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1,*x*-Elimination Reactions: Extending the Limits of a Classical Organic Reaction

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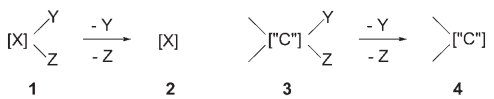
Dedicated to Professor Steen Steenken on the occasion of his 70th birthday

Abstract: α,ω-Dibromo derivatives in which the two terminal carbon atom are separated by an unsaturated spacer unit ("π spacer") undergo 1,*x*-elimination reactions (with $x = 6$, 8, 10, and 14), using Mori's reagent (nBu$_3$SnSiMe$_3$/CsF). The resulting cumulenic intermediates cyclodimerize in a subsequent step yielding novel macrocyclic acetylenic and bridged aromatic compounds (cyclophanes). Thus 1,6-eliminations were carried out with dibromide **17** to yield 1,3,7,9-cyclododecatetrayne (**20**) and with benzylbromide **24** to provide cyclophanes **26** and **27**. By 1,8-eliminations the 16-membered macrocycle **33** could be prepared from enediyne **31**, the benzannelated 1,5-cyclooctadiyne **41** from dibromide **38**, and a mixture of cyclophanes **45** and **46** from the precursor **43**. 1,10-Eliminations were carried out successfully with dibromides **47**, **50**, and **53** yielding the corresponding unsaturated cyclophanes ("cyclophynes") **49**, **52**, and **55**. The influence of the solvent on the cyclodimerization **47**→**49** was investigated, with acetonitrile providing the highest yields. The heterophanes **59a** and **b** were obtained by 1,10-elimination of the precursor dibromides **57a** and **b**, and in an elimination experiment involving a 1:1 mixture of the dibromides **50** and **57b** the "mixed dimer" **60** was isolated, besides the homodimers **52** and **59b**. The method reached its limits with the 1,14-elimination of **68**, **70**, and **74** providing the cyclophanes **69**, **71**, and **75** in varying amounts. Two final debrominations with **76** and **77**, which in principle could undergo 1,16- and 1,20-eliminations reactions, respectively, failed. The structures of the new cyclophanes **49**, **50**, **59a**, and **59b** were established by X-ray structural analysis; all other structure assignments rest on the usual spectroscopic and analytical data.

Keywords: cumulenes · cycloaddition · cyclophanes · dimerization · elimination

Introduction

Some general remarks on elimination reactions: Together with pericyclic reactions, substitutions and redox reactions, elimination reactions—and their converse: additions—belong to the elementary processes of chemistry. In a more general form they may be expressed by the transformation of substrate **1** into **2** (Scheme 1), in which two groups Y and Z are removed from a "carrier" X. X can contain or consist of carbon and/or hetero atoms, Y and Z may be simple atoms (e.g. hydrogen) or complex functional groups. Numerous mechanisms are possible for the transformation, and it may be induced with very different reagents and under a wide variety of conditions. Y and Z may be bonded to one and the same atom or to different positions of the substrate. If X is carbon, the **1**→**2** transformation translates into the conversion of **3** into **4**, in which "C" symbolizes a general organic fragment, which could be called a spacer, and can consist of 1, 2 …, n carbon atoms (C_1-, C_2- …, C_n spacer).



Scheme 1. An elimination reaction in general form.

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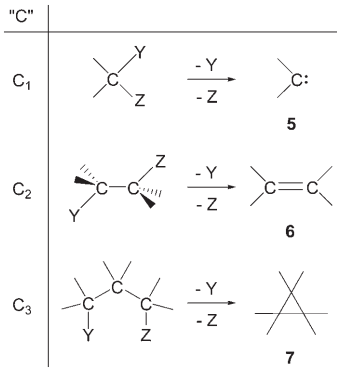
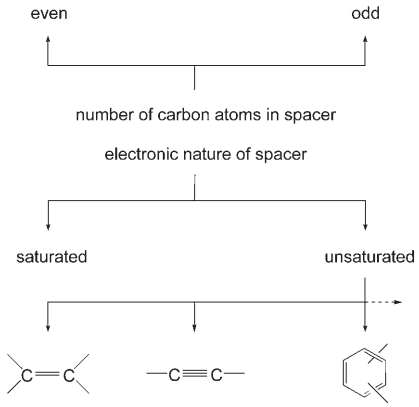
Scheme 2 shows these considerations in greater detail and summarizes the typical text book elimination reactions (without taking their different mechanisms into account), that is, α-elimination to carbenes **5** (the bonds from C_1 may lead to the same atom as in the decomposition of azo compounds), β elimination to olefins **6** and γ elimination to cyclopropane and its derivatives **7**.



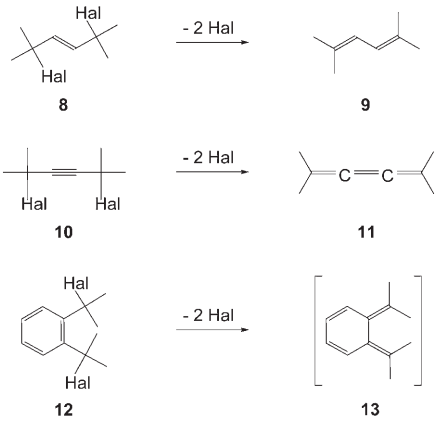
Scheme 2. The classical textbook eliminations.

The main purpose of the present paper consists in demonstrating how the variation of the length and the electronic nature of the spacer element "C" affects product formation. Excluding hetero atoms the spacer unit can either contain an odd or an even number of carbon atoms, and the spacer can be saturated or unsaturated (Scheme 3), the most important unsaturated "separating units" being the double and the triple bond, and the benzene ring.



Scheme 3. A general Scheme for elimination reactions.

As a practical illustration the three well known examples in Scheme 4 may be cited, with halide substituents as leaving groups in all cases. Whereas reductive elimination of 1,4-dihalo-2-butenes **8** furnishes 1,3-butadienes **9**,[1] change of the C_2 spacer to an acetylene moiety (1,4-dihalo-2-butynes, **10**) results in the formation of [3]cumulene **11**.[2]

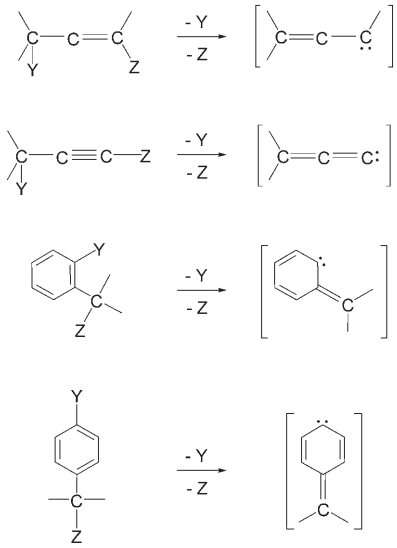


Scheme 4. A selection of known 1,4-elimination reactions.

If a 1,2-disubstituted benzene ring is inserted between the two leaving group carrying carbon atoms, as in the *o*-xylyl-dihalide **12**, the elimination leads to *o*-xylylenes (*o*-quinodimethanes), **13**, long known as very useful diene components for the construction of complex natural[3] and non-natural carbon frameworks.[4]

The unsaturated spacers in **8**, **10**, and **12** can easily be extended by combining them with unsaturated units of either the same or of a different type, thus creating a diene, diyne, enyne, etc. separating unit. Combination with aromatic units could lead to diethynylbenzene or ethynylvinylbenzene spacers, for example. If aromatic or heteroaromatic subunits are employed, though, they must be connected in *ortho*- (1,2-) or *para*- (1,4-) fashion. Any *meta*-substitution pattern results in the formation of non-Kekulé structures[5] after elimination.

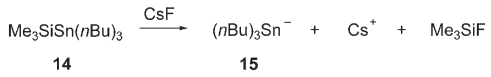
A selection of examples with odd unsaturated spacers is finally listed in Scheme 5; substrates of this type are not discussed in the present publication, but certainly also deserve more attention than they have hitherto attracted.



Scheme 5. Several elimination reactions involving odd spacers.

Results and Discussion

Before the first 1,x-elimination reactions were carried out, we had to decide on both the leaving groups Y and Z to be used, and on the elimination reagent and conditions. Because dibromides have often been employed in 1,4-eliminations of the type presented in Scheme 4 (above), we also decided to concentrate on substrates with Y = Z = Br. Usually these are easy to prepare from their corresponding allylic, propargylic or benzylic alcohols. As far as the actual elimination is concerned, the conditions were more restrictive. Not only are all of the expected products (see below) highly unsaturated, but the intermediates leading to them contain an even higher number of π electrons, and are hence expected to be highly reactive; therefore, a method was needed in which room temperature should not be significantly exceeded. For example, the Hofmann elimination, which has been used successfully in several vinylogous eliminations reactions,[6] was disqualified from the very beginning because it has to be carried out in refluxing toluene. A promising method, however, is the elimination developed by Mori and co-workers,[7] which employs the tributylstannyl anion (**15**), generated in situ by cesium fluoride treatment of tributyl(trimethylsilyl)stannane (**14**, Scheme 6).



Scheme 6. Mori's reagent.

The Japanese group has used this commercially available reagent successfully for numerous 1,2- and 1,4-eliminations, including the preparation of dehydrobenzene, *o*-xylylene (**13**) and other highly unsaturated hydrocarbons and intermediates.[8] In our hands this elimination reagent also turned out to be the reagent of choice.

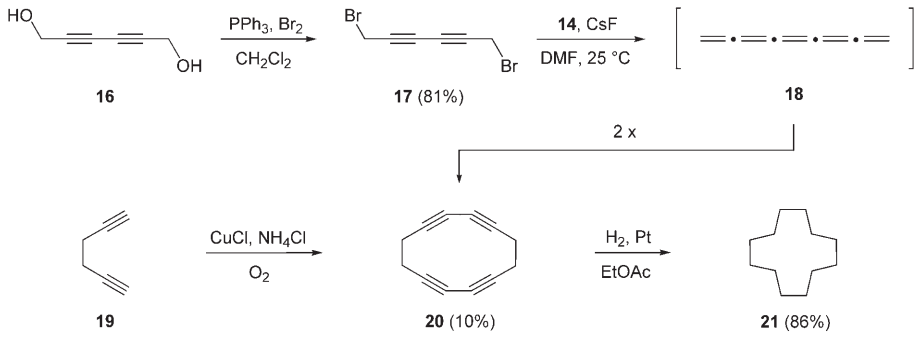
1,6-Eliminations: As a first example of a 1,x-elimination 1,6-dibromo-2,4-hexadiyne (**17**), prepared from the corresponding diol **16** by treatment with triphenylphosphine/bromine in dichloromethane, was subjected to the above treatment with Mori's reagent in DMF at room temperature. We were pleased to isolate a small amount (10%) of 1,3,7,9-cyclododecatetrayne (**20**) from the reaction mixture. Although this hydrocarbon is unstable, it can be purified by chromatography on silica gel and obtained in pure form as a colorless solid, which quickly turns brown (Scheme 7).

The tetrayne was characterized by its NMR spectra and its complete hydrogenation to cyclododecane (**21**). Interestingly, **20** has been prepared previously by Sondheimer and co-workers in the course of their studies on the preparation of cyclic oligomers of 1,5-hexadiyne (**19**),[9,10] which, in turn, served as precursors for their famous higher annulenes. Tetraacetylene **20** could be obtained in small amounts (ca. 10%) by Glaser coupling of **19**, but apparently was never isolated in pure form.

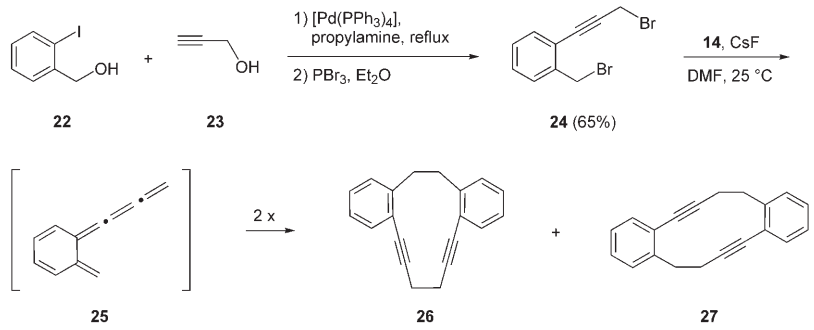
As far as the mechanism of formation of **20** is concerned, the simplest route involves debromination of **17** to provide 1,2,3,4,5-pentahexaene (**18**), which subsequently dimerizes to **20**. There are no experimental hints for the formation of the presumably very reactive (and unknown)[5] cumulene; its tetramethyl derivative, though, has been described in the literature[11] and has been shown to undergo dimerization to the octamethyl derivative of **20**.[12,13] Alternatively, the cyclodimerization of **17** could be initiated by a halogen–metal exchange with **15**, forming an organocesium intermediate that could then couple with a second molecule of **17**. Repetition of these steps on the resulting α,ω-dibromide would ultimately lead to **20**. Whether these two pathways compete (or occur simultaneously) can only be established by detailed mechanistic experiments. Such intermediate bromides could not be isolated in any of our experiments so far.

A 1,6-elimination involving an aromatic spacer element was carried out with the dibromide **24**, readily available by Sonogashira coupling of 2-iodobenzylalcohol (**22**) with propargyl alcohol (**23**), followed by bromination with phosphorus tribromide (total yield 65%, Scheme 8).

Debromination with **14**/CsF under the above conditions furnished a complex product mixture, the components of which could only be partially separated. In the end (after several separation cycles by radial chromatography on silica with petrol ether) only one of the hydrocarbon products could be isolated in pure form in poor yield (2.2%): the [2.6]orthocyclophane **26**. Its structure assignment follows from its spectroscopic and analytical data (see Experimental Section), in particularly from the two singlets for methylene protons at $\delta = 2.75$ ppm (4H, propargylic hydrogen atoms) and 3.07 (4H, benzylic hydrogen atoms), respectively. The isomer of **26**, the [4.4]orthocyclophane **27**, could not be freed from impurities; nevertheless, two triplets ($J = 7.1$ Hz) between $\delta = 2.5$–3.5 ppm are indicative of an absence of a plane of symmetry, and hence coupling between two methyl-



Scheme 7. A 1,6-elimination leading to non-aromatic cyclic hydrocarbons.



Scheme 8. A 1,6-elimintion leading to aromatic cyclic hydrocarbons (cyclophanes).

