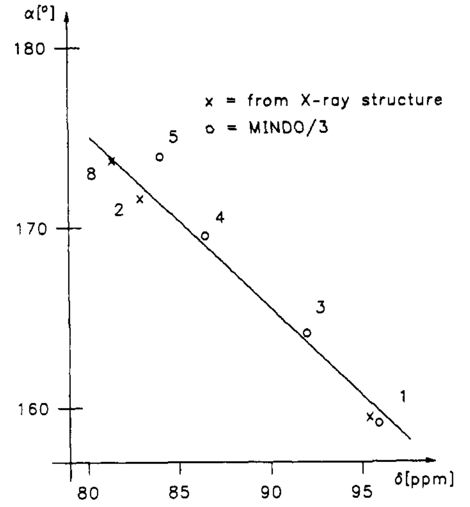


Figure 1. Correlation of the ^{13}C chemical shift of the sp-hybridized carbon atoms adjacent to the ethano bridge with the bending angle α at this center.

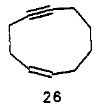
supplemented by values obtained from X-ray results for **1**[4], **2** and **8**.[5] In Figure 1 we have plotted the ^{13}C chemical shift of the sp centers adjacent to the C_2H_4 bridge and the angle (α) at this carbon for **1** and **3–5**. Also included in this diagram are the values of α derived from the X-ray structures of **1**, **2**, and **8** as well as the corresponding ^{13}C values. As can be seen from this figure, a linear correlation is obtained.

To rationalize the ratio of the selenadiazoles obtained from **13** and **17**, respectively (see Scheme II), we have carried out force field calculations[16] on *cis*-cyclodeca-1-en-5-yne (**26**) and *cis*-cyclodeca-1-en-6-yne (**27**) as models for **15** and **16**. As a model for **19** we chose *cis,cis*-cycloundeca-1,5-diene (**28**) and for **20** and **21** *cis,cis*-cycloundeca-1,6-diene (**29**). The calculations predict very similar energies for **26** and **27** and about 2.4 kcal/mol more strain energy for **28** than for **29**. These data suggest the formation of equal amounts of **2** and **4** in the case of **14** and a ratio of about 1:3 for **5** and **6**, respectively. The difference between experiment and prediction excludes arguments based on product stability.

Table I. Geometrical Parameters of **1–8** as Derived from MMX and Semiempirical MO Methods

compd	param	MMX	MINDO/3	MNDO/2	X-ray
1	*a*	2.72	2.65	2.55	2.56
	b	2.72	2.65	2.55	2.56
	α	153.2	157.8	160.6	159.3
	β	153.2	157.8	160.6	159.3
2	*a*	3.0	3.10	2.94	2.99
	b	3.0	3.10	2.94	2.99
	α	172.0	171.7	174.3	171.7
	β	172.0	171.7	174.3	171.7
3	*a*	2.73	2.70	2.58	
	b	3.03	3.01	2.86	
	α	160.0	164.0	166.4	
	β	164.5	166.6	169.6	
4	*a*	2.84	2.76	2.64	
	b	3.53	3.35	3.23	
	α	166.4	169.4	172.3	
	β	166.8	172.6	175.0	
5	*a*	2.92	2.86	2.75	
	b	3.85	3.76	3.65	
	α	171.0	174.0	177.0	
	β	170.0	175.0	177.0	
6	*a*	3.13	3.25	3.08	
	b	3.51	3.53	3.37	
	α	176.0	174.0	175.0	
	β	173.0	174.0	174.0	
7	*a*	3.27	3.43	3.29	
	b	3.89	4.02	3.86	
	α	177.8	178.6	178.6	
	β	174.5	178.8	178.8	
8	*a*	4.36	3.72	3.67	4.06
	b	4.36	3.72	3.67	4.06
	α	168.2	179.8	179.0	173.8
	β	168.2	179.8	179.0	173.8

Thus, explanations based on the kinetics of selenadiazole formation have to be considered. From the proposed mechanism of selenadiazole formation[9,10] it seems likely that the acidity of the α-H atoms next to the semicarbazone functionality will be decisive.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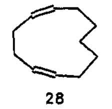
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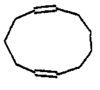
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(17) (a) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285. (b) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899 and 4907.

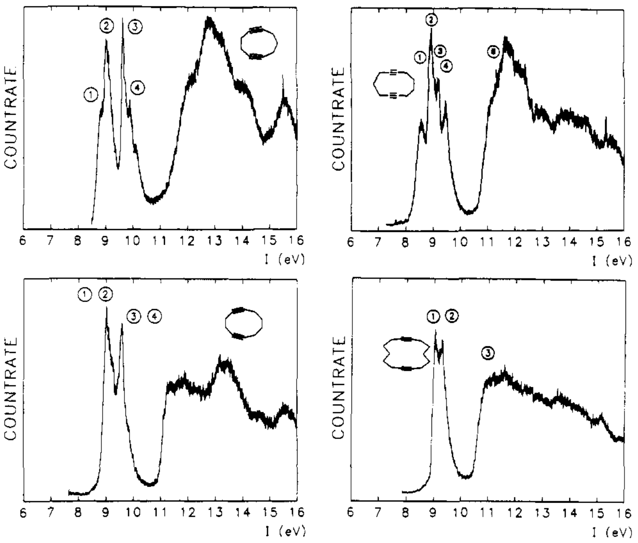

Figure 2. PE spectra of **3**, **4**, **6**, and **9**.

