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Phenylethynyl- and Phenylethenylmetacyclophanes

Derong Cao, Heinz Kolshorn and Herbert Meier*

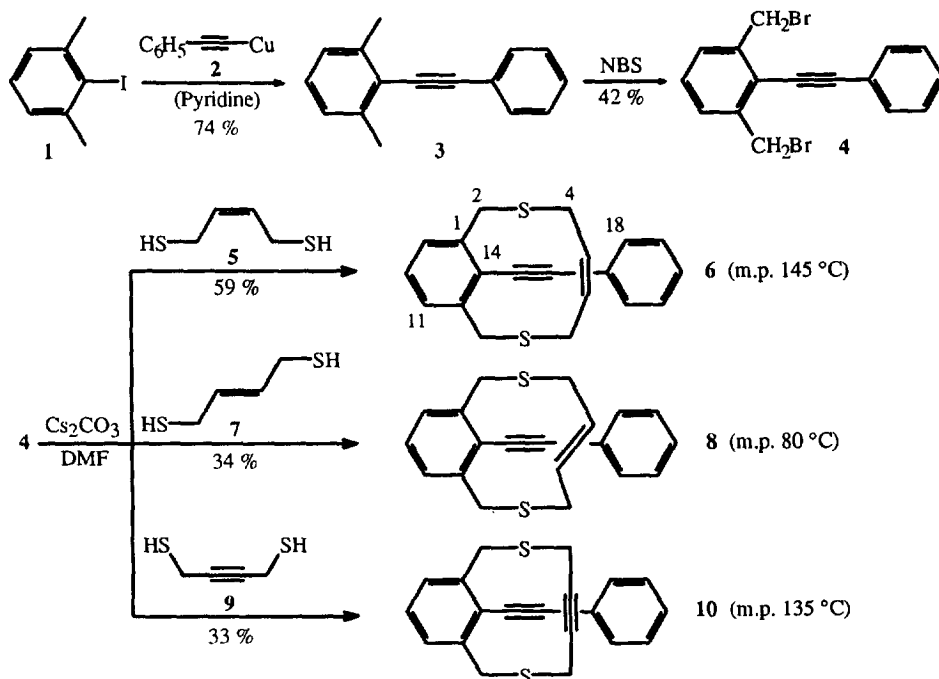
Institute of Organic Chemistry, University of Mainz, J.-J.-Becherweg 18-22

D-55099 Mainz, Germany

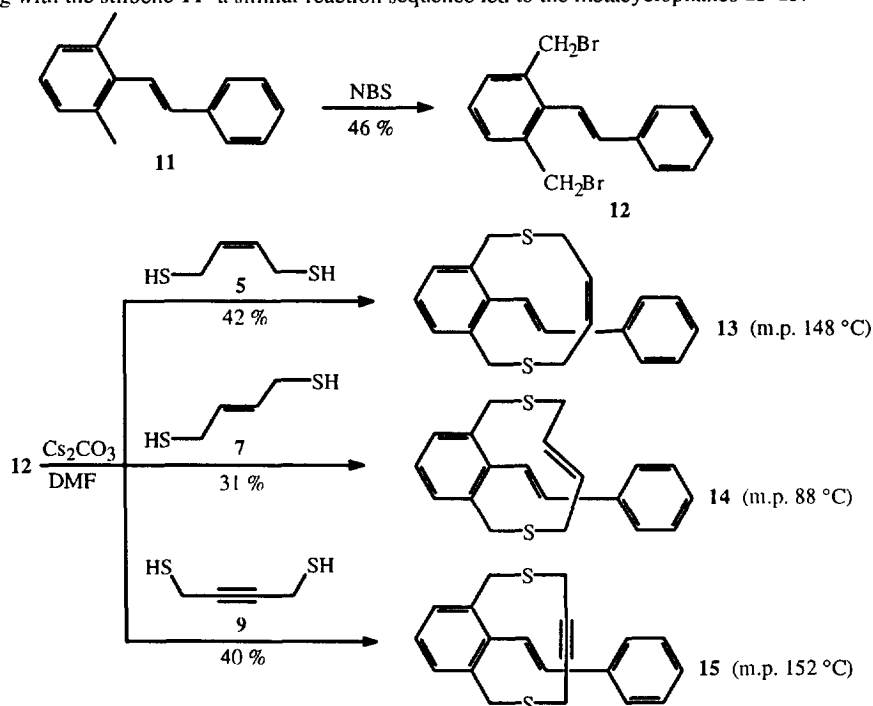
Abstract: The cyclophanes **6,8,10** and **13-15** were synthesized by cesium assisted ring closure reactions. The main interest in these systems concerns the interaction of the unsaturated bridge with the tolan and the stilbene chromophores, respectively.