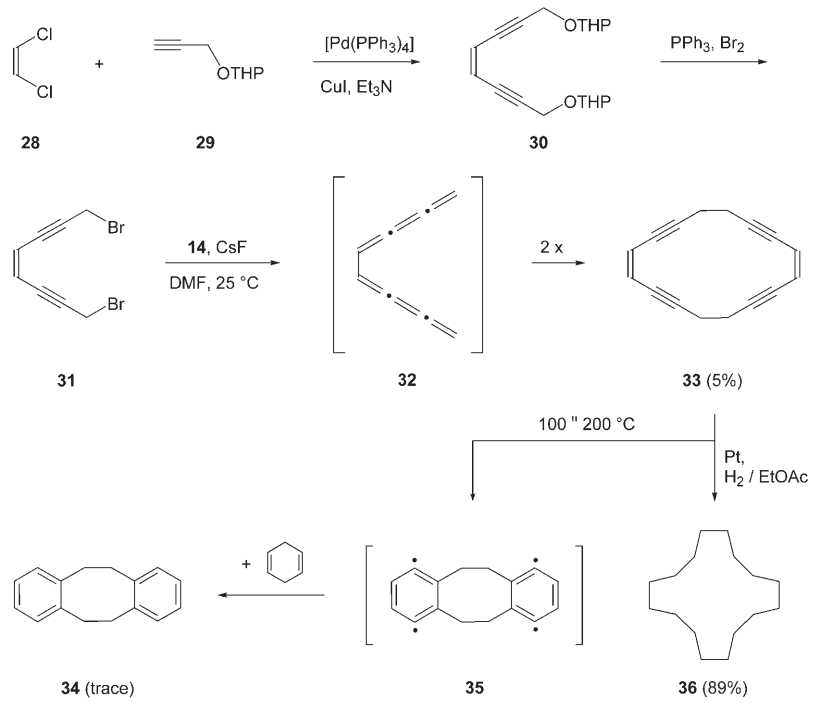
ene groups. The two isomers, which can be regarded as the head-to-head and the head-to-tail dimers of the cumulenic intermediate **25**, are produced in approximately equal amounts (^{1}H NMR analysis).

1,8-Eliminations: The first 1,8-elimination was carried out with the acyclic precursor **31**, obtained from (*Z*)-1,2-dichloroethene (**28**) according to a procedure by König et al. (Scheme 9).[14]

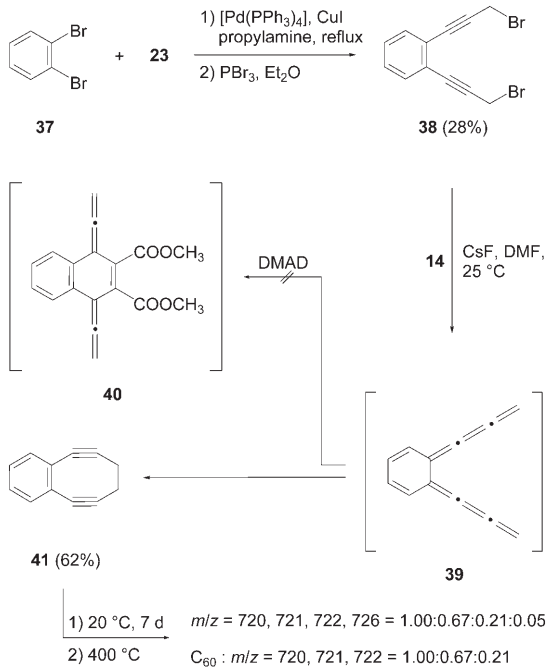
Thus **28** was coupled to the protected propargyl alcohol **29**; the resulting bis-THP-ether **30** yielded the dibromide **31** directly on treatment with triphenylphosphine/bromine. Mori debromination as described above provided a complex and unstable product mixture from which we could isolate cyclohexadeca-1,9-dien-3,7,11,15-tetrayne (**33**) in approximately 5% yield by silica gel chromatography. On removal of residual solvent traces, **33** started to decompose; however, the dimer is stable in dilute solution at low temperatures (−25 °C). The structure assignment of the hydrocarbon, for which we propose the bis-cumulene **32** as a precursor, rests on its mass spectrum (*m*/*z* 204), its ^{1}H NMR spectrum (singlets at $\delta = 5.95$ and 2.58, respectively), and its catalytic hydrogenation to cyclohexadecane (**36**). With its double enediyne structure, the hydrocarbon immediately suggests itself for a double Bergman cyclization.[15] The appropriate experiment (heating of **33** in benzene from 100 to 200 °C in the presence of a huge excess of 1,4-cyclohexadiene) proceeded inconclusively: because of partial peak overlap in the GC/MS spectrum of the pyrolysate, the signals of the expected product **34** could not be assigned unambiguously. Furthermore, lack of material precluded enrichment of the [2.2]orthocyclophane.

An aromatic version of the elimination of **31** was next tried with 1,2-bis-(3-bromo-1-propynyl)benzene (**38**), prepared by coupling *o*-dibromobenzene (**37**) with **23** followed by bromination with phosphorus tribromide; the overall yield of 28% is only mediocre in this case. On treatment of **38** with **14**/CsF no dimer was isolated but instead the cyclized product **40**, this time in excellent yield (62%). Evidently intermediate **39**—if formed at all—prefers ring closure to cycloisomer **41** over dimerization. Since *ortho*-xylylenes have been used as dienes in countless cycloadditions[16] we repeated the experiment in the presence of dimethyl acetylene dicarboxylate (DMAD) as a trapping agent. The expected product **40** or products derived there from (dimers?) were, however, not obtained (Scheme 10).

Although diyne **41** is stable in ether or toluene solution, its crystals, obtained by recrystallization from pentane, rapidly change color from colorless to brown, then black, upon standing, not only in air but also under nitrogen or polyfluorinated silicon oil. If **41** is left standing in air for one week and the resulting product mixture subsequently admitted to the mass spectrometer (temperature of the inlet system up to 400 °C), a mass spectrum is registered with peaks at *m*/*z* 720, 721, and 722 in a ratio of 1:0.67:0.21, practically identical with the signals of C_{60} in that spectral region.[17]



Scheme 9. A 1,8-elimination leading to non-aromatic cyclic hydrocarbons.



Scheme 10. A 1,8-elimination providing an *ortho*-cyclophane.

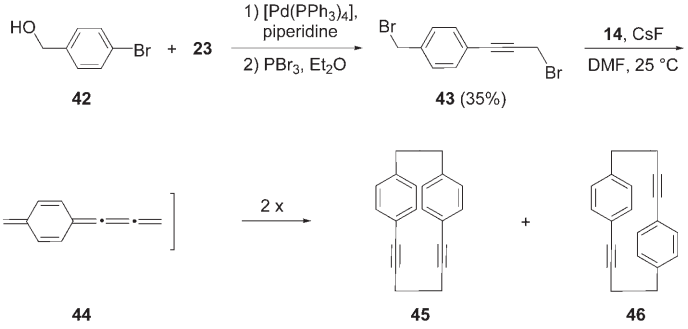
The isomer of **24**, 1-bromomethyl-4-(3-bromo-1-propynyl)-benzene (**43**), prepared from the benzyl alcohol **42** and **23** by Pd-mediated coupling and treatment of the resulting diol with PBr_3, is also structurally preconditioned to undergo a 1,8-elimination (Scheme 11).

Indeed, on treatment with **14**/CsF under the usual conditions, a 1:1 mixture of the two isomeric cyclophanes **45** and **46** is obtained in a combined yield of 4.5%. All attempts to separate the two isomers failed. Still, they can be readily distinguished by the signals for the methylene protons in their ^{1}H NMR spectra, which are registered as singlets for the head-to-head dimer of **44**, hydrocarbon **45**, and as triplets for the head-to-tail dimer **46** (see Experimental Section). Since these signals are well separated, they can also be used to determine the ratio of the two regioisomers, which is approximately 1:1, that is, there is no selectivity in the dimerization of **44**.

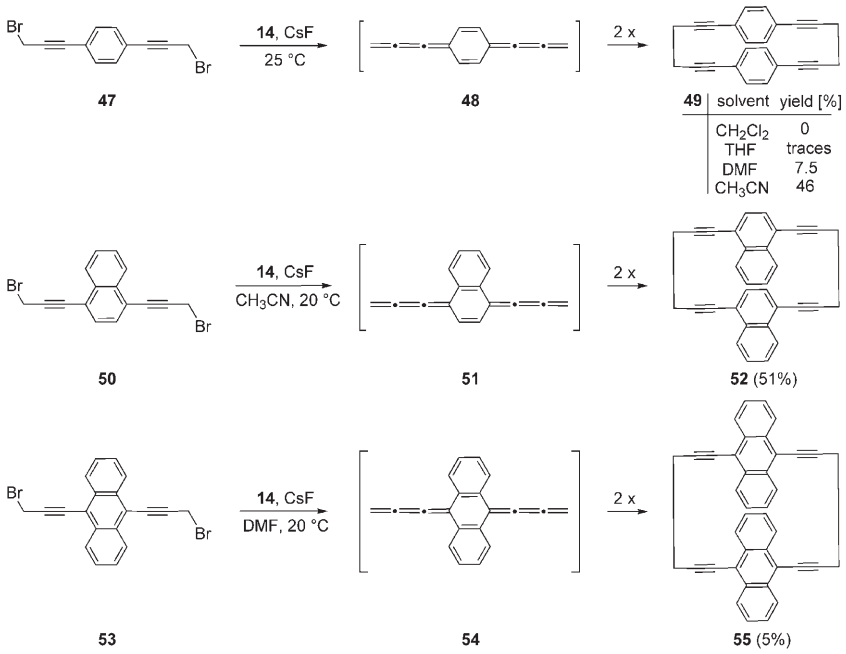
1,10-Eliminations: Two types of 1,10-eliminations were carried out: in the first type an aromatic ring system was part of the spacer unit, whereas in the second category heteroaromatics were included. The two types of eliminations/dimerizations will be discussed in turn.

The chain-extended dibromides **47**, **50**, and **53** were prepared from the corresponding aromatic dihalides by the methods discussed above; in all cases the overall yields for the individual steps were between 80 and 95% (Scheme 12).

The Mori elimination took place as expected and the cyclophanes **49**, **52**, and **55** were obtained in variable yields. The structures of these hydrocarbon were derived from their spectroscopic and analytical data (see Experimental Section); for **49** and **52**, single crystals X-ray structural investigations could be performed (see below). Cyclophane **49** was used as a model system for optimisation, since it is the most readily available macrocycle studied in this series; it is also more stable than many of its analogues. In particular, we varied the solvent used for the debromination step. For the examples described in the literature DMF is usually employed.[7,8] As shown in Scheme 12, it was successful in our example as well. In dichloromethane, no dimerization of **47** took place, and in THF only traces of the [6.6]paracy-



Scheme 11. Paracyclophandiynes by a 1,8-elimination.



Scheme 12. Carbocyclic paracyclophanes by a 1,10-elimination.

clophane tetrayne were obtained. However, when we changed the solvent to acetonitrile, **49** was produced in 46% yield, allowing the preparation of 25 mg batches per experiment. The reason for this drastic increase in yield is unclear at present. It was observed that **14**/CsF forms two phases with acetonitrile, and possibly the cumulenic intermediate **48** migrates into the acetonitrile phase, where, because of concentration effects, intramolecular dimerization is preferred over a side product producing intermolecular oligomerization. Interestingly, in THF we could isolate 1-(3-fluoro-1-propynyl)-4-(1-propnyl)benzene as a side product (5%), a formal 1,10-addition product of HF to **48**. Unfortunately the solvent effect was discovered at a late stage of this investigation, so that most debrominations were performed in DMF.

The X-ray structure of **49** has already been briefly discussed in a short communication describing its formation from **47**.[18] The compound displays two independent molecules, each with crystallographic inversion symmetry (Figure 1) and thus with exactly parallel six-membered rings. The molecular conformations are however different; in molecule 1 the rings are eclipsed (torsion angle C2-C1-C12#1-C11#1 9.9(8)°) with an intercentroid distance of 3.84 Å, but in molecule 2 the larger torsion angle of 41.9(5)° causes the rings to be laterally displaced, with an intercentroid distance of 4.00 Å but a perpendicular separation of only 3.43 Å. The angle between the ring plane and the plane of the immediate substituents in the phane bridges (C3, C10 and equivalents) is 89.1(1)° in molecule 1 but only 55.3(1)° in molecule 2. It is noteworthy that, given the inversion symmetry, this interplanar angle and the torsion angle about the single bond are the only real degrees of freedom in the molecule. The molecular strain is seen not in any non-planarity of the six-membered rings (< 0.02 Å) but rather in the displacement of the substituents out of the ring planes (by 0.21–0.28 Å) and the distorted "linear" bond angles of 169–172° (av. 170.2°) at the triple bond systems.

The main feature of the packing of **49** is a C-H···π interaction from C12–H12B to the centroid of the ring C4′–C9′, with H···Cent 2.82 Å (C–H normalised to 1.08 Å), angle 144°, operator $x,1+y,z$.

A surprising result was also noted in the reductive cyclization of the naphthalene derivative **50**. Not only did the dimerization take place with a surprising yield of 51%, but it provided, as shown by X-ray analysis, one isomer only: the *syn*-configured hydrocarbon **52**. Intuitively one would have predicted the preferred production of the *anti*-isomer, even more so since in the synthesis of the parent system [2.2]-(1,4)naphthalenophane this diastereomer is always produced preferentially[19] or exclusively.[20]

The structure of compound **52** is not of high quality; despite low temperature measurements, the displacement parameters are high, especially around the single bonds of the phane bridges, and libration effects are severe. Combined with the effects of the non-centrosymmetric space group, this makes the data weak, and results should be interpreted with caution. Nevertheless, the unexpected *syn* configuration (Figure 2) is unequivocally established. There is no imposed

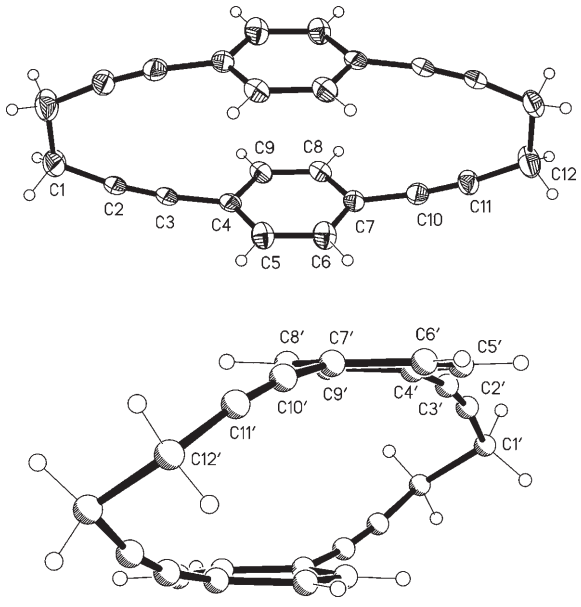


Figure 1. Structure of compound **49** in the crystal. Top: molecule 1; ellipsoids represent 30% probability levels. Bottom: molecule 2, arbitrary radii. Only the asymmetric unit is numbered. Dimensions at the triple bond systems [Å, °; values for two molecules]: C2–C3 1.189(5), 1.186(6), C10–C11 1.176(5), 1.192(5), C1-C2-C3 169.6, 169.1, C2-C3-C4 172.0, 170.4, C7-C10-C11 170.4, 169.8, C10-C11-C12 169.9, 170.7 (all esd's 0.5°).