PE Spectra of 3–9

If one considers carbocyclic diacetylenes as members of the class of cyclophanes (i.e., two π-systems connected by at least two linking units—in the case of **1–9** one may even classify these compounds as the most simple "superphanes"), then an analysis of their electronic structure from a similar approach as documented for the well-known benzenoid cyclophanes[18] seems appropriate. Therefore, we have recorded the PE spectra of the above medium-sized diacetylenes—the PE spectra of **1**,[4] **2**,[5] and **8**[5] have been discussed already. To give an idea of the appearance of the PE spectra we have reproduced those of **3**, **4**, **6**, and **9** in Figure 2. The measured ionization energies of **1–8** are collected in Table II.

On the basis of the assumption of the validity of Koopmans' theorem ($-\epsilon_j = I_{v,j}$),[19] we have correlated the recorded vertical ionization energies, $I_{v,j}$, with the calculated orbital energies of the neutral ground state, $-\epsilon_j$. This assumption allows us to analyze the PE spectra of **3–9** in terms of through-space and through-bond interactions[1b,1c,20] with arguments from perturbation theory.[21]

In the low-energy region (below 11 eV), we anticipate four ionic states for **3–9**, arising from the ionization out of the "in-plane", π_i, and "out-of-plane", π_o, linear combinations of the π-fragments. On top of this the C–C σ orbitals of the $-(CH_2)_n-$ chains have the correct symmetry to interact with either one of the π_i combinations shown below; for an even-numbered n this is π_i^+, and for an odd-numbered n it is the π_i^- combination. Furthermore, the π_o orbitals are prone to destabilizing interactions with the adjacent σ C–H bonds (hyperconjugation). As connection by a single $-CH_2-$ fragment ($n = 1$) or direct conjugation (linear arrangement, $n = 0$) is not considered here, we can use the results obtained from PE spectroscopy to evaluate the different effect of the ethano ($n = 2$), propano ($n = 3$), butano ($n = 4$), and pentano ($n = 5$) bridges, as all possible combinations of these fragments are given in **1–9**. A glance at the low-energy region in the depicted PE spectra shows that the separation and intensities of the ionization bands vary considerably from compound to compound. To account for these differences we will analyze the spectra with the following questions as a guideline:

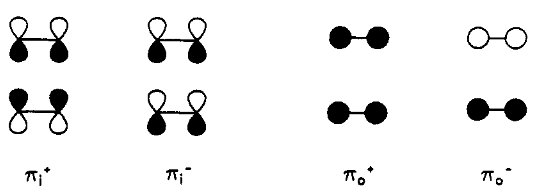

Table II. Ionization Energies, $I_{v,j}$, Assignments and Calculated Energies, $-\epsilon_j$, According to ZDO and MINDO/3 Procedures

compd	$I_{v,j}$	assignment	$-\epsilon_j$ (ZDO)	$-\epsilon_j$ (MINDO/3)
1	9.16	π_o^-		9.37 (π_i^+)
	9.30	π_i^+	9.44	9.43 (π_i^-)
	9.70	π_i^-	9.60	9.53 (π_o^-)
	10.07	π_o^+		10.17 (π_o^+)
3	8.82	π_i^-	9.05	9.33 (π_i^-)
	9.05	π_o^-		9.57 (π_o^-)
	9.67	π_i^+	9.82	9.62 (π_i^+)
	9.90	π_o^+		9.80 (π_o^+)
4				9.42 (π_i^+)
	9.07	π_i^-, π_o^-	9.33	9.54 (π_o^-)
				9.68 (π_i^-)
	9.63	π_i^+, π_o^+	9.46	9.84 (π_o^+)
5				9.51 (π_i^+)
	9.10	π_i^-, π_o^-	9.24	9.54 (π_o^-)
				9.72 (π_i^-)
	9.57	π_i^+, π_o^+	9.56	9.79 (π_o^+)
2	8.47	π_i^-	8.66	9.07 (π_i^-)
	9.12	π_o^-		9.77 (π_o^+)
	9.42	π_o^+		9.79 (π_o^-)
	10.02	π_i^+	10.25	10.31 (π_i^+)
6	8.77	π_i^-	8.90	9.38 (π_i^-)
	9.14	π_o^-		9.63 (π_o)
	9.41	π_o^+		9.66 (π_o)
	9.69	π_i^+	9.90	9.83 (π_i^+)
7	8.80	π_i^-	8.90	9.36 (π_i^-)
	9.13	π_o^-		9.69 (π_o^+)
	9.34	π_o^+		9.62 (π_o^-)
	9.66	π_i^+	9.90	9.89 (π_i^+)
8				9.28 (π_i^+)
	9.13	π_i^-, π_o^-	9.20	9.74 (π_o^-)
				9.79 (π_i^-)
	9.38	π_i^+, π_o^+	9.41	9.89 (π_o^+)

(1) To what extent is the energy separation of the π orbitals influenced by transannular distance?