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Recently we reported on [8]metacyclophanes which contain unsaturated segments in the bridge: triple bonds^{1,2} and cumulated or conjugated double bonds². The $\pi\pi$ interactions between the unsaturated carbon centres and the benzene ring can be avoided in these systems by adopting an "anti" conformation. This result prompted us to introduce phenylethynyl or 2-phenylethenyl groups in C-2 position of the bicycles. The following scheme shows the synthesis of the dithiametacyclophanes **6,8** and **10** which contain a phenylethynyl group. A CC coupling reaction of 2-iodo-1,3-dimethylbenzene (**1**) and copper phenylacetylide (**2**) yielded alkyne **3**, which was brominated to **4**. Cyclization reactions with the dithiols **5,7** and **9** furnished the attempted compounds **6,8** and **10**. Applying the cesium effect ensured reasonable yields for the formation of the 11-membered rings.



Starting with the stilbene **11**³ a similar reaction sequence led to the metacyclophanes **13-15**.



The intramolecular $\pi\pi$ interaction in the metacyclophanes **6,8,10,13,14,15** is directly connected with the molecular dynamics in these systems. Force field calculations (MMX⁴) reveal that there are several energetically close lying minima in each case. All NMR spectra indicate at room temperature a C_s symmetry (Table 1 and 2). However, some signals, particularly of the compounds **8** and **14**, which contain an (*E*)-configured double bond in the bridge, are already broadened. Low temperature measurements prove that the C_s symmetry results from the interconversion of enantiomeric C_1 species by a flip of the bridge during an undisturbed rotation of the phenylethynyl and the phenylethenyl group, respectively. The compounds **6,10,13** and **15** may also exist as C_1 conformers; nevertheless, C_s conformers have to be considered in these examples. Whereas **6** does not give any change in the ¹H and ¹³C NMR spectra on cooling to 213 K, a doubling of all signals is observed for **13**; i.e. that two C_s species are involved in the equilibrium. Obviously the rotating styryl group is sterically more discriminating than the linear phenylethynyl substituent.⁵

The ¹H and ¹³C chemical shifts of the unsaturated segments in the bridge are shifted towards higher field in comparison to the resonance of the compounds without phenylethynyl or phenylethenyl groups.^{1,2} However, more obvious hints for the interaction of the unsaturated bridges with the tolan or stilbene chromophores are given by the UV spectra (Figure 1). The long wavelength absorption maxima of **6,8** and **10** are red-shifted ($488 \leq \Delta\tilde{\nu} \leq 1177 \text{ cm}^{-1}$) compared to the basic chromophore in **3**; the intensity is lower - especially for compound **8** with the (*E*)-configured double bond in the bridge. The latter statement is also valid for compound **14**, but the effect on the absorption maxima of the stilbene systems **13-15** is less pronounced.