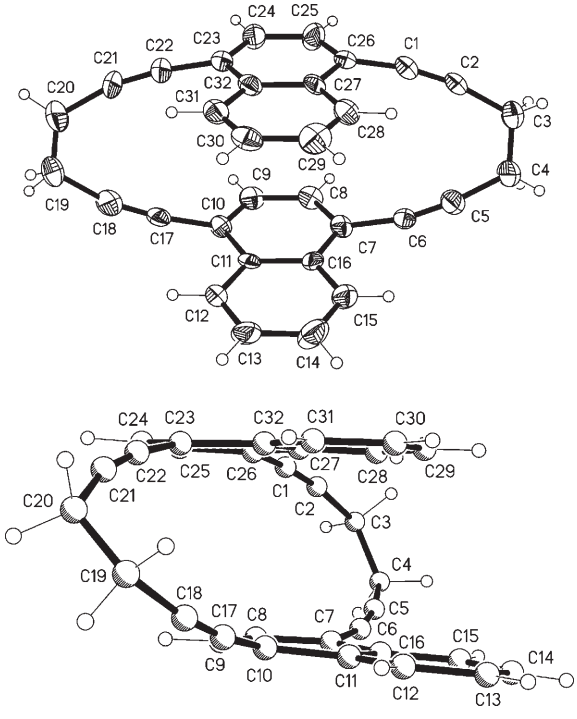


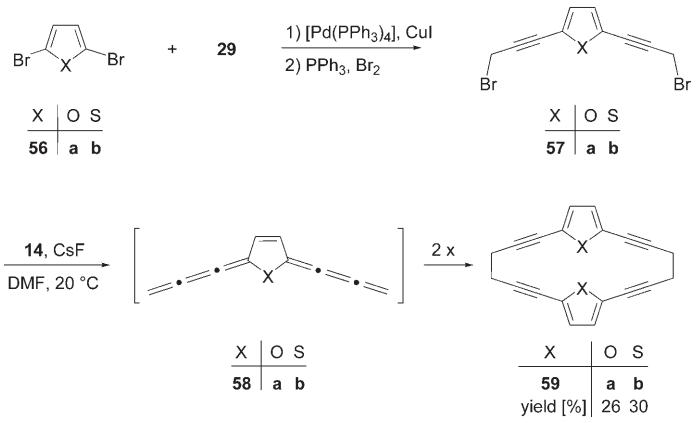
Figure 2. Structure of compound **52** in the crystal, seen from two alternative view directions. Ellipsoids represent 30% probability levels. Dimensions at the triple bond systems [Å, °]: C1–C2 1.193(13), C5–C6 1.168(12), C17–C18 1.176(12), C21–C22 1.184(13), C2-C1-C26 169.2(11), C1-C2-C3 169.0(11), C4-C5-C6 170.7(13), C5-C6-C7 167.9(10), C10-C17-C18 172.3(10), C17-C18-C19 167.0(11), C20-C21-C22 166.5(13), C21-C22-C23 172.4(11).

symmetry, but the naphthalene ring systems are approximately parallel (interplanar angle 4.1(4)°); they are mutually displaced such that the phane-substituted ring C7,8,9,10,11,16 overlaps with the ring C27–C32, with an intercentroid distance of 3.55 Å. The torsion angles about the single bonds are −5(2)° about C3-C4 and −24(2)° about C19−C20 (but see the above caveat). The angles between the naphthalene ring planes and the substituent plane (C1,6,17,22) are 56.6(2) and 60.6(2)°. The substituent atoms are displaced from the ring planes by 0.22–0.28 Å, and the triple bond angles lie in the range 166–173° (av. 169.4°). The packing involves no noteworthy contacts.

The other analytical and spectroscopic data confirm the structure assignment of **52** (see Experimental Section).

The formation of the anthracenophane **55** from dibromide **53** took place as expected (in DMF, Scheme 12). However, this dimer is chemically extremely sensitive. The presence of air is especially detrimental, and the purification of **55** by column chromatography was only successful if both the silica gel and the eluents had been degassed prior to use. Even then the column material turned black during chromatography, and the change to flash vacuum chromatography and coarser silica gel led to no real improvement. From an oxygen-free solution of **55** in $CDCl_3$, yellow-green crystals precipitated in the cold. However, on contact with air and/or in the presence of daylight these were converted into insoluble, black material. [4+4]Cycloadditions of [2.2]anthracenophane have been reported in the literature, and possibly comparable reactions also take place here.[21]

The heterocyclic bis-propargylic bromides **57a** and **b** were prepared by coupling 2,5-dibromofuran (**56a**) and its thiophene analogue **56b** with the protected propargyl alcohol **29** and treating the resulting bis-THP ethers with triphenylphosphine and bromine; in both cases the total yields were in the 60–70% range (Scheme 13). Although the corresponding *N*-methyl pyrrol bis-ether could be prepared, its conversion to the dibromide failed. It should be pointed out that some of these *intermediates could be* ***toxic***; for example, when small amounts of **56a** were inhaled during the preparative work, nausea immediately set in.



Scheme 13. Heteroaromatic paracyclophanes by a 1,10-elimination.

Debromination of **57a** and **b** furnished the heterophanes **59a** and **b** in acceptable yield, although the reaction was carried out in DMF. Again, we postulate the formation of cumulenes (**58a** and **b**) as reactive intermediates. Both dimers (for the spectroscopic data see the experimental section) were stable enough to be recrystallized, allowing the preparation of single crystals suitable for X-ray structural analysis (see below). The two heterophanes can be kept under inert gas for several months at room temperature; however, when exposed to air the surface of the crystals turns brown within minutes and black on extended oxygen contact.

The furan derivative **59a** displays crystallographic inversion symmetry (Figure 3) and the rings are thus exactly parallel. The torsion angle of 48.9(2)° about C5−C6 leads to an extreme lateral displacement of the rings (intercentroid distance 5.98 Å). In contrast to the previous two structures, in which the ring systems subtended large angles to the plane of their four immediate substituents, the furan rings lie approximately parallel to the plane of C3, C8 and their equivalents (interplanar angle 10.4(1)°). The intramolecular O···O distance is 3.645(2) Å. The geometrical requirements of the five-membered rings are significantly different from those of the six-membered rings in the two previous structures; the vectors corresponding to an extension of the substituent bonds (here C8−C9 and C2#1-C3#1) subtend an angle of 55° rather than being approximately parallel to each other. It seems that this is sufficient to relieve the worst of the strain seen in **49** and **52**; the ring substituents lie only 0.03–0.06 Å out of the ring plane, and the triple bond angles are almost ideally linear at 176.3–177.3°. There are no exceptional intermolecular contacts.

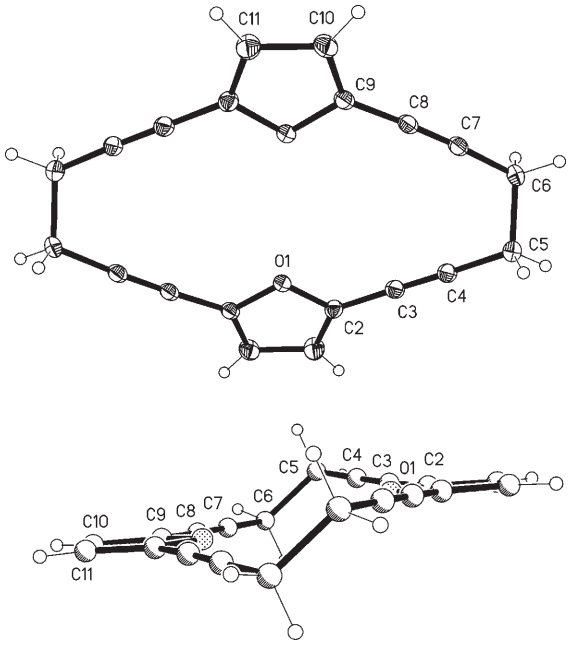


Figure 3. Structure of compound **59a** in the crystal, seen from two alternative view directions. Ellipsoids represent 30% probability levels. Only the asymmetric unit is numbered. Dimensions at the triple bond systems [Å, °]: C3−C4 1.193(2), C7−C8 1.192(2), C2-C3-C4 176.34(16), C3-C4-C5 176.96(16), C6-C7-C8 177.06(15), C7-C8-C9 177.30(15).

Having rationalised the structure of **59a** to some extent, it is disappointing that the structure of **59b** is so irregular and does not conform to the same principles. The molecule (Figure 4) has no imposed symmetry and the interplanar

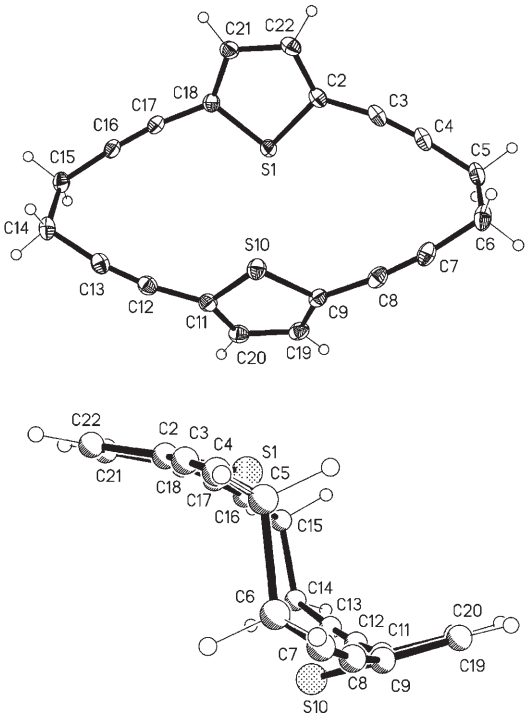
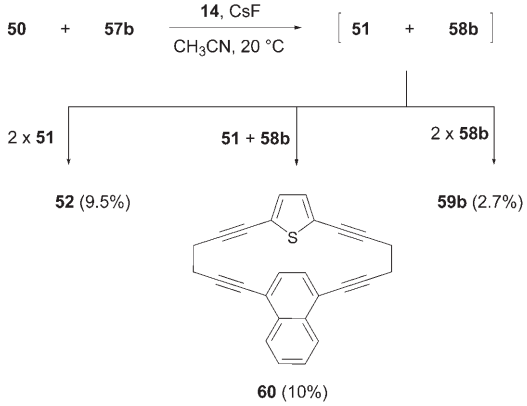


Figure 4. Structure of compound **59b** in the crystal, seen from two alternative view directions. Ellipsoids represent 30% probability levels. Dimensions at the triple bond systems [Å, °]: C3–C4 1.188(3), C7–C8 1.191(3), C12–C13 1.185(3), C16-C17 1.195(3), C2-C3-C4 169.5(2), C3-C4-C5 172.6(2), C6-C7-C8 170.8(2), C7-C8-C9 172.6(2), C11-C12-C13 171.0(2), C12-C13-C14 171.4(2), C15-C16-C17 174.7(2), C16-C17-C18 172.4(2).

angle between the thiophene rings is 25.5(1)°; the intercentroid distance is 5.00 Å and the intramolecular S···S distance is 3.4966(5) Å. The torsion angles about C5–C6 and C14–C15 are 52.5(3) and −49.0(3)° respectively. The intervector angles C2–C3/C17–C18 and C8–C9/C11–C12 are both 38° (appreciably less than in **59a**). In other respects the two rings differ considerably. For the ring based on S1, the substituents C3 and C17 lie only 0.08 and 0.11 Å out of the ring plane and the interplanar angle to the plane of all four substituent atoms (C3,8,12,17) is 39.9(1)°. For the ring based on S10, the corresponding distances are 0.21, 0.28 Å for C8 and C12, and the corresponding angle is 65.4(1)°. The triple bond angles of 169.5–174.7° (av. 171.9°) show some strain. It is possible that the following intermolecular contacts may be associated with the irregularities: C20-H20···Cent(S1-ring) with H···Cent 2.70, angle 139°, operator $^1/_2-x,^1/_2+y,z$; C6-H6B···S1 with H···S 2.71, angle 144°, operator $^1/_2+x,^1/_2-y,1-z$; C21-H21···S10 with H···S 2.82, angle 149°, operator $1-x,-^1/_2+y,^1/_2-z$.

In a final 1,10-elimination a crossing experiment was carried out. Thus an equimolar mixture of the dibromides **50** and **57b** was treated in acetonitrile with the Mori reagent at room temperature. Since the debromination should lead to a mixture of **51** and **58b** we expected the formation of one hetero- and two homodimers (Scheme 14).



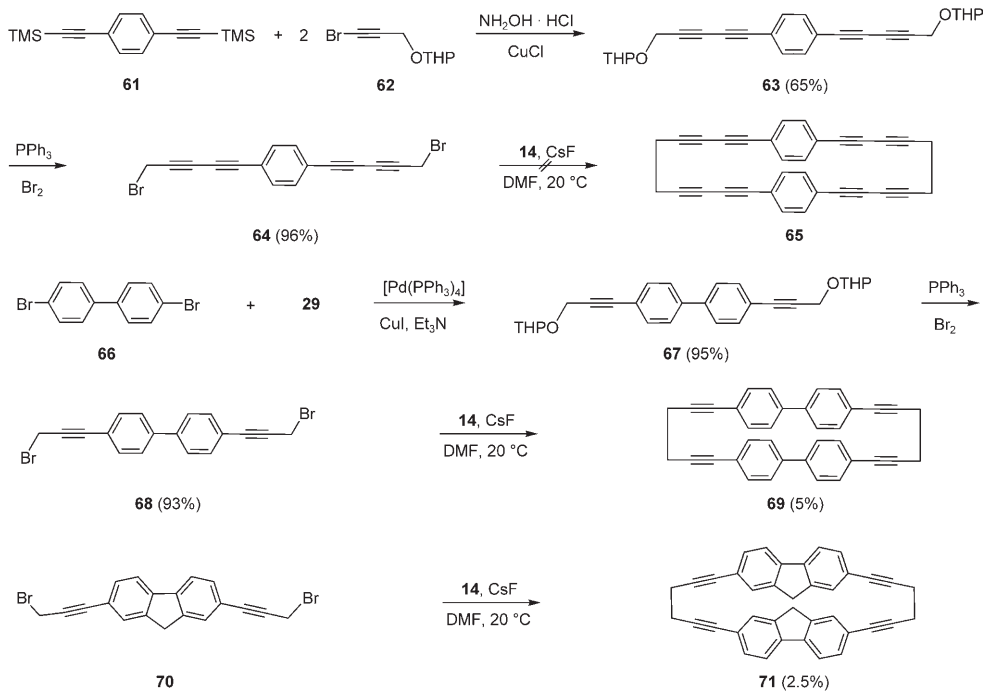
Scheme 14. Mixed paracyclophanes by a crossing experiment.

This is indeed the case. The homodimers **52** (9.5%) and **59b** (2.7%) were identified by comparison with the authentic products (see above), and the structure of the main product **60** (10%; product composition by ^{1}H NMR analysis) was derived from its spectroscopic data (see Experimental Section). Unfortunately a complete separation of the three cyclodimers was not possible: on silica gel the three compounds possess practically the same R_f values. They could be enriched, however, when the silica gel had been impregnated with picric acid. The separation is additionally made difficult by the instability of **60**.

1,14- and higher eliminations: Not unexpectedly, with growing distance between the two groups to be eliminated it becomes more difficult to observe and isolate 1,x-elimination products. Still, as several of the following examples demonstrate the process does not yet break down.

Whereas the starting dibromide **64** could be prepared readily and in good yield *via* the doubly protected tetrayne **63** (itself obtain by Cadiot–Chodkiewicz coupling of **61** with the 1-bromo alkyne **62**, Scheme 15), its debromination did not yield the desired cyclophane **65**.

From the product mixture we could isolate an extremely unstable component that might have been **65** (soluble in organic solvents, R_f value comparable with structurally similar compounds such as **49**). However, it decomposed to a black, insoluble material before we could obtain its spectroscopic data. The feasibility of 1,14-eliminations when the number of triple bonds is reduced in starting materials and products was demonstrated with the biphenyl derivative **68**, prepared by the established protocol from the commercial substrate **66** via the bis-ether **67**. The cyclophane could not only be purified by column chromatography, but it is stable under



Scheme 15. 1,14-Eliminations leading to novel extended paracyclophanes.