(2) Can the different effect of even- or odd-numbered bridges easily be discerned? Are the larger butano and pentano chains at all effective?

(3) If a combination of both odd- and even-numbered linking units is present (as in **3** or **5**), which group dominates?

(4) Which effect is more pronounced, through-space or through-bond interaction?

(5) Can the ordering of the π_o orbitals be assigned with certainty?

(6) Can our results on symmetry and sequence of the energy levels of the four highest occupied MO's be used to predict reactivity toward electrophilic attack on the acetylenic moieties? In other words, when do we expect a reaction to proceed in the plane of the ring and when will it commence from above the plane?

To answer some of these questions we will draw on the results obtained from our previous studies on **2** and **8**[5] and supplement these with further calculations on an empirical as well as semiempirical level for the remaining diacetylenes. For 1,6-cyclodecadiyne (**2**), we expect strong interactions between the σ skeleton and the π_i^- linear combinations to dominate the through-space interaction.

In order to estimate the energy of the π_i bands, taking only the most important contributions into consideration, we have carried out LCFO (linear combination of fragment orbitals) calculations with the parameters listed below. The basis energy of the triple bond was deduced from the PE spectra of a number of open-chain diacetylenes.[22]

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$$\langle \pi_i | H | \pi_i \rangle = -10.3 \text{ eV} \tag{1}$$

For the basis energy of the localized C–C single bonds, the value

$$\langle \sigma_n | H | \sigma_n \rangle = -14.0 \text{ eV} \tag{2}$$

was selected. This value has been used in a similar investigation of the PE spectra of several cyclophanes.[23]

The off-diagonal terms

$$\langle \pi_i | H | \sigma \rangle = -1.33 \text{ eV} \tag{3}$$

$$\langle \sigma_n | H | \sigma_m \rangle = -2.0 \text{ eV} \tag{4}$$

stem from interaction energies between localized orbitals of cyclic diacetylenes calculated by the MINDO/3 method. To account for the through-space interactions between the triple bonds we have assumed an exponential dependence of the matrix element

$$\langle \pi_i^1 | H | \pi_i^2 \rangle = -1.75 e^{-0.45d} \text{ eV} \tag{5}$$

where d denotes the (mean) distance between the π-bonds derived from MNDO calculations or, if available, X-ray data (see Table I). The cross terms of eqs 3–5 have been adjusted in order to reproduce the experimental data. The out-of-plane π orbitals have not been included since in this simple approach their energies vary only if hyperconjugation with the adjacent C–H bonds is also considered.

The results of the calculations are given in Table II. Although this procedure neglects the hydrogen atoms as well as the individual molecular geometry, the good agreement between the calculated and experimental values shows that the complex interplay of through-space and through-bond effects can be explained qualitatively on this level.[24]

In addition to the empirical method, we have used the MINDO/3 procedure,[17a] which has proven quite reliable in predicting PE bands of many unsaturated hydrocarbons. Studies on **1** have revealed[4] that the ethano bridges cause a sequence π_i^+ above π_i^-, opposite to the ordering that is expected solely from through-space interaction. This sequence has been ascribed to a strong interaction between π_i^+ and the σ-skeleton. In **2** on the other hand, the sequence π_i^- on top of π_i^+ is predicted.[5] Here the propano bridge interacts strongly with π_i^- and thus reinforces the through-space ordering.

To correlate the superimposed effects in these systems we have divided the nine diacetylenes into two groups (see Figure 3a,b). The criterion imposed is the length of the methylene chain relevant to the discussion, which is always drawn on the left-hand side of the depicted formula (we will concentrate on $n = 2$ and $n = 3$ and consider the larger butano or pentano bridges as relatively ineffective for through-bond interaction; for the justification of this assumption, see below). The cycles containing an even-numbered n have been collected in Figure 3a and those with an odd-numbered n in Figure 3b.

This classification lets us distinguish a number of effects. (1) The effect of transannular overlap is nicely accounted for by the exponential decline of the relative split assigned to the out-of-plane orbitals. Starting at **1** with a strong split, $\Delta(\pi_o^+/\pi_o^-) = 0.9$ eV, this difference is reduced to $\Delta = 0.3$ eV in **2** and remains at about 0.25 eV in all larger rings. For instance, the spectrum of 1,7-cyclododecadiyne (**8**) is more or less identical with that of the next higher symmetrical homologue, 1,8-cyclotetradecadiyne (**9**) ($I_{v,j}$ = 9.07 and 9.34 eV). Thus, we conclude that a transannular distance of $d \approx 3$ Å or less is necessary to induce through-space interaction.