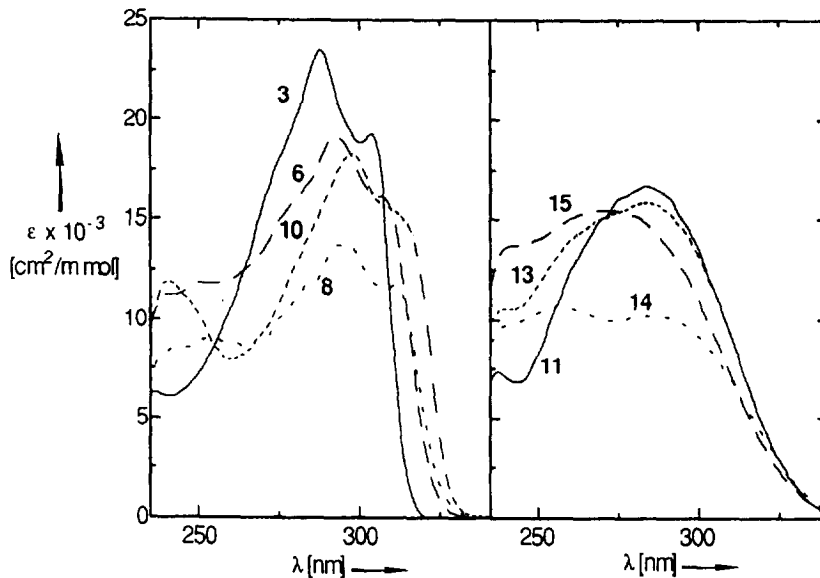


Figure 1. UV absorption spectra of the series **3,6,8,10** and the series **11,13,14,15** in CH_2Cl_2 .

In comparison to **11** the long wavelength band is rather somewhat blue-shifted, particularly for **15** ($\Delta\tilde{\nu} = 2270 \text{ cm}^{-1}$). Apparently the stilbene moiety can partly evade the $\pi\pi$ interaction by torsion. Thus the effect of the bridge on the two chromophores is different. Until now $\pi\pi$ interactions in cyclophanes were mainly observed in paracyclophanes and their styryl derivatives.⁶⁻⁸

Table 1. ^1H and ^{13}C NMR data of **6,8**, and **10** (δ values measured at room temperature in CDCl_3); the numbering illustrated in formula **6** corresponds only partly to the nomenclature

	2-H	$^2J[\text{Hz}]$	4-H	$^2J[\text{Hz}]$	5-H	11-H	12-H	18-H	19-H	20-H
6	3.54/4.66	-12.3	2.73/3.75	-15.5	4.63	7.27	7.17	7.58	7.39	7.39
8	3.76/4.49	-12.4	2.82 ^{a)} /3.15 ^{a)}		4.80 ^{a)}	7.24	7.24	7.63	7.38	7.38
10	3.90/4.51	-12.6	2.95/3.22	-15.8	---	7.20	7.26	7.61	7.35	7.35

	C-1	C-2	C-4	C-5	C-11,18,19	C-12,20	C-14,17	C-15,16
6	141.9	33.5	27.7	128.5	128.6/128.6/131.4	128.7/129.0	122.9/123.7	87.5/99.6
8	138 ^{a)}	34.0	33.6 ^{a)}	127.9	128.5/129.3/131.4	128.5/129.3	123.4/127.2	86.9/98.7
10	138.6	36.0	19.9	78.8	128.4/129.2/131.4	128.1/128.4	123.6/126.4	86.5/99.4

a) broad signals

Table 2. ^1H and ^{13}C NMR data of **13**, **14**, and **15** (δ values measured at room temperature in CDCl_3)

	2-H	4-H	5-H	11-H	12-H	15-H	16-H	18-H	19-H	20-H
	$^2\text{J}[\text{Hz}]$	$^2\text{J}[\text{Hz}]$				$^3\text{J}[\text{Hz}]$				
13	3.62	2.48 ^{a)}	5.01 ^{a)}	7.30	7.20	6.38	7.43	7.50	7.40	7.30
	4.34	2.85 ^{a)}				16.4				
	-12.1	-14.3								
14	3.78	2.82 ^{a)}	4.71 ^{a)}	7.23	7.18	6.50	7.79	7.58	7.41	7.32
	4.13	3.07 ^{a)}				16.5				
	-12.9	-14.8								
15	3.82	2.94	---	7.13	7.19	6.58	8.00	7.58	7.39	7.29
	4.19	3.05				16.6				
	-12.8	-15.7								
	C-1	C-2	C-4	C-5	C-11, 18, 19		C-12, 15, 16, 20		C-14, 17	
13	136.0	31.6	26.2	136.0	126.5		126.4	127.5	136.9	
					128.7		128.0	129.3	139.5	
					129.5					
14	134.8	34.3	32.9	135.2	126.5		126.4	127.5	137.5	
					128.6		127.5	127.7	141.2	
					129.8					
15	134.9	35.9	19.4	77.8	126.6		127.0	127.1	137.5	
					128.7		127.6	132.7	142.1	
					129.8					

a) broad signals

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