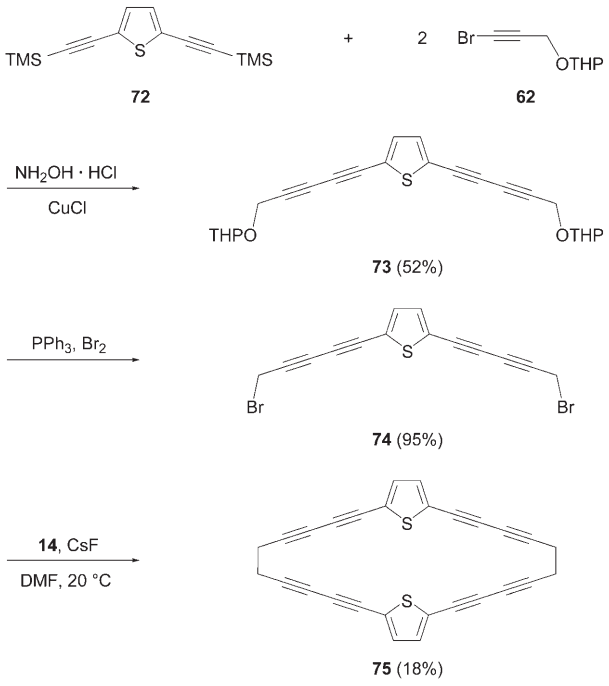
inert gas for extended periods of time. Unfortunately we could not obtain crystals of X-ray quality; its structure is clearly shown by the spectroscopic data (Experimental Section). Formally connecting two *ortho*-positions in **68** by a methylene group leads to **70**, which on debromination with Mori reagent in DMF provides small amounts of the fluorenophane **71** (2.5%). The determination of its exact structure (*syn*- or *trans*-configured, see **52** and **59a**, **b** above), awaits the preparation of single crystals for X-ray structural analysis. Provided that sufficient amounts of the hydrocarbon can be obtained, its conversion into metallocenophanes is also of interest.

For a final 1,14-elimination we prepared the thiophene derivative **74** from the diacetylene **72** as described in Scheme 16. Again, the preparation of the precursor compounds could be carried out in satisfactory yields.

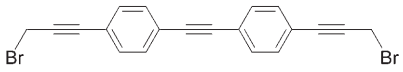
Dimerization of **74** to the thiaphane **75** took place in acceptable yield (18%), although the compound could not be obtained free of solvent. Like its sister molecule **65** it quickly decomposes to a black material and, as in **71**, the orientation of the (hetero)aromatic decks remains undetermined for the time being.

In a last series of experiments we tried to find experimental hints for the occurrence of a 1,16- and a 1,20-elimination, and selected the two dibromides **76** and **77** (Scheme 17) for that purpose.

Both precursors were again prepared without problems from commercially or easily available substrates by the coupling processes described above. However, in neither case did the debromination lead to cyclodimerization products. Since lack of stability is an unlikely cause for this, we propose that the above concept of "extended eliminations" has reached its limit with **74**, that is, with a 1,14-elimination process.



Scheme 16. Preparation of an extended thiaphane by 1,14-elimination.



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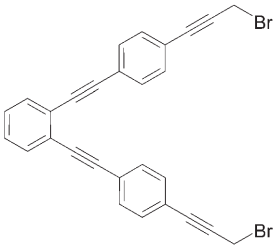

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Scheme 17. Attempted 1,16- and 1,20-eliminations.

Conclusion

Recently the concept of "expanded structures" has received increasing attention in the chemical literature. Typical examples are the [*N*]pericyclynes,[22] "exploded" radialenes,[23] expanded cubanes[24] or the aromatic ring carbomers.[25] With this publication we wish to extend this concept in the literal sense and suggest applying it to chemical reactivity as well. For example 1,12-additions of organocuprates to extended unsaturated esters have already been reported.[26] In the area of substitutions reactions, several 1,5-processes have been described.[27]

It appears likely that many other examples can be designed and subsequently developed in the chemical laboratory.

Experimental Section

General remarks: Column chromatography: Silica gel 60 (70–230 mesh, Merck); aluminium oxide, activity II–III (Woelm). Melting points: Kofler hot stage (uncorr.) NMR: Bruker AC 200 (^{1}H: 200 MHz; ^{13}C: 50.3 MHz); Bruker AM 300 (^{1}H: 300 MHz; ^{13}C: 75.5 MHz); Bruker WM 400 and Bruker AM 400 (^{1}H: 400 MHz; ^{13}C: 100.6 MHz) in $CDCl_3$, TMS as internal standard. IR: Perkin-Elmer 1420 as KBr pellets. MS: Finnigan MAT 84530 (70 eV, EI). UV: Beckman UV 5230.

General procedure 1 (GP 1): **Preparation of propargyl bromides**: Bromine (1.2 equiv) was added under nitrogen at 0 °C to a solution of triphenylphosphine (1.2 equiv) in anhydrous dichloromethane (100 mL). After stirring for 5–10 min a slightly yellow homogenous solution had formed, to which the appropriate propargyl alcohol (1 equiv) or its THP ether (see GP 2) was added, if necessary dissolved in a small amount of dichloromethane. After stirring for 1 h at 0 °C, the reaction was completed by stirring for an additional hour at room temperature. The solution was passed through a pad of silica gel, and the solvent was removed by rotary evaporation. For further purification the propargyl bromides were purified by chromatography on silica gel.

General procedure 2 (GP 2): **Coupling of halides with 2-(2-propynyloxy)-3,4,5,6-tetrahydro-2*H*-pyran (29)**: The appropriate aryl halide (5 mmol), ether **29** (6.25 mmol), 1–4 mol % of $[Pd(PPh_3)_4]$, and 2–8 mol % of CuI were dissolved in anhydrous triethylamine (50 mL), and the solution heated to 80 °C for 1–8 h. The reaction mixture was hydrolyzed with saturated aqueous ammonium chloride solution (300 mL), and extracted several times with Et_2O. The combined organic layers were filtered through a short silica gel column and the solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography.

General procedure 3 (GP 3): **Elimination reactions with Mori's reagent**: The dihalide (1 mmol) and cesium fluoride (1.5 mmol) were dissolved at room temperature under nitrogen in the appropriate anhydrous solvent (in most experiments: DMF). To this solution was added tributyl(trimethylsilyl)stannane (**14**, 1.5 mmol) within 1 h. After stirring for an additional 4 h at room temperature dichloromethane (100 mL) was added to the reaction mixture, followed by 10 % aqueous ammonia solution (300 mL), and the aqueous phase was thoroughly extracted with dichloromethane. The organic phases were combined, dried, and filtered through silica gel. The elimination product (hydrocarbon) was purified by column chromatography (silica gel).

1,6-Dibromo-2,4-hexadiyne (17): According to GP 1 1,6-dihydroxy-2,4-hexadiyne (**16**, 1.33 g (12.1 mmol) was treated in dichloromethane (100 mL) with triphenylphosphine (7.6 g, 29.0 mmol) and bromine (1.33 g, 29.0 mmol). After work-up **17** (2.3 g, 81 %) was isolated as a colorless oil that solidifies in the refrigerator. M.p. ca. 0 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.99$ ppm (s, 4H, 1-, 6-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 13.96$ (t, C-1, -6), 70.29 (s, C-3, -4), 75.27 ppm (s, C-2, -5); IR (film): $\tilde{\nu} = 2954$ (s), 2924 (s), 2852 (s), 2256 (w), 2155 (w), 1198 (s), 608 cm^{-1} (vs); UV (acetonitrile): λ_{max} (log ε) = 200 (4.41), 262 nm (3.65); MS (70 eV): *m*/*z* (%): 238 (20) [M^+], 236 (38) [M^+], 234 (20) [M^+], 157 (98), 155 (100), 76 (52); elemental analysis calcd (%) for $C_6H_4Br_2$: C 30.55, H 1.71; found: C 30.42, H. 1.58.

1,3,7,9-Cyclododecatetrayne (20): According to GP 3 **17** (1.00 g, 4.24 mmol) was treated with **14** (2.31 g, 6.36 mmol) and cesium fluoride (0.97 g, 6.36 mmol) in DMF (70 mL), giving **20** (64 mg, 10 %) as colorless plates that turned brown in air and then black quickly. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.63$ ppm (s, -CH_2-); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 19.84$ (t, C-5, -6, -11, -12), 72.94 (s, C-3, -3, -8, -9), 86.58 ppm (s, C-1, -4, -7, -10); GC/MS (40 eV): *m*/*z* (%): 152 (100) [M^+], 76 (54). A sample of **20** (16 mg, 0.11 mmol) was dissolved in degassed ethyl acetate (50 mL) and hydrogenated over Pt under normal pressure at room temperature. After 12 h the catalyst was removed by filtration, the solvent was removed in vacuo and the residue (15 mg, 86 %) identified as cyclododecane by GC/MS comparison with an authentic sample.

[2.6]Orthocyclophan-1,5-diyne (26)

a) *ortho*-(3-Bromopropynyl)benzyl bromide (24): A solution of *ortho*-iodobenzyl alcohol (**22**, 5.0 g, 21.3 mmol), propargyl alcohol (**23**, 2.5 mL, 46.5 mmol), and $[Pd(PPh_3)_4]$ (1.23 g, 1 mmol) in anhydrous propylamine (100 mL) was refluxed under nitrogen for 1.5 h. The reaction mixture was cooled to room temperature and hydrolyzed with saturated aqueous ammonium chloride solution (200 mL). After thorough extraction with Et_2O and dichloromethane the organic phases were combined, the solution filtered through a pad of silica gel, and the solvent evaporated in vacuo. Column chromatography (silica gel, Et_2O) provided *o*-(3-hydroxypropynyl)benzyl alcohol (3.2 g, 93 %) as colorless crystals. M.p. 63 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.44$ (s, 1H, OH), 3.77 (s, 1H, OH), 4.42 (s, 2H, -CH_2-), 4.74 (s, 2H, -CH_2-), 7.22–7.41 ppm (m, 4H, arom. H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 51.17$ (t), 63.65 (t), 82.97 (s), 92.02 (s), 121.35 (s), 127.59 (d), 127.87 (d), 128.73 (d), 132.28 (d), 142.29 ppm (s); IR (KBr): $\tilde{\nu} = 3314$ (vs), 3307 (vs), 2232 (vw), 1635 (s), 1629 (s), 1042 (vs), 1025 (vs), 757 cm^{-1} (vs); UV (acetonitrile): λ_{max} (log ε) = 196 (sh, 4.21), 206 (4.36), 244 (4.07), 250 nm (sh, 4.00); MS (70 eV): *m*/*z* (%): 162 (8) [M^+], 144 (78), 115 (100); elemental analysis calcd (%) for $C_{10}H_{10}O_2$ (162.19): C 74.05, H 6.21; found: C 74.32, H 6.22.

To a solution of this diol (3.0 g, 18.5 mmol) in anhydrous Et_2O (40 mL), cooled to 0 °C, was added under nitrogen PBr_3 (1.3 mL, 13.6 mmol) to which pyridine (0.1 mL) had been added. After stirring for 1 h at 0 °C, the reaction mixture was refluxed for an additional hour. To the cooled solution was added saturated aqueous sodium bicarbonate solution (100 mL), and the mixture was thoroughly extracted with Et_2O. The combined organic phases were filtered through silica gel, the solvent was removed by rotary evaporation, and the remaining crude product purified by column chromatography (silica gel, petrol ether): **24** (3.7 g, 70 %) as colorless needles. M.p. 37 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.21$ (s, 2H, -CH_2-), 4.64 (s, 2H, -CH_2-), 7.26–7.44 ppm (m, 4H, arom. H);

^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.93$ (t), 31.52 (t), 83.75 (s), 89.74 (s), 121.93 (s), 128.40 (d), 129.36 (d), 129.74 (d), 132.79 (d), 139.66 ppm (s); IR (KBr): $\tilde{\nu} = 3058$ (w), 3026 (w), 2221 (m), 1485 (vs), 1449 (s), 1218 (vs), 1202 (vs), 1192 (vs), 765 cm^{-1} (vs); UV (acetonitrile): λ_{max} (log ε) = 218 (4.39), 258 nm (4.10); MS (70 eV): *m/z* (%): 290 (12) [M^+], 288 (19) [M^+], 286 (12) [M^+], 209 (98), 207 (100), 128 (98); elemental analysis calcd (%) for $C_{10}H_{10}Br_2$: C 41.71, H 2.80; found: C 41.23, H 2.99.

b) Debromination of 24 to 26: According to GP 3 **24** (1.0 g, 3.48 mmol) was treated with cesium fluoride (0.58 g, 3.85 mmol) and **14** (1.39 g, 3.85 mmol) at 0 °C. After stirring for 24 h at room temperature the reaction mixture was hydrolyzed and worked-up (see GP 3). After solvent removal in vacuo the remaining oil was purified by radial chromatography (silica gel, petrol ether), giving **26** (10 mg, 2.2 %) as colorless, microcrystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.75$ (s, 4H, -CH_2CH_2-), 3.07 (s, 4H, -CH_2CH_2-), 7.16–7.39 ppm (m, 4H, arom. H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 19.66$ (t), 37.72 (t), 81.05 (s), 91.87 (s), 122.94 (s), 125.99 (d), 128.11 (d), 129.24 (d), 131.50 (d), 144.72 ppm (s); IR (KBr): $\tilde{\nu} = 3061$ (w), 3018 (w), 2923 (m), 2191 (w), 1705 (s), 1483 (s), 1449 (s), 1069 (s), 1043 cm^{-1} (s); UV (acetonitrile): λ_{max} (log ε) = 210 (4.58), 240 (4.32), 252 nm (4.10); MS (70 eV): *m/z* (%): 256 (100) [M^+], 241 (58), 228 (28); HRMS: *m/z*: calcd for $C_{20}H_{16}$: 256.12500, found: 256.125. The isomer **27** could never be completely separated from side-products. The ^{1}H NMR data mentioned in the main section indicated its formation, as do signals in the IR and MS spectra comparable to those reported for **26**.

1,9-Cyclohexadecadien-3,7,11,15-tetrayne (33): According to GP 3 (*Z*)-1,8-dibromo-4-octen-2,6-diyne (**31**, 1.0 g, 3.81 mmol), prepared from (*Z*)-1,2-dichloroethene (**28**) by the method of König et al.,[14] was debrominated with **14** (2.07 g, 5.72 mmol) and cesium fluoride (0.87 g, 5.72 mmol) in DMF (50 mL). After work-up hydrocarbon **33** (ca. 40 mg, 5 %) was obtained, which started to decompose rapidly at room temperature. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.58$ (s, 8H, -CH_2CH_2-), 5.95 ppm (s, 4H, -CH=CH-); GC/MS (40 eV): *m/z* (%): 204 (35) [M^+], 202 (100), 189 (15), 152 (10), 102 (268), 76 (30).

A sample of **33** (10.0 mg, 0.05 mmol) was dissolved in degassed ethyl acetate (20 mL), and the solution hydrogenated under normal pressure over platinum for 20 h at room temperature. After solvent removal by rotary evaporation **36** (10 mg, 89 %) was obtained, identical in its GC/MS behavior with a sample prepared by hydrogenation of commercial cyclohexadeca-1,3-diene.