(2) As is evident from the two figures, the ethano bridge (Figure 3a) leads to an overall more closely spaced band structure, which can be traced back to destabilization of the π_i^+ orbital while the π_i^- combination remains unaffected. In contrast, all compounds with a propano bridge (Figure 3b) show one band at an energy below $I_{v,j} = 9$ eV, which, according to the calculations, is due to an ionization event from the π_i^- combination. The virtually identical PE spectra of **4** and **5** as well as those of **6** and **7** confirm our assumption that the butano or pentano bridges do not influence the ordering of the four highest occupied MO's to any extent and justify our classification ($n = 2$ or $n = 3$) as shown in Figure 3a,b. An explanation for this behavior can be traced back to the fact that the longer methylene chains contain a large number of

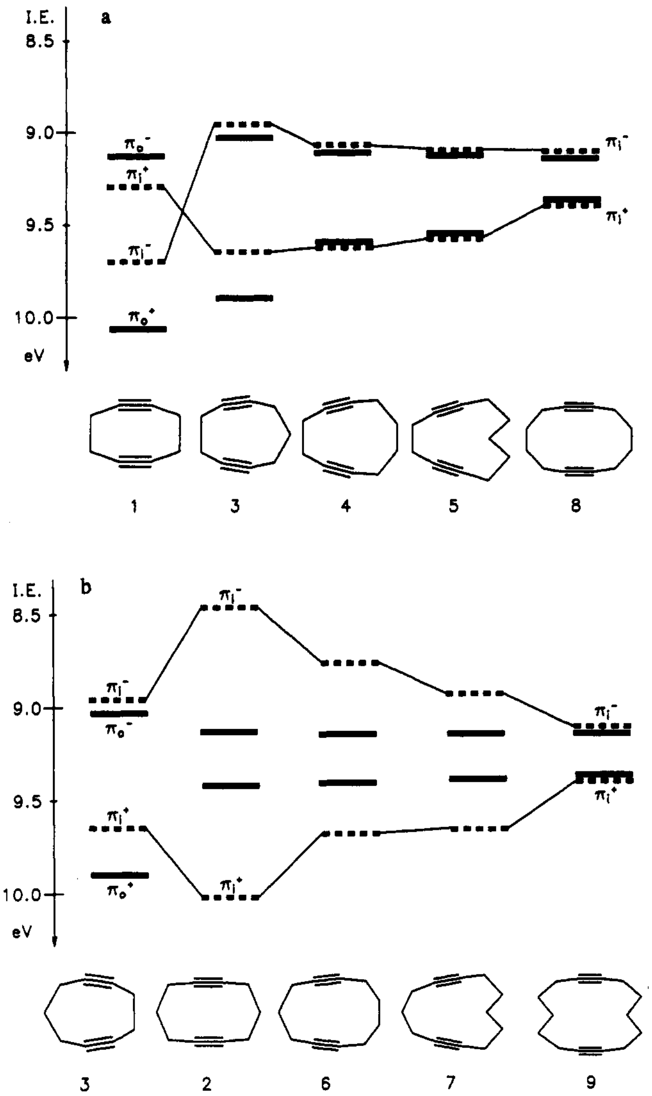

Figure 3. (a) Correlation of the ionization energies of the cyclic diacetylenes **1**, **3**, **4**, **5**, and **8** containing even-numbered ethano ($n = 2$) or butano bridges ($n = 4$) (on right) based on the results of LCFO calculations. (b) Correlation of the ionization energies of the cyclic diacetylenes **3**, **2**, **6**, **7**, and **9** containing odd-numbered propano ($n = 3$) or pentano bridges ($n = 5$) (on right) based on the results of LCFO calculations.

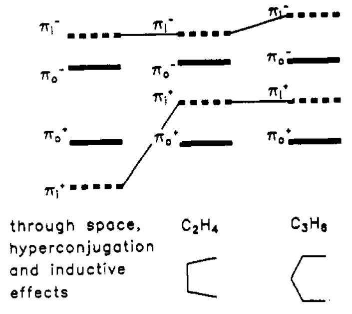

Figure 4. The interplay of through-space and through-bond effects leading to the observed band structure in **3**.

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fragment σ orbitals that belong to different symmetry groups and thus allow for interaction with both the bonding and the antibonding combinations of the π orbitals.

(3) 1,5-Cyclononadiyne (**3**) is represented in both figures. Here the effects of both bridges are competing with each other. Through-space interaction, inductive effect, and hyperconjugation place π_i^+ below π_i^- and π_o^+ below π_o^- (see left of Figure 4). Interaction with the C_2H_4 bridge moves π_i^+ on top of π_o^+, leaving the other levels unchanged (middle of Figure 4). The propano bridge on the other hand only destabilizes π_i^- ($I_{v,j}$ = 8.85 eV), and thus the sequence shown on the right of Figure 4 is obtained.

(4) From the above discussion, a picture emerges that indicates that if an ethano or propano bridge is present, through-bond interaction will dominate through-space interaction even though the latter should be substantial because of the small transannular distance. This effect is especially pronounced in 1,5-cyclooctadiyne (**1**). According to our calculations, in this case the strong through-space interaction caused by the small transannular distance (d = 2.56 Å) is overruled by through-bond interaction with the ethano bridge. Thus, we conclude that the natural orbital sequence in **1** is reversed (see Figure 3a), and the bonding π_i^+ combination lies at lower ionization energy than its antibonding π_i^- counterpart (for a different interpretation, see ref 4). For larger rings neither effect plays an important part in the relative order of the π-MO's.

