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[2.2]Paracyclophanes

[2.2]Paracyclophanes in Polymer Chemistry and Materials Science

*Henning Hopf**

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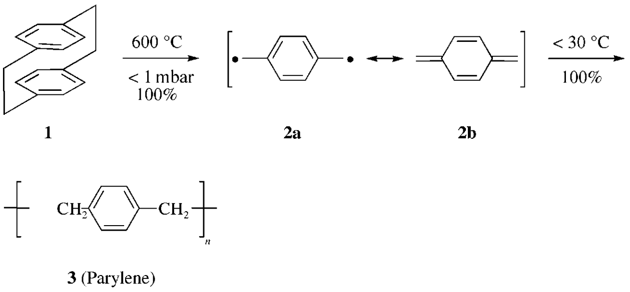
After a long period as model compounds in basic research [2.2]paracyclophanes are quickly gaining in practical importance. They can be incorporated into numerous polymeric systems in which they either lose (the so-called Parylenes) or retain their layered structure, and they can be used for the construction of unsaturated molecular scaffolds characterized not only by conventional (lateral) π-electron overlap but also by cofacial π-electron interactions. Surfaces generated from and with [2.2]paracyclophanes possess interesting biological, photophysical, and optoelectronic properties.

Although [2.2]paracyclophane (**1**, Scheme 1) will celebrate its 60th birthday next year,[1] there are no indications that this hydrocarbon is getting old. On the contrary, interest in this prototypical layered organic molecule is growing steadily. Whereas originally the investigation of its structural, spectroscopic, and chemical properties stood in the focus of numerous research projects,[2–7] in recent years interest is beginning to shift more and more to applications. Among these, the use of chiral cyclophanes as ligands for stereoselective synthesis[8] and the use of phanes in materials science, in particular polymer chemistry, stand out. The present Minireview summarizes the most important developments in the latter field.

[2.2]Paracylophane (**1**) and several of its simple derivatives have been used as monomers for the preparation of aromatic polymers for quite a while. In the Gorham process, developed in the mid-1960s,[9,10] **1** is quantitatively cleaved by vacuum vapor-phase pyrolysis at 600 °C to generate two molecules of *p*-xylylene (**2**, *p*-quinodimethane), the all-carbon analogue of *p*-benzoquinone. In a subsequent step the highly reactive **2** spontaneously polymerizes on surfaces (metals, glass, paper, plastics, ceramics etc.) maintained below 30 °C (Scheme 1).

The resulting linear poly-*p*-xylylenes **3** (trade name: Parylene), formed in quantitative yield, are crystalline polymers (molecular mass up to 500 000 g mol^{-1}) of outstanding conformity and uniform thickness. Coatings as thin as 0.1 μm without voids and pinholes have been reported. These coatings are thermally stable at temperatures of around 220 °C for extended periods of time and possess excellent dielectric properties that make the material a unique insulator. The polymer resists attack from most acids, bases, and solvents; it is a most effective inhibitor of fungal and bacterial growth. Parylene is widely used for the coating of printed circuits, for barrier coatings, in corrosion control, and as a dry lubricant. Since Parylene is prepared from a gas, it can penetrate spaces that conventional coatings cannot cover such as small crevices and spaces inside very fine tubes. The polymer conforms to virtually any shape, including sharp edges and points. Starting the dissociation/polymerization process with substituted derivatives of **1** furnishes the corresponding derivatives of **3**. In practice—besides the parent system **3** (Parylene N)—the most often used derivatives are Parylene C (prepared from monochloro-[2.2]paracyclophane) and Parylene D (from dichloro-[2.2]paracyclophane).[11]