For a Bergman cyclization a few mg of **33** was dissolved in 1,4-cyclohexadiene (1 mL) and the solution heated in a sealed ampoule to 200 °C. Analysis of the pyrolysate by GC/MS revealed peaks that agreed with those expected for **34**, but since no authentic material was available for comparison the experiment remained ambiguous.

3,4-Benzocycloocta-3-en-1,5-diyne (41)

a) 1,2-Bis-(3-bromo-1-propynyl)benzene (38): A mixture of PBr_3 (1.66 mL, 17.7 mmol) and pyridine (0.1 mL) was added under nitrogen at 0 °C to a solution of 1,2-bis-(3-hydroxy-1-propynyl)benzene (4.50 g, 24.2 mmol), prepared from the coupling of propargyl alcohol (**23**) with *ortho*-dibromobenzene (**37**) according to ref. [28]), in anhydrous Et_2O (20 mL). After stirring for 1 h at that temperature the bromination was completed by refluxing the reaction mixture for 1 h. The red product mixture was hydrolyzed with saturated aqueous sodium bicarbonate solution (100 mL), and the aqueous phase was thoroughly extracted with Et_2O. The combined organic phases were filtered through silica gel, and the solvent was removed. Column chromatography (silica gel, dichloromethane/petrol ether 5:2) furnished colorless **36** (4.5 g, 60 %) as low melting needles. M.p. 30–33 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.22$ (s, 4H, -CH_2-), 7.28–7.43 ppm (AA′BB′-m, 4H, arom. H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 15.06$ (t), 84.93 (s), 88.36 (s), 125.05 (s), 128.78 (d), 131.91 ppm (d); IR (KBr): $\tilde{\nu} = 3061$ (w), 3008 (w), 2227 (w), 1719 (m), 1655 (m), 1637 (m), 1592 (m), 1480 (s), 1440 (s), 1291 (s), 1202 (vs), 983 (s), 759 (vs), 609 cm^{-1} (vs); UV (acetonitrile): λ_{max} (log ε) = 198 (4.27), 243 (4.44), 268 nm (4.12); MS (70 eV): *m/z* (%): 314 (10) [M^+], 312 (20) [M^+], 310 (10) [M^+], 233 (82), 231 (83), 152 (100); elemental analysis calcd (%) for $C_{12}H_8Br_2$: C 46.20, H 2.58; found: C 46.21, H 2.42.

b) Debromination of 38 to 41: According to GP 3 **38** (1.0 g, 3.2 mmol) was debrominated with **14** (3.50 g, 9.6 mmol) and cesium fluoride (1.47 g, 9.6 mmol). After work-up (see GP 3), the crude product was pre-purified by column chromatography on silica gel with dichloromethane. A second chromatography (silica gel, pentane) provided **41** (0.3 g, 62 %) as colorless needles. The hydrocarbon polymerized quickly at room temperature yielding a solid material that did not melt below 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.99$ (s, 4H, -CH_2CH_2-), 7.27–7.28 ppm (AA′BB′-m, 4H, arom. H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 20.98$ (t), 96.14 (s), 110.99 (s), 126.59 (d), 127.42 (d), 131.74 ppm (s); IR (KBr): $\tilde{\nu} = 3079$ (w), 2922 (w), 2159 (s), 1555 (vs), 1540 (m), 1450 (vs), 1438 (vs), 1420 (vs), 1282 (s), 1033 (s), 751 cm^{-1} (vs); UV (acetonitrile): λ_{max} (log ε) = 200 (4.38), 222 (4.28), 232 (4.43), 250 nm (sh, 4.12); MS (70 eV): *m/z* (%): 152 (100) [M^+], 126 (18). When the debromination experiment was repeated in the presence of dimethyl acetylene dicarboxylate as trapping reagent no addition product(s) was (were) obtained.

[2.6]Paracyclophan-1,5-diyne (45) and [4.4]paracyclophan-1,11-diyne (46)

a) *p*-(3-Bromopropynyl)-benzyl bromide (43): As described for the conversion of **22** into **24** above, *p*-bromobenzyl alcohol (**42**) was converted into dibromide **43** in an overall yield of 35 %. After chromatography (silica gel, petrol ether) it was obtained in the form of colorless needles. M.p. 64 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.16$ (s, 2H, -CH_2-), 4.47 (s, 2H, -CH_2-), 7.34–7.41 ppm (AA′XX′-m, 4H, $J_m = 3.5$, $J_p = 8.3$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 15.03$ (t), 32.69 (t), 85.03 (s), 86.07 (s), 122.22 (s), 128.99 (d), 132.21 (d), 138.42 ppm (s); IR (KBr): $\tilde{\nu} = 3030$ (vw), 2970 (vw), 2266 (vw), 2215 (w), 1508 (m), 1412 (m), 1276 (m), 1225 (s), 1194 (s), 841 (s), 603 cm^{-1} (vs); UV (hexane): λ_{max} (log ε) = 196 (4.44), 204 (sh, 4.38), 266 nm (4.37); MS (70 eV): *m/z* (%): 290 (8) [M^+], 288 (14) [M^+], 286 (7) [M^+], 209 (80), 207 (82), 128 (100); elemental analysis calcd (%) for $C_{10}H_8Br_2$: C 41.71, H 2.80; found: 41.23, H 2.70.

b) Debromination of 43 to 45/46: According to GP 3 **43** (1.0 g, 3.47 mmol) was debrominated with **14** (1.26 g, 3.47 mmol) and cesium fluoride (0.53 g, 3.47 mmol) in anhydrous DMF (50 mL) at −30 °C. The reaction mixture was brought to room temperature and stirred for 2 d. After work-up as described above, the product mixture was pre-purified by column chromatography on silica gel with dichloromethane and subsequently fractionated by radial chromatography (silica gel, petrol ether): 1:1 mixture of **45** and **46** (20 mg, 4.5 %) as colorless needles. The following spectroscopic data were derived from the hydrocarbon mixture. ^{1}H NMR (400 MHz, $CDCl_3$) for **45**: $\delta = 2.67$ (s, 4H, -CH_2CH_2-), 2.98 (s, 4H, -CH_2CH_2-), 6.82–6.91 ppm (AA′XX′-m, 8H, arom. H); ^{13}C NMR (100 MHz, $CDCl_3$) for **45**: $\delta = 19.74$ (t), 34.33 (t), 86.09 (s), 92.7 (s), 121.82 (s), 128.99 (d), 130.96 (d), 139.25 ppm (s); ^{1}H NMR (400 MHz, $CDCl_3$) for **46**: $\delta = 2.68$ (t, 4H, $J = 7.0$ Hz, -CH_2CH_2-), 2.92 (t, 4H, $J = 7.0$ Hz, -CH_2CH_2-), 6.51–6.82 ppm (m, 4H, arom. H); ^{13}C NMR (100 MHz, $CDCl_3$) for **46**: $\delta = 20.30$ (t), 33.01 (t), 88.12 (s), 94.75 (s), 121.82 (s), 130.85 (d), 131.10 (d), 140.35 ppm (s); IR (KBr) for **45**/**46**: $\tilde{\nu} = 3073$ (w), 3038 (w), 2947 (s), 2924 (vs), 2855 (s), 2216 (w), 1506 (vs), 1408 (m), 1095 (m), 815 (s), 723 cm^{-1} (s); UV (acetonitrile) for **45**/**46**: λ_{max} (log ε) = 194 (4.60), 198 (4.59), 240 (sh, 4.33), 246 (4.38), 260 nm (4.05); MS (70 eV) for **45**/**46**: *m/z* (%): 256 (76) [M^+], 241 (20), 152 (8), 128 (100), 102 (18); HRMS: *m/z*: calcd for $C_{20}H_{16}$: 256.1252; found: 256.125.

[6.6]Paracyclophan-1,5,13,17-tetrayne (49)

a) 1,4-Bis-(3-bromo-1-propynyl)benzene (47): A solution of 1,4-dibromobenzene (10.0 g, 42.3 mmol), propargyl alcohol (**23**, 7.6 mL, 0.13 mol) and of [$Pd(PPh_3)_4$] (1.27 g, 1.1 mmol) in propylamine (130 mL) was refluxed under nitrogen for 3 d. For work-up the reaction mixture was hydrolyzed with saturated aqueous sodium bicarbonate solution (200 mL), extracted thoroughly with Et_2O, and the combined organic phases dried with magnesium sulfate. Solvent removal provided a solid residue that was recrystallized from Et_2O to yield colorless plates (7.5 g, 94 %). M.p. 122 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.39$ (s, 4H, -CH_2-), 7.37 ppm (s, 4H, arom. H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 52.74$ (t), 86.43 (s), 92.27 (s), 125.86 (s), 134.1 ppm (d); IR (KBr): $\tilde{\nu} = 3359$ (s), 3363 (s), 2904 (w), 2241 (w), 1507 (s), 1497 (s), 1440 (m), 1425 (s), 1030 (vs), 839 cm^{-1} (s); UV (acetonitrile): λ_{max} (log ε) = 196 (4.36), 212 (4.26), 218 (4.24), 268 (4.56), 280 (4.60), 294 nm (3.36); MS (70 eV): *m/z* (%): 186 (100) [M^+], 169 (12), 157 (32), 128 (44); elemental analysis calcd (%) for $C_{12}H_8O_2$: C 77.40, H 5.41; found: C 77.55, H 5.40. To a solution of this diol (5.0 g, 26.9 mmol) in anhydrous Et_2O (30 mL) was added a mixture of PBr_3

(1.85 mL) and pyridine (0.1 mL) at 0 °C. After stirring for 30 min at this temperature the reaction was completed by refluxing the mixture for further 30 min. The product mixture was hydrolysed (100 mL of saturated aqueous sodium bicarbonate solution), the phases were separated and the aqueous phase thoroughly extracted with ether. The combined organic layers were dried (magnesium sulfate), the solvent was removed in vacuo, and the residue purified by column chromatography (silica gel, petrol ether): **47** (5.7 g, 68 %) as colorless needles. M.p. 103 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.16$ (s, 4H, -CH_2-), 7.38 ppm (s, 4H, arom. H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.9$ (t), 85.97 (s), 86.20 (s), 122.55 (s), 131.72 ppm (d); IR (KBr): $\tilde{\nu} = 3000$ (w), 2926 (vw), 2270 (vw), 2218 (m), 1505 (m), 1274 (m), 1199 (vs), 831 (s), 601 cm^{-1} (s); UV (hexane): λ_{max} (log ε) = 196 (4.46), 218 (4.24), 282 (4.54), 290 nm (sh, 4.51); MS (70 eV): *m*/*z* (%): 314 (10) [M^+], 312 (20) [M^+], 310 (9), [M^+], 233 (95), 231 (93), 152 (100); elemental analysis calcd (%) for $C_{12}H_8Br_2$: C 46.20. H 2.58; found: C 46.30, H 2.80.

b) Debromination of 47 to 49: According to GP 3 **47** (1.0 g, 3.2 mmol) was debrominated with cesium fluoride (0.34 g, 3.5 mmol) and **14** (1.3 g, 3.5 mmol) in anhydrous DMF (50 mL). The reaction mixture was stirred for 6 h at 0 °C, followed by 12 h at room temperature. After work-up (see above) the solvent was removed by rotary evaporation, and the residue purified by column chromatography (alumina, pentane) and recrystallization (methanol): **49** (40 mg, 7.5 %) as colorless needles. M.p. 190 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.69$ (s, 8H, -CH_2CH_2-), 6.92 ppm (s, 8H, arom. H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 19.32$ (t), 85.58 (s), 91.96 (s), 123.00 (s), 130.72 ppm (d); IR (KBr): $\tilde{\nu} = 3034$ (vw), 2909 (w), 2835 (w), 2217 (w), 1503 (s), 834 cm^{-1} (vs); UV (hexane): λ_{max} (log ε) = 194 (4.56), 212 (4.45), 264 (4.76), 286 nm (4.30); MS (70 eV): *m*/*z* (%): 304 (100) [M^+], 276 (16), 152 (62); HRMS: *m*/*z*: calcd for $C_{24}H_{16}$: 304.1252; found: 304.125. When the experiment was repeated in acetonitrile the yield increased to 245 mg (46 %). Although several attempts were undertaken, we could not obtain a satisfactory elemental analysis of **49**.

***syn*-[6.6](1,4)Naphthalenocyclophan-1,5,18,22-tetrayne (52)**

a) 1,4-Bis-(3-bromo-1-propynyl)naphthalene (50): According to GP 2 1,4-dibromonaphthalene (3.0 g, 10.5 mmol) was coupled with THP-ether **29** (3.68 g, 26.3 mmol) in the presence of [Pd(PPh_3)$_4$] (0.363 g, 0.315 mmol) and cuprous iodide (0.120 g, 0.63 mmol) in triethylamine (100 mL); reaction time 4 h at 80 °C. After work-up (see above, GP 2), 3.8 g (90 %) of the bis-THP ether of 1,4-bis(3-hydroxy-1-propynyl)naphthalene was obtained, colorless solid. M.p. 75 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.56$–1.92 (m, 12H, THP-ring), 3.57–3.63 (m, 2H, THP-ring), 3.91 (m, 2H, THP-ring), 4.62 and 4.67 (AX-q, $J = 15.9$ Hz, 4H, propargyl-CH_2-), 4.98 (t, $J = 3.3$ Hz, 2H, -$CH(O)_2$), 7.50–7.60 and 8.32–8.36 (AA′BB′-m, 4H, arom. H), 7.61 ppm (s, 2H, arom. H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 19.04 (t), 25.34 (t), 30.29 (t), 54.66 (t), 62.08 (t), 83.59 (s), 91.63 (s), 96.12 (s), 121.12 (s), 126.47 (d), 127.14 (d), 129.87 (d), 133.06 ppm (s); IR (KBr): $\tilde{\nu} = 3065$ (vw), 2945 (w), 2226 (vw), 1447 (w), 1202 (m), 1026 cm^{-1} (s); UV (hexane): λ_{max} (log ε) = 192 (4.56), 212 (4.17), 242 (4.68), 324 (4.40), 340 nm (4.44); MS (70 eV): *m*/*z* (%): 404 (16) [M^+], 304 (43), 262 (20), 204 (51), 203 (98), 202 (100), 85 (14); elemental analysis calcd (%) for $C_{26}H_{28}O_4$: C 77.20, H 6.98; found: C 76.82, H. 7.01. According to GP 1 this bis-ether (2.4 g, 5.94 mmol) was treated with triphenylphosphine (3.74 g, 14.3 mmol) and bromine (0.73 g, 14.3 mmol) in dichloromethane (100 mL). After work-up **50** (2.06 g, 95 %) was obtained as colorless needles (cyclohexane). M.p. 105 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 4.32 (s, 4H, -CH_2-), 7.61 (s, 2H, arom. H), 7.61–8.33 ppm (AA′BB′-m, 4H, arom. H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 15.03$ (t), 84.54 (s), 90.72 (s), 120.93 (s), 126.31 (d), 127.51 (d), 129.95 (d), 133.04 ppm (s); IR (KBr): $\tilde{\nu} = 3050$ (vw), 2212 (w), 1565 (w), 1369 (m), 1198 (s), 761 (s), 605 (s); UV (acetonitrile): λ_{max} (log ε) = 192 (4.35), 242 (4.38), 330 (4.19), 344 nm (4.19); MS (70 eV): *m*/*z* (%): 364 (14) [M^+], 362 (28) [M^+], 360 (15) [M^+], 283 (86), 281 (85), 202 (100); elemental analysis calcd (%) for $C_{16}H_{10}Br_2$: C 53.08, H 2.78; found: C 53.23, H 2.72.

b) Debromination of 50 to 52: According to GP 3 **50** (0.82 g, 2.25 mmol) was treated with **14** (2.45 g, 6.75 mmol) and cesium fluoride (2.04 g, 13.5 mmol) in acetonitrile (100 mL). After work-up (see above) **52** (230 mg, 51 %) was isolated as colorless prisms (dichloromethane), decomp. at 100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.91$ (s, 8H, -CH_2CH_2-), 6.75 (s, 4H, arom. H), 7.21–8.11 ppm (AA′BB′-m, 8H, arom. H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 19.86$ (t), 84.64 (s), 95.71 (s), 121.12 (s), 125.90 (d), 126.06 (d), 128.62 (d), 132.37 ppm (s); IR (KBr): $\tilde{\nu} = 3059$ (w), 2925 (w), 2212 (w), 1568 (w), 1384 (m), 836 (s), 764 cm^{-1} (s); UV (acetonitrile): λ_{max} (log ε) = 192 (4.71), 210 (4.43), 234 (4.87), 316 (4.54), 346 nm (4.28); MS (70 eV): *m*/*z* (%): 404 (100) [M^+], 387 (14), 215 (10), 202 (52); elemental analysis calcd (%) for $C_{32}H_{20}$: C 95.02, H 4.98; found: C 94.57, H 4.97.