(5) It is difficult to rationalize the result that the MINDO/3 procedure calculates the antibonding π_o^- combination to be at higher orbital energy than the bonding π_o^+ combination for all even-numbered n. For odd n the natural order (π_o^+ below π_o^-) also varies strongly (see Table II). Thus the assignments of these MO's have been made only tentatively. Furthermore, there is a discrepancy between the ordering of the $\pi_i^{+/-}$ levels when comparing the results obtained for **4**, **5**, and **8** (see Table II). While the semiempirical calculations predict π_i^+ to be at lower orbital energy than π_i^- (strong influence of the ethano or butano bridge), the LCFO analysis comes to the opposite conclusion (π_i^+ at higher energy, i.e., natural order). In Figure 3a we have assigned the bands from the results of the latter procedure.

(6) If reaction with an electrophile at the triple bonds of the discussed compounds is primarily influenced by the HOMO/LUMO interaction, then only **2**, and to a lesser extent **6** and **7**, should show a pronounced differentiation concerning the direction of attack of the incoming electrophile. In these cases, the HOMO is of the in-plane type and lies at exceptionally high values as compared to the remaining p orbital combinations (the HOMO energy is separated by 0.65 eV (**2**), 0.37 eV (**6**), and 0.33 eV (**7**) from the remaining bands). All other compounds show a relatively close spacing of MO energies, and consequently any selectivity based on the MO sequence alone is more than questionable. On top of the electronic effects, one must consider steric restraints imposed by the length of the connecting moieties, which will direct the mode of reaction irrespective of any electronic contributions. To study these influences we are currently investigating the reaction of a number of electrophiles with **2**–**8**.

Conclusions

We have presented two complementary methods to prepare medium-sized cyclic diacetylenes. For **1**–**5** we have found a correlation between the angle at the sp center next to the ethano bridge and the ^{13}C shift of this C atom. The PE spectroscopic investigations reveal a strong splitting of the in-plane π-bands in the cases of **2**, **3**, and **6**, i.e., in those molecules where at least one propano group connects the two acetylene moieties. Our investigations furthermore show that the ethano and butano bridges lead to a small splitting between the π-bands.

Experimental Section

Preparation of the Bissemicarbazones 18 and 23. To a solution of 0.05 mol of the cyclic dione (**17**, **22**) in 200 mL of dry ethanol was added a 3-fold amount of semicarbazide–acetate in 250 mL of ethanol. After 30 h at room temperature, the precipitate was filtered off and washed with ethanol. 1,6-Cycloundecanedione bissemicarbazone (**18**) was obtained in 70% yield, and 1,7-cyclododecanedione bissemicarbazone (**23**) was obtained in 94% yield. **18**: mp 218 °C dec; IR (KBr) ν 3465, 3100, 2943, 1640, 1587, 1470 cm^{-1}. **23**: mp 230 °C dec; IR (KBr) ν 3454, 3186, 2926, 1682, 1582, 1463 cm^{-1}. Anal. Calcd for $C_{14}H_{26}N_6O_2$: C, 54.20; H, 8.40; N, 27.10. Found: C, 54.53; H, 8.64; N, 25.91.

Preparation of the Cyclic Bis[1,2,3]selenadiazoles 19, 20, 21, 24, and 25 from the Cyclic Semicarbazones 18 and 23. To a suspension of 0.048 mol of **18** or **23** in freshly distilled dioxane was added a saturated SeO_2/H_2O *solution (3-fold molar amount) dropwise.* The addition was carried out in the dark with stirring. After 24 h, the red suspension was concentrated, and 500 mL of $CHCl_3$ was added. The $CHCl_3$ solution was washed three times with 150 mL of water. The water phase was extracted with 100 mL of $CHCl_3$. After filtration over Celite, the $CHCl_3$ solutions were dried with $MgSO_4$ and the solvent was evaporated. Further purification was achieved by flash chromatography on silica gel, with $CHCl_3$ in the case of 4,5,6,7,11,12,13,14-octahydrocyclododeca[1,2-*d*:7,8-*d'*]bis[1,2,3]selenadiazole (**24**) and 4,5,6,7,8,12,13,14-octahydrocyclododeca[1,2-*d*:9,8-*d'*]bis[1,2,3]selenadiazole (**25**) and with ether in the case of 4,5,6,10,11,12-hexahydro-13*H*-cycloundeca[1,2-*d*:6,7-*d'*]bis[1,2,3]selenadiazole (**19**), 4,5,6,7,11,12-hexahydro-13*H*-cycloundeca[1,2-*d*:8,7-*d'*]bis[1,2,3]selenadiazole (**20**), and 4,5,6,7,8,12-hexahydro-13*H*-cycloundeca[1,2-*d*:9,8-*d'*]bis[1,2,3]selenadiazole (**21**). The mixture **19**–**21** was obtained as ochre-colored crystals (TLC, silica gel/ether yields three spots in a ratio ≈ 10:1:10). The yellow oil of **24** and **25** can be crystallized by adding acetone (TLC, silica gel/ether yields two spots in a ratio ≈ 5:1). The yield was 20% for **19**–**21** and 15% for **24** + **25**. MS (**19**–**21**) (CI/CH_4) m/z 403, 391, 363, 335, 283 (each peak shows the isotopic pattern of $C_{11}H_{14}N_4Se_2$), 313, 301, 273, 245, 227 (each peak shows the isotopic pattern of $C_{11}H_{16}ON_2Se$).

