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Phenylethynyl- and Phenylethenylmetacyclophanes

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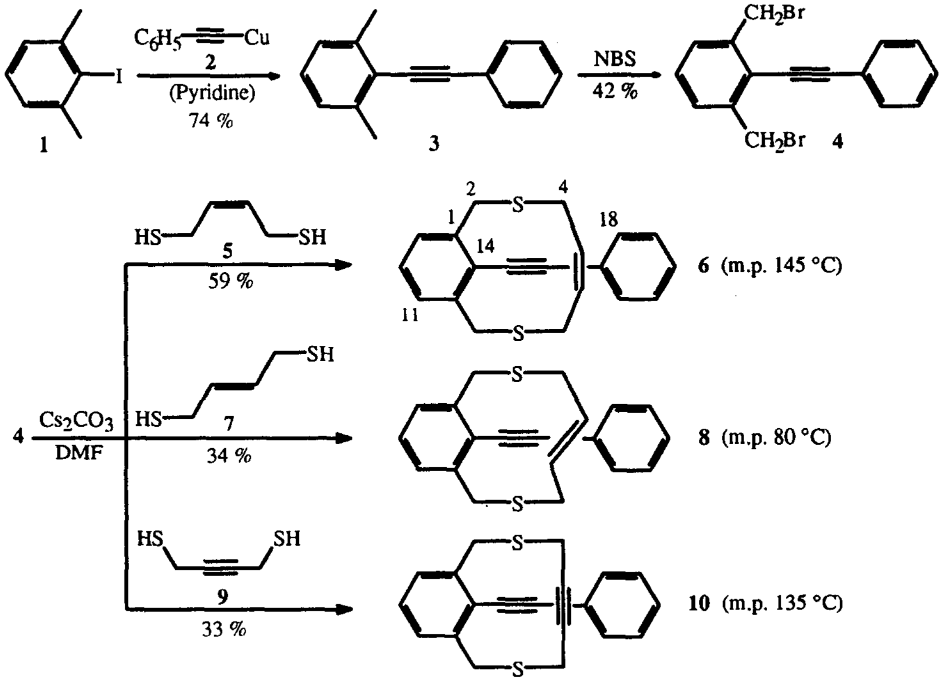
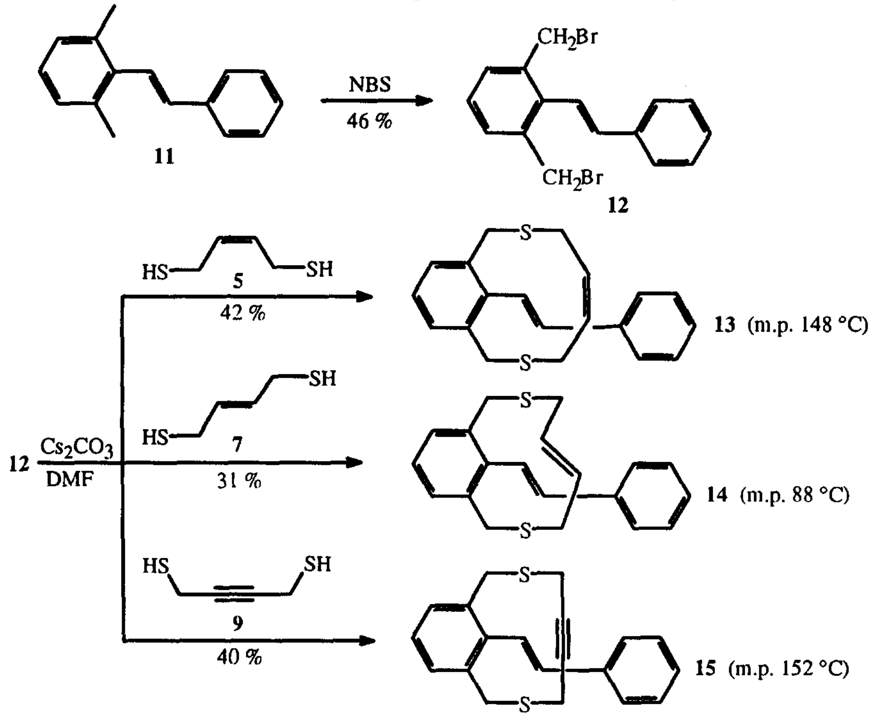
Abstract: The cyclophanes **6,8,10** and **13-15** were synthesized by cesium assisted ring closure reactions. The main interest in these systems concerns the interaction of the unsaturated bridge with the tolan and the stilbene chromophores, respectively.

Recently we reported on [8]metacyclophanes which contain unsaturated segments in the bridge: triple bonds[1,2] and cumulated or conjugated double bonds[2]. 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 ππ interaction in the metacyclophanes **6**,**8**,**10**,**13**,**14**,**15** is directly connected with the molecular dynamics in these systems. Force field calculations (MMX[4]) 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*)-configurated 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 ^{13}C 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 ^{13}C 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 ($488 \leq \Delta\tilde{\nu} \leq 1177$ cm^{-1}) compared to the basic chromophore in **3**; the intensity is lower - especially for compound **8** with the (*E*)-configurated 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.

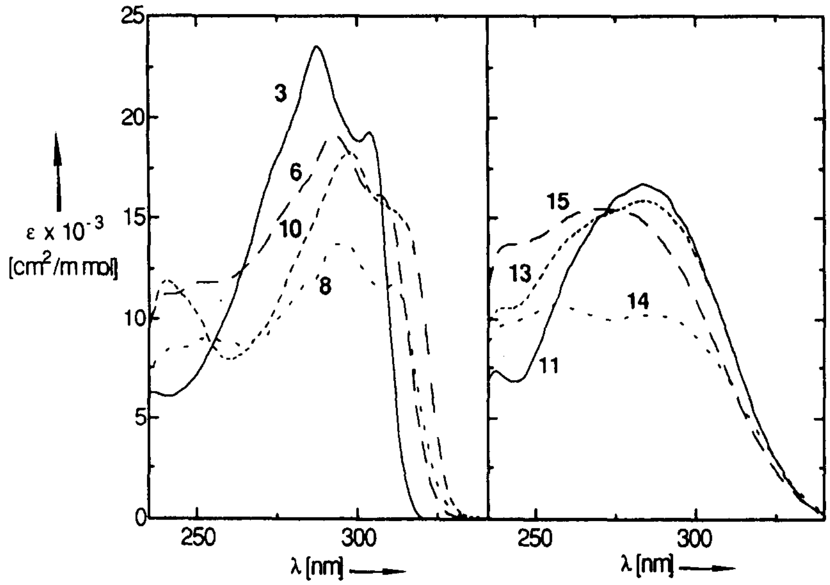


Figure 1. UV absorption spectra of the series **3,6,8,10** and the series **11,13,14,15** in CH_2Cl_2.

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

Table 1. ^{1}H 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[Hz]	4-H	^2J[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. ^{1}H 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}J[Hz]	^{2}J[Hz]				^{3}J[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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