[6.6](9,10)Anthracenophan-1,5,24,28-tetrayne (55)

a) 9,10-Bis-(3-bromo-1-propynyl)anthracene (53): According to GP 2 9,10-diiodoanthracene (2.3 g, 5.35 mmol) was coupled with **29** (1.65 g, 11.8 mmol) in the presence of [Pd(PPh_3)$_4$] (0.247 g, 0.21 mmol) and cuprous iodide (0.1 g, 0.53 mmol) in triethylamine (100 mL) for 8 h at 80 °C. After work-up (see above) the bis-THP ether of 9,10-bis-(3-hydroxy-1-propynyl)anthracene (1.90 g, 78 %) was obtained as yellow-orange prisms. M.p. 113 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.50$–1.97 (m, 12H, THP-ring), 3.52–3.66 (m, 2H, THP-ring), 3.96–4.02 (m, 2H, THP-ring), 4.83 (s, 4H, propargyl-CH_2-), 5.10 (t, $J = 3.3$ Hz, 2H, -$CH(O)_2$), 7.57–7.60 and 8.54–8.58 ppm (AA′BB′-m, 8H, arom. H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 19.13$ (t), 25.39 (t), 30.40 (t), 55.18 (t), 62.20 (t), 82.35 (s), 97.09 (d), 98.06 (s), 118.04 (s), 126.71 (d), 127.06 (d), 132.19 ppm (s); IR (KBr): $\tilde{\nu} = 3058$ (w), 2940 (w), 2202 (vw), 1436 (s), 1389 (s), 1208 (s), 1119 (vs), 1079 (vs), 1039 (vs), 768 cm^{-1} (vs); UV (acetonitrile): λ_{max} (log ε) = 192 (4.23), 218 (3.80), 268 (4.86), 366 (3.39), 384 (3.79), 406 (4.13), 430 nm (4.24); MS (70 eV): *m*/*z* (%): 454 (36) [M^+], 354 (24), 252 (100), 239 (51), 85 (10); elemental analysis calcd (%) for $C_{30}H_{30}O_4$: C 79.27, H 6.65; found: C 78.94, H 6.71.

According to GP 1 this bis-ether (1.40 g, 3.08 mmol) was treated with triphenylphosphine (1.94 g, 7.39 mmol) and bromine (1.18 g, 7.39 mmol) in dichloromethane (50 mL). After work-up (see GP 1) **53** (1.13 g, 96 %) was obtained as yellow-orange prisms (dichloromethane). M.p. 172 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.50$ (s, 4H, -CH_2-), 7.60–8.54 ppm (AA′BB′-m, 8H, arom. H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 15.32$ (t), 83.65 (s), 96.95 (s), 117.69 (s), 126.89 (d), 127.13 (d), 132.11 ppm (s); IR (KBr): $\tilde{\nu} = 3060$ (vw), 2207 (s), 1436 (m), 1203 (s), 1192 (s), 761 cm^{-1} (vs); UV (acetonitrile): λ_{max} (log ε) = 192 (4.60), 268 (4.92), 390 (3.96), 410 (4.22), 434 nm (4.34); MS (70 eV): *m*/*z* (%): 414 (7) [M^+], 412 (14) [M^+], 410 (6) [M^+], 333 (54), 331 (54), 252 (98), 250 (100); elemental analysis calcd (%) for $C_{20}H_{12}Br_2$: C 58.29, H 2.93; found: C 58.31, H 2.96.

b) Debromination of 53 to 55: According to GP 3 **53** (0.8 g, 1.94 mmol) was treated with **14** (1.06 g, 2.91 mmol) and cesium fluoride (0.44 g, 2.91 mmol) in DMF (70 mL). After work-up (see above) **55** (24 mg, ca. 5 %) was obtained as yellow needles. As soon as the solvent had been removed completely, the hydrocarbon started to decompose (transformation first into brown, then black material). This instability prevented the recording of a mass spectrum and determination of an elemental analysis. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.18$ (s, 8H, -CH_2CH_2-), 7.96–8.00 ppm (AA′BB′-m, 16H, arom. H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 20.53$ (t), 84.07 (s), 101.05 (s), 117.88 (s), 124.95 (d), 126.37 (d), 130.75 ppm (s); IR (KBr): $\tilde{\nu} = 2923$ (w), 1622 (s), 760 cm^{-1} (s); UV (acetonitrile, qualitative): $\lambda_{max} = 192$, 256, 372, 388, 404, 428, 442 nm.

[6.6](2,5)Furanophan-1,5,11,15-tetrayne (59a)

a) 2,5-Bis-(3-bromo-1-propynyl) furan (57a): According to GP 2 2,5-dibromofuran (**56a**, 8.0 g, 35.4 mmol) was coupled with **29** (12.38 g, 88.4 mmol) in the presence of [Pd(PPh_3)$_4$] (0.41 g, 0.35 mmol) and cuprous iodide (0.134 g, 0.70 mmol) in triethylamine (100 mL) for 7 h at 80 °C. After work-up (see GP 2) the bis-THP ether of 2,5-bis-(3-hydroxy-1-propynyl)furan (9.8 g, 80 %) was isolated as a colorless oil, which solidified around 0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.43$–1.81 (m, 12H, THP-ring), 3.45–3.50 (m, 2H, THP-ring), 3.75–3.81 (m, 2H, THP-ring), 4.38–4.43 (AB-q, $J = 16.2$ Hz, 4H, propargyl-CH_2-), 4.78 (t, $J = 3.3$ Hz, 2H, -$CH(O)_2$), 6.47 ppm (s, 2H, -CH=); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 18.86$ (t), 25.23 (t), 30.08 (t), 54.30 (t), 61.64 (t), 75.55 (s), 90.36 (s), 96.78 (d), 116.32 (d), 136.93 ppm (s); IR (film): $\tilde{\nu} = 3119$ (w), 2943 (s), 2870 (m), 2852 (m), 1515 (m), 1389 (s), 1121 (vs), 1058 (s), 1028 (vs), 901 cm^{-1} (s); UV (acetonitrile): λ_{max} (log ε) = 204 (4.02), 280 (4.45), 284 (4.45), 296 nm (4.42); MS (70 eV): *m*/*z* (%): 344 (40) [M^+], 243 (100),

144 (40), 115 (60), 85 (39); elemental analysis calcd (%) for $C_{20}H_{24}O_5$: C 69.75, H 7.02; found: C 69.55, H 7.06.

A sample of the bis-protected ether (1.60 g, 4.65 mmol), was treated according to GP 1 with triphenylphosphine (2.92 g, 11.2 mmol) and bromine (1.79 g, 11.2 mmol) in dichloromethane (100 mL). After work-up (see GP 2 above) the dibromide **57a** (1.22 g, 97%) was obtained as colorless needles (dichloromethane). M.p. 79–82°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.15$ (s, 4H, -CH_2-), 6.60 ppm (s, 2H, =CH-); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.11$ (t), 76.17 (s), 98.49 (s), 117.22 (d), 136.95 ppm (s); IR (KBr): $\tilde{\nu} = 3154$ (s), 3125 (s), 3002 (s), 2954 (s), 2226 (m), 1516 (s), 1200 (s), 1010 (vs), 801 cm^{-1} (vs); UV (acetonitrile): λ_{max} (log ε) = 192 (4.13), 300 nm (4.45); MS (70 eV): *m*/*z* (%): 304 (12) [M^+], 302 (22) [M^+], 300 (12) [M^+], 223 (98), 221 (100), 142 (64); elemental analysis calcd (%) for $C_{10}H_6Br_2O$: C 39.78, H 2.00; found: C 39.94, H 1.92.

b) Debromination of 57a to 59a: According to GP 3 **57a** (1.00 g, 3.31 mmol) was treated with **14** (1.80 g, 4.96 mmol) and cesium fluoride (0.754 g, 4.96 mmol) in DMF (50 mL). After work-up (see above) **59a** (122 mg, 26%) was obtained as colorless plates (dichloromethane/methanol). M.p. 100°C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.71$ (s, 8H, -CH_2CH_2-), 6.39 ppm (s, 4H, -CH=); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 19.19 (t), 73.52 (s), 92.43 (s), 113.43 (s), 137.77 ppm (d); IR (KBr): $\tilde{\nu} =$ 3127 (w), 3114 (w), 2953 (s), 2915 (s), 2850 (m), 2227 (w), 2172 (w), 1702 (m), 1520 (s), 1418 (s), 1308 (s), 1192 (s), 1005 (vs), 787 cm^{-1} (vs); UV (acetonitrile): λ_{max} (log ε) = 206 (4.26), 264 (4.51), 272 (4.67), 286 (4.25), 298 nm (4.18); MS (70 eV): *m*/*z* (%): 284 (100) [M^+], 226 (38), 114 (14); HRMS: calcd for $C_{20}H_{12}O_2$: 284.083, found 284.083.

[6.6](2,5)Thiophenophan-1,5,11,15-tetrayne (59b)

a) 2,5-Bis-(3-bromo-1-propynyl)thiophene (57b): According to GP 2 2,5-dibromothiophene (**56b**, 5.00 g, 20.7 mmol) was coupled with **29** (7.23 g, 88.4 mmol) in the presence of [Pd(PPh_3)$_4$] (0.48 g, 0.41 mmol) and cuprous iodide (0.078 g, 0.41 mmol) in triethylamine (80 mL) for 7 h at 60°C. After work-up (see above) the bis-THP ether of 2,5-bis-(3-hydroxy-1-propynyl)thiophene (5.75 g, 77%) was isolated as a colorless solid. M.p. 50°C (cyclohexane); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.51$–1.90 (m, 12H, THP-ring), 3.53–3.58 (m, 2H, THP-ring), 3.83–3.89 (m, 2H, THP-ring), 4.44–4.51 (AB-q, $J = 15.9$ Hz, 4H, propargyl-CH_2-), 4.85 (t, $J = 3.3$ Hz, 2H, -$CH(O)_2$), 7.05 ppm (s, 2H, -CH=); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 18.09$ (t), 25.27 (t), 30.14 (t), 54.67 (t), 61.89 (t), 78.44 (s), 90.08 (s), 96.90 (d), 123.98 (s), 132.05 ppm (d); IR (film): $\tilde{\nu} = 2942$ (s), 2870 (m), 2851 (m), 2222 (w), 1343 (m), 1201 (s), 1120 (vs), 1056 (vs), 1026 (vs), 902 cm^{-1} (s); UV (acetonitrile): λ_{max} (log ε) = 208 (3.97), 216 (4.02), 300 (4.41), 304 nm (4.41); MS (70 eV): *m*/*z* (%): 360 (14) [M^+], 260 (60), 259 (40), 159 (100), 85 (66); elemental analysis calcd (%) for $C_{20}H_{24}O_4S$: C 66.64, H 6.71, S 8.89; found: C 66.48, H 6.81, S (8.88).

A sample of the bis-protected ether (2.50 g, 6.94 mmol), was treated according to GP 1 with triphenylphosphine (4.36 g, 16.6 mmol) and bromine (2.66 g, 16.7 mmol) in dichloromethane (100 mL). After work-up (see above) the dibromide **57b** (2.07 g, 95%) was obtained as colorless needles (dichloromethane/pentane). M.p. 62°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.16$ (s, 4H, -CH_2-), 7.08 ppm (s, 2H, -CH=); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.84$ (t), 79.25 (s), 89.34 (s), 124.01 (s), 132.73 ppm (d); IR (KBr): $\tilde{\nu} = 3004$ (w), 2994 (w), 2223 (s), 1198 (vs), 809 cm^{-1} (s); UV (acetonitrile): λ_{max} (log ε) = 192 (4.28), 316 nm (4.45); MS (70 eV): *m*/*z* (%): 320 (10) [M^+], 318 (20) [M^+], 316 (9) [M^+], 239 (100), 237 (98), 158 (92); elemental analysis calcd (%) for $C_{10}H_6SBr_2$: C 37.77, H 1.90, S 10.08; found: C 37.42, H 1.90, S 10.29.

b) Debromination of 57b to 59b: According to GP 3 **57b** (1.00 g, 3.15 mmol) was treated with **14** (1.72 g, 4.73 mmol) and cesium fluoride (0.714 g, 4.73 mmol) in DMF (50 mL). After work-up (see above) **59b** (150 mg, 30%) was isolated as colorless needles (dichloromethane/methanol). M.p. 120°C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.70$ (s, 8H, -CH_2-), 6.89 ppm (s, 4H, -CH=); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 19.89 (t), 77.21 (s), 95.32 (s), 125.25 (s), 129.01 ppm (d); IR (KBr): $\tilde{\nu} =$ 2929 (w), 2210 (w), 1450 (m), 1188 (m), 1045 (m), 933 (m), 817 (s), 809 cm^{-1} (s); UV (acetonitrile): λ_{max} (log ε) = 210 (4.32), 218 (4.40), 296 nm (4.55); MS (70 eV): *m*/*z* (%): 316 (100) [M^+], 158 (33); elemental analysis calcd (%) for $C_{20}H_{12}S_2$: C 75.91, H 3.82, S 20.26; found: C 75.48, H 3.73, S 19.83.

Cross-dimerization

[6.6](1,4)Naphthaleno-(2.5)-thiophenophan-1,5,11,15-tetrayne (60): According to GP 3 a mixture of **50** (0.569 g, 1.57 mmol) and **57b** (0.550 g, 1.57 mmol) was treated with **14** (3.42 g, 4.71 mmol) and cesium fluoride (1.42 g, 9.42 mmol) in acetonitrile (100 mL). Yield: 110 mg of a mixture of **52** (9.5%), **59b** (2.7%), and **60** (10%), the ratio being determined by ^{1}H NMR analysis. The mixed dimer **60** is an unstable compound that decomposed during column chromatography on silica gel. Its NMR spectra were determined in the above mixture, subtracting the signals for the known cyclodimers **52** and **59b**.