Pyrolysis of the Cyclic Bis[1,2,3]selenadiazoles. To a solution of 2 g of the bis[1,2,3]selenadiazole mixtures (**19**–**21** or **24**, **25**) in CH_2Cl_2 was added 30 g of copper powder (electrolytical quality). The solvent was removed in such a way that the solid material covered the walls of the flask. The pyrolysis was carried out under argon. The apparatus was connected to a Schlenk flask cooled by liquid nitrogen. For pyrolysis the flask was immersed in a heated (180 °C) oil bath. The pyrolysate was dissolved in CCl_4 and chromatographed on silica gel. By this technique the following compounds (yields) were obtained: 1,5-cycloundecadiyne (**5**) (32%); 1,6-cycloundecadiyne (**6**) (25%); 1,6-cyclododecadiyne (**7**) (4%); and 1,7-cyclododecadiyne (**8**) (27%). Properties of **5**–**8**. **5**: ^1H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 4 H), 2.21 (t, 4 H, ^3J = 6.25 Hz), 1.88 (q, 2 H, ^3J = 6.97 Hz), 1.53 (q, 4 H, ^3J = 6.61 Hz); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 17.98 (t, CH_2), 18.88 (t, CH_2), 24.18 (t, CH_2), 25.71 (t, CH_2), 81.01 (s, C), 84.04 (s, C); GC–MS (EI) m/z 146 (M^+, 3), 145 ($M^+ - H$, 14), 131 ($M^+ - CH_3$, 70), 117 (100), 91 (95), 39 (64); IR (CCl_4) ν 2925, 2860, 2224, 1435, 1331 cm^{-1}; UV/vis (cyclohexane) λ_{max} (log ϵ) 228 (sh, 1.65), 238 (sh, 1.46). Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.34; H, 9.94. **6**: ^1H NMR (300 MHz, $CDCl_3$) δ 2.3 (m, 4 H), 2.1 (m, 4 H), 1.65 (m, 6 H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 19.18 (t, CH_2), 20.02 (t, CH_2), 27.06 (t, CH_2), 27.63 (t, CH_2), 80.35 (s, C), 81.76 (s, C); GC–MS (EI) m/z 146 (M^+, 13), 145 ($M^+ - H$, 11), 131 ($M^+ - CH_3$, 41) 117 ($M^+ - C_2H_5$, 100), 91 (71), 39 (46); IR (CCl_4) ν 2930, 2860, 2290, 2235, 1435, 1360 cm^{-1}; UV/vis (cyclohexane) λ_{max} (log ϵ) 227 (sh, 2.1), 237 (sh, 1.94). Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.50; H, 9.81. **7**: ^1H NMR (300 MHz, $CDCl_3$) δ 2.3 (m, 4 H), 2.22 (m, 4 H), 1.85 (q, 2 H, ^3J = 7.17 Hz), 1.71 (m, 2 H), 1.45 (q, 4 H, ^3J = 6.74 Hz); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 17.71 (t, CH_2), 19.66 (t, CH_2), 24.24 (t, CH_2), 24.33 (t, CH_2), 27.30 (t, CH_2), 80.17 (s, C), 81.52 (s, C); GC–MS (EI) m/z 160 (M^+, 4), 159 ($M^+ - H$, 6), 145 ($M^+ - CH_3$, 7), 131 ($M^+ - C_2H_5$, 62), 117 ($M^+ - C_3H_7$, 100), 91 (66), 39 (36); IR (CCl_4) ν 2918, 2852, 2224, 1450, 1435 cm^{-1}; GC–HRMS (EI). Calcd for $C_{12}H_{16}$ (M) 160.1252, found 160.1249. **8**: The data are identical with those from the literature.[8]

Semicarbazone of 5-Cyclononyne. A suspension of 44.4 g (0.4 mol) of semicarbazide–hydrochloride and 34.5 g (0.42 mol) of sodium acetate was refluxed for 20 min in dry ethanol. After addition of 13.6 g (0.1 mol) of 5-cyclononynone, the suspension was refluxed for 4 h. After removal of the solvent, the residue was treated with H_2O and CH_2Cl_2 to dissolve all of the solid white material. The two phases were separated, and the water solution was washed three times with CH_2Cl_2. The organic solvents were washed with saturated $NaHCO_3$ solution and dried over $MgSO_4$. After evaporation of the solvent, a colorless solid material was obtained. Recrystallization from methanol yielded 15.5 g of the semicarbazone of 5-cyclononynone (**11**) (80%) as colorless needles: mp 192–193 °C; ^1H NMR (90 MHz, $CDCl_3$) δ 8.20 (s, 1 H), 5.64 (m, 2 H), 1.90–2.50 (m, 12 H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 158.2, 156.2, 86.1, 85.4, 36.8, 32.4, 27.0, 25.9, 19.5, 18.0; MS (70 eV) m/z 193 (11), 149 (12), 132 (28), 119 (46), 105 (29), 91 (100), 79 (53), 72 (46); IR (KBr) ν 3460, 3200, 2922, 1672, 1570, 1452 cm^{-1}. Anal. Calcd for $C_{10}H_{15}N_3O$: C, 62.15; H, 7.82; N, 21.74. Found: C, 62.17; H, 7.83; N, 21.85.

Semicarbazone of 5-Cyclodecynone. A suspension of 22.0 g (0.2 mol) of semicarbazide–hydrochloride and 17.2 g (0.21 mol) of dry sodium acetate was refluxed in 200 mL of dry ethanol for a short period of time. The resulting sodium chloride was filtered and washed with hot ethanol. To the ethanolic solution of semicarbazide–acetate was added 15.0 g (0.1 mol) of 5-cyclodecynone, and the mixture was refluxed for 1 h. Cooling slowly to −20 °C yielded 15.9 g (77%) of crystals of the semicarbazone of cyclodecynone **14**: mp 217–219 °C; MS (70 eV) m/z 207 (14), 148 (38), 133 (40), 119 (28), 105 (44), 91 (100), 79 (52), 41 (52); IR (KBr) ν 3457, 1684, 1576, 1451 cm^{-1}. Anal. Calcd for $C_{11}H_{17}N_3O$: C, 63.74; H, 8.27; N, 20.27. Found: C, 62.70; H, 8.29; N, 20.40.

7,8-Didehydro-5,6,9,10-tetrahydro-4*H*-cyclonona-1,2,3-selenadiazole (12) and 7,8-Didehydro-4,5,6,7,10,11-hexahydrocyclodeca-1,2,3-selenadiazole (16). To a solution of 30 mmol of semicarbazone (**11** or **14**) in 400 mL of dioxane was added a concentrated solution of SeO_2 in water (52 mL) under stirring, dropwise at room temperature. After 16 h an additional 1.5 g of solid SeO_2 was added, and the stirring was continued for 4 h. After concentration of the solvent to 50 mL, 700 mL of CH_2Cl_2 was added. The organic phase was washed with water, dried with $MgSO_4$, and the solvent evaporated. The residue was chromatographed over a short column of silica gel with CH_2Cl_2. The orange colored raw material was recrystallized from pentane in the case of **12**. In the case of the 10-membered ring, both isomers **16** and **15** were obtained, in a ratio of 14:1. Recrystallization from pentane yielded pure **16**. Yields: 48% **12**, 37% **16**. **12**: colorless, photolabile crystals, mp 70–71 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.23–2.50 (m, 2 H), 3.10–3.20 (m, 2 H), 3.32–3.36 (m, 2 H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 163.6, 156.5, 89.7, 85.4, 30.5, 28.4, 26.1, 22.4, 17.8; MS (70 eV) m/z 197 (8.2), 117 (100), 115 (100), 103 (17), 91 (100), 79 (45), 65 (45), 51 (57), 39 (100), 28 (100); IR (KBr) ν 2922, 1500, 1444, 1428, 1330, 1306, 1264 cm^{-1}; UV (pentane) λ_{max} (log ϵ) 240 (3.97), 293 (2.79). Anal. Calcd for $C_9H_{10}N_2Se$: C, 48.01; H, 4.48; N, 12.44. Found: C, 48.00; H, 4.31; N, 12.44. **16**: colorless, photolabile crystals, mp 66–67 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.29–3.34 (m, 4 H), 2.34–2.44 (m, 4 H), 2.11–2.17 (m, 2 H), 1.54–1.62 (m, 2 H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 161.4, 156.8, 87.1, 79.5, 28.5, 26.3, 25.7, 25.4, 21.9, 18.4; MS (CI/CH_4) m/z 281, 269, 241, 211, 197, 171, 161, 117, 104; IR (KBr) ν 2926, 2268, 2216, 1501, 1440, 1331, 1307, 1263 cm^{-1}; UV (cyclohexane) λ_{max} (log ϵ) 241 (3.92), 297 (2.70). Anal. Calcd for $C_{10}H_{12}N_2Se$: C, 50.22; H, 5.06; N, 11.71. Found: C, 50.41; H, 5.16; N, 11.79.

Preparation of 1,5-Cyclononadiyne (3) and 1,5-Cyclodecadiyne (4). To a solution of 10 mmol of the selenadiazoles **12** (2.25 g) and **16** (2.37 g) in CH_2Cl_2 was added 20 g of copper powder (electrolytical quality). The solvent was removed in such a way that the solid material covered the wall of the flask. The pyrolysis was carried out under vacuum (0.1 Torr) by immersing the flask in a heated (200 °C) oil bath. After a few seconds, the product, together with the educt, was distilled over and trapped in a cooled flask (liquid nitrogen). The mixture was separated by chromatography on silica gel (0.040–0.063) with CCl_4 as solvent. The following yields were obtained: 65 mg of **3** (9.2%) and 506 mg of **4** (56%). The yields are related to the decomposed selenadiazole. **3**: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.34–2.39 (m, 8 H), 1.93–1.97 (m, 2 H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 92.0, 85.2, 30.6, 19.7, 19.6; MS m/z 118 (15), 117 (100), 91 (54), 51 (31), 39 (57); IR (CCl_4) ν 2920, 2263, 2206, 1259 cm^{-1}. **4**: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.35–2.37 (m, 4 H), 2.15–2.16 (m, 4 H), 1.72–1.79 (m, 4 H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 86.38 (s), 80.63 (s), 27.51 (t), 20.32 (t), 18.82 (t); GC–MS m/z 132 (22), 131 (42), 117 (100), 104 (95), 91 (89), 78 (56), 51 (45), 39 (51); IR (KBr) ν 2939, 2851, 2286, 2228, 1450, 1440 cm^{-1}.