Compound 60: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.76$–2.79 (m, 8H, -CH_2 CH_2-), 6.56 (s, 2H, thiophene ring), 7.51–8.33 (AA′BB′-m, 4H, unsubst. naphthalene ring), 7.57 ppm (s, 2H, subst. naphthalene ring); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 19.28$ (t), 20.16 (t), 76.30 (s), 84.32 (s), 93.14 (s), 97.01 (s), 122.14 (s), 124.93 (s), 126.84 (d), 126.76 (d), 128.09 (d), 129.66 (d), 134.13 ppm (s).

Attempted preparation of [10.10]paracyclophan-1,3,7,9,17,19,23,25-octayne (65)

a) 1,4-Bis-(5-bromo-1,3-pentadiynyl)benzene (64): To methanol (150 mL) and aqueous ethylamine solution (70%, 50 mL) was added 1,4-bis(trimethylsilylethynyl)benzene (**61**, 4.00 g, 14.8 mmol), and the mixture was stirred for 30 min at room temperature. Subsequently hydroxylamine hydrochloride (200 g) and cuprous chloride (0.3 g) were added, followed by the addition of 1-bromopropargyl THP ether **62** (7.1 g, 32.6 mmol). After stirring for 1 h at room temperature, the reaction temperature was raised to 55°C, and the mixture stirred for an additional hour. For work-up the cooled solution was poured into saturated aqueous ammonium chloride solution (400 mL), and the coupling product **63** isolated by careful extraction with Et_2O. The combined organic phases were filtered through a pad of silica gel, the solvent was removed by rotary evaporation and the remaining solid purified by column chromatography on silica gel with dichloromethane to yield 1,4-bis-(5-tetrahydropyran-2-yloxy-1,3-pentadiynyl)benzene (**63**, 3.86 g, 65%) as colorless needles. M.p. 88°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.51$–188 (m, 12H, THP-ring), 3.53–3.58 (m, 2H, THP-ring), 3.81–3.97 (m, 2H, THP-ring), 4.41 (ps-s, 4H, propargyl-CH_2-), 4.48 (ps-t, $J = 3.3$ Hz, 2H, -$CH(O)_2$), 7.42 ppm (s, 4H, arom. H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 18.89$ (t), 25.24 (t), 30.11 (t), 54.56 (t), 61.99 (t), 70.16 (s), 75.90 (s), 77.00 (s), 80.26 (s), 96.96 (d), 122.30 (s), 132.44 ppm (d); IR (KBr): $\tilde{\nu} = 2943$ (m), 2240 (w), 1344 (m), 1149 (s), 1022 (s), 872 (s), 816 cm^{-1} (s); UV (acetonitrile): λ_{max} (log ε) = 196 (4.73), 228 (4.74), 292 (4.50), 306 (4.76), 328 nm (4.90); MS (70 eV): *m*/*z* (%): 402 (35) [M^+], 302 (100), 234 (28), 218 (64), 202 (95), 85 (45); elemental analysis calcd (%) for $C_{26}H_{26}O_4$: C 77.59, H 6.51; found: C 77.58, H 6.53.

b) 1,4-Bis-(5-bromo-1,3-pentadiynyl)benzene (64): According to GP 1 **63** (1.00 g, 2.49 mmol) was treated with triphenylphosphine (1.56 g, 5.97 mmol) and bromine (0.96 g, 5.97 mmol) in dichloromethane (70 mL). After work-up (see above) **64** (0.86 g, 96%) was obtained as slightly yellow needles (dichloromethane). M.p. 138°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.06$ (s, -CH_2-), 7.50 ppm (s, 4H, arom. H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.23$ (t), 70.93 (s), 75.68 (s), 78.30 (s), 78.81 (s), 122.21 (s), 132.23 ppm (d); IR (KBr): $\tilde{\nu} = 2984$ (w), 2240 (w), 2217 (w), 1403 (m), 1195 (s), 830 cm^{-1} (s); UV (acetonitrile): λ_{max} (log ε) = 200 (4.70), 238 (4.26), 314 (4.72), 334 nm (4.75); MS (70 eV): *m*/*z* (%): 362 (10) [M^+], 360 (24) [M^+], 358 (11) [M^+], 281 (60), 279 (60), 200 (100), 100 (38); elemental analysis calcd (%) for $C_{16}H_8Br_2$: C 53.38, H 2.24; found: 53.36, H 2.29.

c) Attempted debromination of 64: According to GP 3 several attempts were undertaken to debrominate **64** to the cyclophane **65**. Although a spot was detected on the TLC plate having a R_f value in agreement with the expected hydrocarbon, in no case could this material be enriched or even purified. In all cases it was observed that this spot turned brown, and later black quickly.

[6.6]Biphenylparacyclophan-1,5,15,19-tetrayne (69)

a) 4,4′-Bis-(3-tetrahydropyran-2-yloxy-1-propynyl)biphenyl (67): According to GP 2 4,4′-dibromobiphenyl (**66**, 5.0 g, 16.0 mmol) was coupled with

29 (5.61 g, 40.0 mmol) in the presence of $[Pd(PPh_3)_4]$ (0.370 g, 0.32 mmol) and cuprous iodide (0.122 g, 0.64 mmol) in triethylamine (200 mL); **67** (6.5 g, 95%) as colorless needles (dichloromethane). M.p. 112°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.52–1.92 (m, 12H, THP-ring), 3.55–3.60 (m, 2H, THP-ring), 3.87–3.93 (m, 2H, THP-ring), 4.47–4.54 (AB-q, J = 15.7 Hz, 4H, propargyl-CH_2-), 4.91 (t, J = 3.3 Hz, 2H, -$CH(O)_2$), 7.49–7.54 ppm (AA′BB′-m, 8H, arom. H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.00 (t), 25.33 (t), 30.24 (t), 54.75 (t), 61.96 (t), 85.50 (s), 86.06 (s), 96.85 (d), 122.00 (s), 126.72 (d), 132.26 (d), 140.10 ppm (s); IR (KBr): $\tilde{\nu}$ = 3072 (w), 2943 (s), 2924 (s), 2869 (s), 2223 (vw), 1495 (s), 1117 (s), 1024 cm^{-1} (vs); UV (acetonitrile): λ_{max} (log ε) = 204 (4.65), 216 (sh, 4.38), 296 nm (4.70); MS (70 eV): *m*/*z* (%): 430 (18) [M^+], 346 (10), 329 (38), 246 (45), 230 (100), 85 (22); elemental analysis calcd (%) for $C_{28}H_{30}O_4$: C 78.11, H 7.02; found: C 77.96, H 7.04.

b) 4,4′-Bis-(3-bromo-1-propynyl)biphenyl (68): According to GP 1 **67** (4.00 g, 9.3 mmol) was treated with triphenylphosphine (5.84 g, 22.3 mmol) and bromine (3.57 g, 22.3 mmol) in dichloromethane (200 mL). After work-up (see above) **68** (3.35 g, 93%) was obtained as colorless needles (cyclohexane). M.p. 115°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.19 (s, 4H, -CH_2-), 7.50–7.56 ppm (AA′BB′-m, 8H, arom. H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.22 (t), 85.15 (s), 86.38 (s), 121.48 (s), 126.85 (d), 132.35 (d), 140.46 ppm (s); IR (KBr): $\tilde{\nu}$ = 3040 (vw), 2222 (w), 1495 (m), 1204 (s), 824 cm^{-1} (vs); UV (acetonitrile): λ_{max} (log ε) = 202 (4.70), 220 (sh, 4.38), 304 nm (4.75); MS (70 eV): *m*/*z* (%): 390 (12) [M^+], 388 (21) [M^+], 386 (10) [M^+], 309 (62), 307 (63), 228 (100); elemental analysis calcd (%) for $C_{18}H_{12}Br_2$: C 55.71, H 3.12; found: C 55.69, H. 3.08.

c) Debromination of 68 to 69: According to GP 3 **68** (0.530 g, 1.36 mmol) was treated with **14** (0.741 g, 2.04 mmol) and cesium fluoride (0.308 g, 2.04 mmol) in DMF (100 mL). After work-up (see above) **69** (13.8 mg, 5%) was obtained as colorless platelets (dichloromethane). M.p. 150°C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.75 (s, 8H, -CH_2CH_2-), 7.05–7.17 ppm (m, 16, arom. H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.39 (t), 84.89 (s), 91.09 (s), 122.83 (s), 126.19 (s), 131.79 (d), 139.30 ppm (s); IR (KBr): $\tilde{\nu}$ = 2922 (m), 2215 (vw), 1491 (m), 820 cm^{-1} (s); UV, qual. (acetonitrile): λ_{max} = 200, 288 nm; MS (70 eV): *m*/*z* (%): 456 (100) [M^+], 228 (74); HRMS: *m*/*z*: calcd for $C_{32}H_{24}$: 456.187; found: 456.187.

[6.6](2,7)Fluorenophan-1,5,15,19-tetrayne (71)

a) 2,7-Bis-(3-bromo-1-propynyl)-9*H*-fluorene (70): According to GP 2 2,7-dibromofluorene (5.0 g, 15.4 mmol) was coupled with **29** (5.40 g, 38.6 mmol) in the presence of $[Pd(PPh_3)_4]$ (0.36 g, 0.31 mmol) and cuprous iodide (0.116 g, 0.31 mmol) in triethylamine (200 mL) for 7 h at 80°C. After work-up (see above) the bis-THP ether of 2,7-bis-(3-hydroxy-1-propynyl)fluorene (6.6 g, 97%) was isolated as colorless needles (dichloromethane). M.p. 94°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.42–1.92 (m, 12H, THP-ring), 3.55–3.60 (m, 2H, THP-ring), 3.83 (s, 2H, fluorene-CH_2), 3.87–3.93 (m, 2H, THP-ring), 4.48–4.54 (AB-q, J = 15.7 Hz, 4H, propargyl-CH_2), 4.92 (t, J = 3.3 Hz, 2H, -$CH(O)_2$), 7.46 (d, J_o = 7.9 Hz, 2H, arom. H), 7.60 (s, 2H, arom. H), 7.66 ppm (d, J_o = 7.9 Hz, 2H, arom. H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.02 (t), 25.35 (t), 30.26 (t), 36.42 (t), 54.80 (t), 61.96 (t), 85.36 (s), 86.28 (s), 96.81 (d), 119.90 (d), 121.19 (s), 128.35 (d), 130.79 (d), 141.18 (s), 143.33 ppm (s); IR (KBr): $\tilde{\nu}$ = 3066 (w), 2938 (s), 2924 (s), 2870 (m), 2226 (w), 1468 (s), 1131 (s), 1117 (s), 1033 (s), 1025 cm^{-1} (s); UV (acetonitrile): λ_{max} (log ε) = 210 (4.63), 294 (4.56), 304 (4.68), 312 (4.63), 320 (4.65), 324 nm (4.88); MS (70 eV): *m*/*z* (%): 442 (30) [M^+], 358 (13), 341 (39), 258 (63), 242 (100), 203 (48), 85 (21); elemental analysis calcd (%) for $C_{29}H_{30}O_4$: C 78.71, H 6.83; found: C 78.81, H 6.82.

The bis-ether (1.99 g, 4.5 mmol) was treated according to GP 1 with triphenylphosphine (2.83 g, 10.8 mmol) and bromine (1.73 g, 10.8 mmol) in dichloromethane (10 mL). After work-up (see above) the dibromide **70** (1.68 g, 93%) was isolated as colorless needles (dichloromethane). M.p. 171°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.84 (s, 2H, fluorene-CH_2), 4.24 (s, 4H, propargyl-CH_2), 7.45 (dd, J_o = 7.9, J_m = 0.4 Hz, 2H, arom. H), 7.61 (d, J_m = 0.4 Hz, 2H, arom. H), 7.68 ppm (d, J_o = 7.9 Hz, 2H, arom. H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.54 (t), 36.50 (t), 84.61 (s), 87.32 (s), 120.16 (d), 120.75 (s), 128.51 (d), 130.98 (d), 141.59 (s), 143.50 (s) ppm; IR (KBr): $\tilde{\nu}$ = 3002 (w), 2216 (m), 1468 (s), 1202 (s), 813 cm^{-1} (s); UV (acetonitrile): λ_{max} (log ε) = 206 (4.60), 308 (4.61), 332 nm (4.79); MS (70 eV): *m*/*z* (%): 402 (8) [M^+], 400 (20) [M^+], 398 (10) [M^+], 312 (64), 319 (63), 240 (100); elemental analysis calcd (%) for $C_{19}H_{12}Br_2$: C 57.04, H 3.02; found: C 57.18, H 3.03.

b) Debromination of 70 to 71: According to GP 3 **70** (1.00 g, 2.50 mmol) was treated with **14** (1.36 g, 3.75 mmol) and cesium fluoride (0.566 g, 3.75 mmol) in DMF (100 mL). After work-up (see above) **71** (15 mg, 2.5%) was obtained as colorless platelets (dichloromethane). M.p. 140°C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.74 (s, 4H, fluorene-CH_2), 2.75 (s, 8H, -CH_2CH_2-), 6.99 (s, 4H, arom. H), 7.40 (d, J_o = 8.0 Hz, 4H, arom. H), 7.66 ppm (d, J_o = 8.0 Hz, 4H, arom. H); IR (KBr): $\tilde{\nu}$ = 3053 (w), 2927 (w), 2908 (w), 2223 (w), 1467 (s), 821 cm^{-1} (s); UV, qual. (acetonitrile): λ_{max} = 194, 202, 296, 302, 318, 330 nm; MS (70 eV): *m*/*z* (%): 480 (100) [M^+], 240 (52); HRMS: *m*/*z*: calcd for $C_{38}H_{24}$: 480.1879; found: 480.187.