General Procedure for the Preparation of 2a–8a. To a solution of 2.28 mmol of the diynes **2–8** in 20 mL of degassed pentane was added dropwise 5.56 mmol of $Co_2(CO)_8$ in 60 mL of dry pentane at room temperature. After the mixture was stirred for 2 h, all of the diyne had disappeared in the solution and precipitated as a complex. To complete crystallization the mixture was cooled to −20 °C, and the solvent was filtered off. Crystallization from CH_2Cl_2 yielded between 80 and 90%. **2a**: dark-red plates, mp 200–201 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.98–3.02 (m, 8 H), 2.00–2.09 (m, 4 H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 200.4, 96.9, 32.3, 31.3; IR (pentane) ν 2095, 2042, 2033, 2011, 2000, 1991, 1980 cm^{-1}. Anal. Calcd for $C_{22}H_{12}Co_4O_{12}$: C, 37.53; H, 1.72. Found: C, 37.39; H, 1.76. **3a**: dark-violet needles, mp 103–106 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.32 (m, 4 H), 3.14–3.18 (m, 4 H), 2.01–2.10 (m, 2 H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 200.2, 97.1, 95.8, 37.0, 33.7, 28.8; IR (pentane) ν 2085, 2052, 2046, 2029, 2011 cm^{-1}. Anal. Calcd for $C_{21}H_{10}Co_4O_{12}$: C, 36.55; H, 1.46. Found: C, 36.69; H, 1.60. **4a**: dark-red plates, mp 90–93 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.02–3.53 (m br, 7 H), 1.55–2.08 (m br, 5 H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 200.5, 200.2, 200.1, 199.6, 98.2, 97.7, 37.8, 32.7, 29.6; IR (pentane) ν 2284, 2162, 2082, 2048, 2024, 2008 cm^{-1}. Anal. Calcd for $C_{22}H_{12}Co_4O_{12}$: C, 37.53; H, 1.72. Found: C, 37.77; H, 1.83. **5a**: dark-red needles, mp 88–91 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.42 (br, 4 H), 3.17 (s, 4 H), 1.79 (m, 4 H), 1.66 (m, 2 H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 26.79 (t, CH_2), 29.24 (t, CH_2), 35.66 (t, CH_2), 37.85 (t, CH_2), 97.37 (s, C), 97.73 (s, C), 200.25 (s, CO); IR (pentane) ν 2082, 2048, 2024, 2008 cm^{-1}. Anal. Calcd for $C_{23}H_{14}Co_4O_{12}$: C, 38.47; H, 1.96. Found: C, 38.60; H, 1.99. **6a**: dark-red crystals, mp 126–128 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.20 (t, 4 H, $J = 6.63$ Hz), 3.11 (s, 4 H), 2.05 (q, 2 H), 1.81 (s, 4 H), 1.55 (s, 4 H, H_2O); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 29.66 (t, CH_2), 32.03 (t, CH_2), 33.29 (t, CH_2), 35.54 (t, CH_2), 96.98 (s, C), 97.46 (s, C), 200.12 (s, CO); IR (pentane) ν 2082, 2048, 2024, 2008 cm^{-1}. Anal. Calcd for $C_{23}H_{14}Co_4O_{12}$: C, 38.47; H, 1.96. Found: C, 38.62; H, 1.92. **7a**: dark-red crystals, mp 90–92 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.13 (s br), 3.04 (s br), 1.96 (m br), 1.76 (m br), 1.62 (m br), 1.26 (br), 0.85 (br); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 200.27 (CO), 97.76 (C), 97.13 (C), 35.42 (CH_2), 34.85 (CH_2), 34.31 (CH_2), 29.69 (CH_2), 28.05 (CH_2); IR (pentane) ν 2086, 2051, 2027, 2011 cm^{-1}. Anal. Calcd for $C_{24}H_{16}Co_4O_{12}$: C, 39.37; H, 2.20. Found: C, 39.02; H, 2.28. **8a**: dark-red crystals, mp 192 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.12 (s br), 1.80 (s br), 1.53 (s br); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 200.18 (CO), 97.94 (C), 34.07 (CH_2), 29.21 (CH_2); IR (pentane) ν 2086, 2050, 2027, 2011 cm^{-1}. Anal. Calcd for $C_{24}H_{16}Co_4O_{12}$: C, 39.37; H, 2.20. Found: C, 36.54; H, 2.05.

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