[10.10](2,5)Thiophenophan-1,3,7,9,15,17,21,23-octayne (75)

a) 2,5-Bis-(5-tetrahydropyran-2-yloxy-1,3-penadiynyl) thiophene (73): As described for the preparation of **63** above, the bis-ether **73** was prepared from 2,5-bis-(trimethylsilylethynyl)thiophene (**72**, 5.5 g, 20.0 mmol; prepared according to ref. [29]) and **62** (9.64 g, 44.0 mmol) using methanol (150 mL), aqueous ethylamine solution (70%, 50 mL), hydroxylamine hydrochloride (2.0 g) and cuprous chloride (0.3 g). After work-up (see above) **73** (4.2 g, 52%) was obtained as a yellow, glassy solid. M.p. 37°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.48–1.86 (m, 12H, THP-ring), 3.50–3.56 (m, 2H, THP-ring), 3.78–3.84 (m, 2H, THP-ring), 4.39 (s, 4H, propargyl-CH_2), 4.80 (t, J = 3.3 Hz, 2H, -$CH(O)_2$), 7.12 ppm (s, 2H, -CH=); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.87 (t), 25.23 (t), 30.10 (t), 54.53 (t), 61.97 (t), 69.95 (s), 69.97 (s), 78.79 (s), 82.20 (s), 96.95 (d), 124.19 (s), 134.06 ppm (d); IR (KBr): $\tilde{\nu}$ = 2942 (m), 2870 (w), 2229 (w), 1344 (m), 1202 (m), 1121 (s), 1045 cm^{-1} (s); UV (acetonitrile): λ_{max} (log ε) = 196 (4.77), 226 (4.27), 236 (4.54), 248 (4.15), 260 (4.01), 344 (4.56), 362 nm (4.66); MS (70 eV): *m*/*z* (%): 408 (30) [M^+], 308 (100), 307 (44), 207 (56), 163 (45), 85 (44); elemental analysis calcd (%) for $C_{24}H_{24}O_4S$: C 70.56, H 5.92; found: C 70.26, H 5.99.

b) 2,5-bis-(5-bromo-1,3-pentadiynyl)thiophene (74): According to GP 1 **73** (1.00 g, 2.45 mmol) was treated with triphenylphosphine (1.54 g, 5.88 mmol) and bromine (0.94 g, 5.88 mmol) in dichloromethane (100 mL). After work-up (see above) **74** (0.85 g, 95%) was isolated as yellow, thin needles (cyclohexane). M.p. 95°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.06 (s, 4H, -CH_2-), 7.15 ppm (s, 2H, -CH=); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.11 (t), 70.23 (s), 71.77 (s), 78.61 (s), 80.18 (s), 124.22 (s), 134.47 ppm (d); IR (KBr): $\tilde{\nu}$ = 3098 (w), 2949 (w), 2225 (m), 1193 (s), 799 cm^{-1} (s); UV (acetonitrile): λ_{max} (log ε) = 194 (4.71), 242 (4.44), 346 (4.60), 368 nm (4.58); MS (70 eV): *m*/*z* (%): 368 (15) [M^+], 366 (28) [M^+], 364 (16) [M^+], 287 (81), 285 (79), 206 (100), 161 (26), 103 (25); elemental analysis calcd (%) for $C_{14}H_6Br_2S$: C 45.93, H 1.65, S 8.76; found: C 45.72, H 1.69, S 8.39.

c) Debromination of 74 to 75: According to GP 3 **74** (0.78 g, 2.13 mmol) was treated with **14** (2.32 g, 6.39 mmol) and cesium fluoride (1.93 g, 12.78 mmol) in acetonitrile (50 mL). After work-up (see above) **75** (80 mg, 18%) was isolated, as an unstable yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.65 (s, 8H, -CH_2CH_2-), 7.04 ppm (s, 4H, -CH=); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.59 (t), 68.14 (s), 68.70 (s), 79.86 (s), 85.41 (s), 125.22 (s), 131.88 ppm (s).

Bis-(4-(3-bromo-1-propynyl)-phenyl)acetylene (76)

a) Bis-(4-bromophenyl)acetylene: A mixture of 1-bromo-4-ethynylbenzene (2.0 g, 11.0 mmol), 1-bromo-4-iodobenzene (3.13 g, 11.0 mmol), and $[Pd(PPh_3)_4]$ (0.254 g, 0.22 mmol) was stirred under nitrogen in propylamine and pyridine (1:1, 50 mL) for 24 h at room temperature. For hydrolysis saturated aqueous ammonium chloride solution was added (300 mL), and the reaction mixture thoroughly extracted with dichloromethane. The combined extracts were filtered through a pad of silica gel, the solvent was removed in vacuo, and the remaining solid purified by column chromatography on silica gel with pentane to yield the dibromide (2.83 g, 77%) as colorless plates (dichloromethane). M.p. 176°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.50 ppm (AA′BB′-m, arom. H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 89.41 (s), 121.88 (s), 122.78 (s), 131.69 (d),

132.99 ppm (d); MS (70 eV): *m/z* (%): 338 (52) [M^+], 336 (100) [M^+], 334 (54) [M^+], 176 (59).

b) Bis-(4-(3-tetrahydro-2*H*-2-pyranyloxy-1-propynyl)acetylene: According to GP 2 the above dibromide (2.0 g, 5.95 mmol) was coupled with **29** (1.84 g, 13.11 mmol) in the presence of [$Pd(PPh_3)_4$] (0.21 g, 0.19 mmol) in propylamine (50 mL) by heating the reaction mixture for 18 h under reflux. After work-up (see GP 2) the bis-protected propargyl ether (2.65 g, 98%) was isolated as colorless needles (dichloromethane). M.p. 125 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.55–1.91 (m, 12H, THP-ring), 3.54–3.60 (m, 2H, THP-ring), 3.86–3.92 (m, 2H, THP-ring), 4.46–4.53 (AB-q, J = 15.8 Hz, 4H, propargyl-CH_2-), 4.89 (t, J = 3.3 Hz, 2H, -$CH(O)_2$), 7.41–7.51 ppm (AA′BB′-m, 8H, arom. H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.06 (t), 25.39 (t), 30.30(t), 54.77 (t), 62.06 (t), 85.42 (s), 87.20 (s), 90.75 (s), 122.82 (s), 123.01 (s), 131.46 (d), 131.80 ppm (d); IR (KBr): $\tilde{\nu}$ = 2940 (m), 2849 (w), 2238 (w), 1517 (s), 1200 (s), 1120 (s), 1029 (s), 841 cm^{-1} (s); UV (acetonitrile): λ_{max} (log ε) = 198 (4.67), 218 (4.34), 312 (4.80), 334 nm (4.80); MS (70 eV): *m/z* (%): 454 (25) [M^+], 354 (23), 353 (28), 270 (35), 254 (100), 85 (15); elemental analysis calcd (%) for $C_{30}H_{30}O_4$: C 79.29, H 6.65; found: C 79.18, H 6.62.

c) Bis-(4-(3-bromo-1-propynyl)phenyl)acetylene (76): According to GP 1 the above bis-THP ether (2.00 g, 4.40 mmol) was treated with triphenylphosphine (2.77 g, 10.56 mmol) and bromine (1.69 g, 10.56 mmol) in dichloromethane (100 mL). After work-up (see GP 1) **76** (1.54 g, 85%) was obtained as slightly yellow needles (dichloromethane). M.p. 194 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.17 (s, 4H, propargyl-CH_2), 7.41–7.48 ppm (AA′BB′-m, 8H, arom. H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.08 (t), 86.19 (s), 86.25 (s), 90.96 (s), 122.23 (s), 123.36 (s), 131.56 (d), 131.89 ppm (d); IR (KBr): $\tilde{\nu}$ = 2998 (w), 2216 (w), 1517 (s), 1202 (s), 839 (s), 609 cm^{-1} (s); UV (acetonitrile): λ_{max} (log ε) = 198 (4.72), 220 (4.34), 318 (4.79), 338 nm (4.74); MS (70 eV): *m/z* (%): 414 (10) [M^+], 412 (20) [M^+], 410 (9) [M^+], 333 (61), 331 (60), 252 (100), 215 (84), 163 (13), 126 (33), 84 (56); elemental analysis calcd (%) for $C_{20}H_{12}Br_2$: C 58.29, H 2.93; found: C 58.46, H 2.93.

d) Debromination of 76: On debromination of **76** according to GP 3 no dimeric hydrocarbons could be isolated from the reaction mixture.

8,10-Bis-(4-(3-bromo-1-propynyl)phenyl-*ortho*-diethynylbenzene (77)

a) 1-(4-Bromophenyl)-3-tetrahydro-2*H*-2-pyranyloxy-1-propyne: According to GP 2 1-bromo-4-iodobenzene (5.0 g, 35.3 mmol) and **29** (5.93 g, 42.4 mmol) were coupled in the presence of [$Pd(PPh_3)_4$] (0.800 g, 0.71 mmol) in anhydrous propylamine (80 mL) at room temperature (reaction time: 24 h). After work-up (see above) the THP-ether (8.69 g, 84%) was isolated by kugelrohr distillation (170 °C, 1 Torr) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.53–1.90 (m, 6H, THP-ring), 3.53–3.58 (m, 1H, THP-ring), 3.84–3.90 (m, 1H, THP-ring), 4.42–4.50 (AB-q, J = 15.8 Hz, 2H, propargyl-CH_2), 4.79 (t, J = 3.4 Hz, 1H, $CH(O)_2$), 7.28–7.43 ppm (m, 4H, arom. H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.95 (t), 25.30 (t), 30.19 (t), 54.63 (t), 61.89n (t), 84.61 (s), 86.36 (s), 96.83 (d), 121.63 (s), 122.60 (s), 131.45 (d), 133.19 ppm (s); IR (KBr): $\tilde{\nu}$ = 2943 (s), 2870 (m), 2246 (w), 1486 (s), 1120 (s), 1026 (s), 1011 (s), 824 cm^{-1} (s); UV (acetonitrile): λ_{max} (log ε) = 198 (4.39), 250 (4.40), 260 nm (4.36); MS (70 eV): *m/z* (%): 296 (7) [M^+], 294 (8) [M^+], 195 (100), 193 (99), 115 (52), 85 (43); elemental analysis calcd (%) for $C_{14}H_{15}O_2Br$: C 56.97, H 5.12; found: C 56.87, H 5.14.

b) 8,10-Bis-(4-phenyl-1-(3-tetrahydro-2*H*-2-pyranyloxy-1-propyne)-*ortho*-diethynylbenzene: A mixture of *ortho*-diethynylbenzene (0.89 g, 7.0 mmol), the bromide (4.6 g, 15.49 mmol) prepared under a), and [$Pd(PPh_3)_4$] (0.69 g, 0.62 mmol) in propylamine (80 mL) was heated under reflux for 24 h. Work-up as described under GP 2 provided the bis-THP-ether (1.7 g, 44%), amorphous solid (dichloromethane). M.p. 91 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.49–1.91 (m, 12H, THP-ring), 3.54–3.59 (m, 2H, THP-ring), 3.86–3.92 (m, 2H, THP-ring), 4.46–4.53 (AB-q, J = 15.8 Hz, 4H, propargyl-CH_2), 4.90 (t, J = 3.4 Hz, 2H, -$CH(O)_2$), 7.29–7.31 and 7.53–7.56 (AA′BB′-m, 4H, *ortho*-subst. arom. ring), 7.33–7.43 and 7.47–7.52 ppm (AA′BB′-m, 8H, *para*-subst. arom. ring); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.99 (t), 25.33 (t), 30.23 (t), 54.70 (t), 85.37 (s), 87.19 (s), 89.98 (s), 93.21 (s), 96.86 (d), 122.78 (s), 123.15 (s), 125.57 (s), 128.20 (d), 131.39 (d), 131.71 (d), 131.77 ppm (d); IR (KBr): $\tilde{\nu}$ = 2940 (s), 2214 (w), 1510 (m), 1119 (s), 1024 (s), 836 cm^{-1} (s); UV (acetonitrile): λ_{max} (log ε) = 196 (4.74), 280 (4.763), 294 (4.98), 330 nm (4.53); MS (70 eV): *m/z* (%): 554 (7) [M^+], 470 (20), 452 (15), 386 (38), 368 (36), 352 (42), 339 (77), 326 (50), 176 (35), 85 (100); elemental analysis calcd (%) for $C_{38}H_{34}O_4$: 82.28, H 6.18; found: C 82.26, H 6.22.

c) 8,10-Bis-(4-(3-bromo-1-propynyl)phenyl-*ortho*-diethynylbenzene (77): According to GP 1 the bis-THP-ether (1.40 g, 2.53 mmol), prepared as above, was treated with triphenylphosphine (1.59 g, 6.07 mmol) and bromine (0.97 g, 6.07 mmol) in dichloromethane (50 mL). After work-up (see GP 1) **77** (1.1 g, 85%) was obtained as a colorless powder (dichloromethane). M.p. 117 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.18 (s, 4H, -CH_2-), 7.31–7.35 and 7.53–7.57 (AA′BB′-m, 4H, *ortho*-subst. arom. ring), 7.39–7.43 and 7.48–7.51 ppm (AA′BB′-m, 8H, *para*-subst. arom. ring); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.09 (t), 86.19 (s), 86.29 (s), 90.34 (s), 93.18 (s), 122.21 (s), 123.75 (s), 125.61 (s), 128.38 (d), 131.53 (d), 131.88 (d), 131.92 ppm (d); IR (KBr): $\tilde{\nu}$ = 2996 (w), 2213 (w), 1508 (s), 1201 (s), 834 (s), 750 (s), 608 cm^{-1} (s); UV (acetonitrile): λ_{max} (log ε) = 196 (4.78), 296 (4.95), 332 nm (4.56); MS (70 eV): *m/z* (%): 514 (22) [M^+], 512 (40) [M^+], 510 (22) [M^+], 352 (62), 351 (100), 350 (92), 176 (60); elemental analysis calcd (%) for $C_{28}H_{16}Br_2$: C 65.65, H 3.15; found: 65.67, H 3.20.

d) Debromination of 77: On debromination of **77** according to GP 3 no dimeric hydrocarbons could be isolated from the reaction mixture.

X-Ray structure determinations: Crystal data and refinement details are presented in Table 1. Data collection and reduction: Crystals were mounted in inert oil on glass fibres and transferred to the cold gas stream of the diffractometer (**52**, **59a**: Stoe STADI-4; **59b**: Siemens P4, with appropriate low temperature attachments). Measurements were performed with monochromated $Mo_{K\alpha}$ radiation. Structure refinement: The structures were refined anisotropically against F^2 (program SHELXL-97, G. M. Sheldrick, University of Göttingen). Hydrogen atoms were included with a riding model. For **52**, intensity data were weak and displacement parameters were therefore restrained with the commands DELU and SIMU. In the absence of significant anomalous scattering, the Flack parameter is meaningless.

Table 1. Crystallographic data for compounds **52**, **59a**, and **59b**.

	52	**59a**	**59b**
formula	$C_{32}H_{20}$	$C_{20}H_{12}O_2$	$C_{20}H_{12}S_2$
M_r	404.48	284.30	316.42
habit	yellow tablet	colourless tablet	colourless tablet
cryst. size [mm]	0.45×0.4×0.11	0.8×0.35×0.15	0.5×0.4×0.18
crystal system	orthorhombic	monoclinic	orthorhombic
space group	*Pca*2$_1$	*P*2$_1$/*c*	*Pbca*
cell constants:			
a [Å]	9.265(2)	9.060(3)	13.1532(12)
b [Å]	14.683(3)	9.864(3)	15.1378(18)
c [Å]	15.750(3)	8.670(2)	15.6714(16)
α [°]	90	90	90
β [°]	90	107.91(2)	90
γ [°]	90	90	90
V [Å^3]	2142.6	737.2	3120.6
Z	4	2	8
ρ_x [Mg m^{-3}]	1.254	1.281	1.347
μ [mm^{-1}]	0.07	0.08	0.33
F(000)	848	296	1312
T [°C]	−130	−130	−100
$2\theta_{max}$	50	55	50
refl. measured	3859	1811	3256
refl. indep.	1957	1700	2743
R_{int}	0.097	0.018	0.028
parameters	289	100	199
restraints	301	0	0
$wR(F^2$, all refl.)	0.193	0.114	0.072
$R(F, >4\sigma(F))$	0.076	0.044	0.034
S	1.03	1.02	0.86
max. $\Delta\rho$ [e Å^{-3}]	0.23	0.22	0.18

CCDC-645858 (**52**), -645859 (**59a**), -645860 (**59b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The structure determination of compound **49** was reported in our earlier communication,[18] and the data were deposited under the number CSD-401565; the Cambridge refcode is ZEZSIG.

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