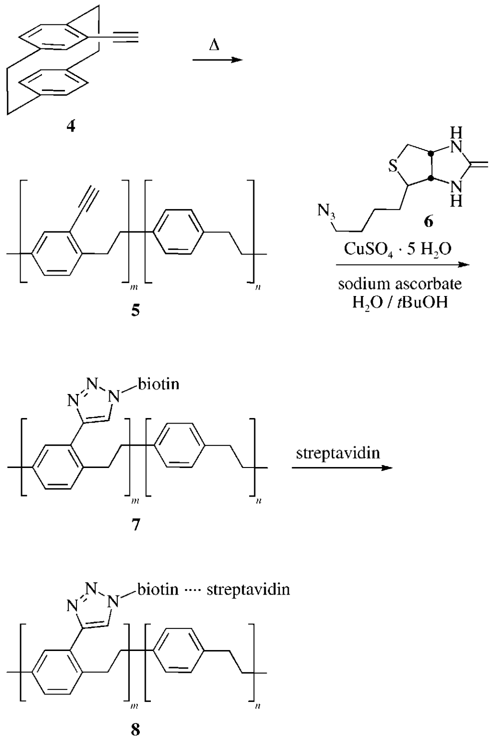
In fact, the introduction of novel substituents into **1**–**3** has made the Gorham polymerization (which uses no other



Scheme 1. The Gorham process for preparing Parylenes.

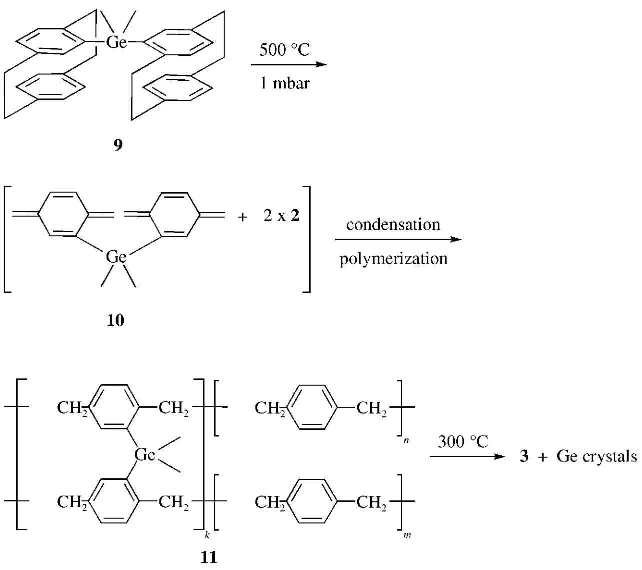
[*] Prof. Dr. H. Hopf
Institut für Organische Chemie
Technische Universität Braunschweig
Hagenring 30, 38106 Braunschweig (Germany)
Fax: (+49) 531-391-5388
E-mail: h.hopf@tu-bs.de

chemicals than those mentioned above) an actively investigated technology even today. In a recent application[12] various acetylenic [2.2]paracyclophanes such as 4-ethynyl-[2.2]paracyclophane (**4**)[13] were subjected to gas-phase vacuum pyrolysis at 680 °C/0.5 mbar. The resulting polymer **5** was then treated with biotinazide (**6**) to yield the cycloaddition product **7** in a click reaction (Scheme 2). Biotin is known to form a noncovalently bonded complex with streptavidin, thus allowing the fixation of biomolecules to the reactive polymer film (as in **8**). In principle bioactive surfaces as described here could be employed for the preparation of novel biomaterials (biosensors, microarrays).



Scheme 2. Preparation of biologically active surfaces by the Gorham route.

The use of a cyclophane derivative as a "carrier" for metal atoms is demonstrated by another example.[14] Chemical vapor deposition of the germanium derivative **9** under the usual conditions yields copolymer films **11**, presumably via bis *p*-xylylene **10** (Scheme 3). The structure of **11** was established by analytical and spectral data. When the polymer was annealed at 300 °C for 20 min its Ge–C bonds were destroyed and Parylene (**3**) was produced as well as germanium grains (diameter approximately 1 μm according to the X-ray pattern of the pyrolysis product) embedded in the poly(*p*-xylylene) matrix. This new hybrid material displays decreased electrical resistance relative to **3**, and is sensitive to air humidity in spite of the relatively low metal content of the crystals (ca. 4 vol %). Traditionally metal–polymer systems have been obtained by the treatment of polymer films with metal vapors or by the reduction of metal salts in solution in the presence of polymers.

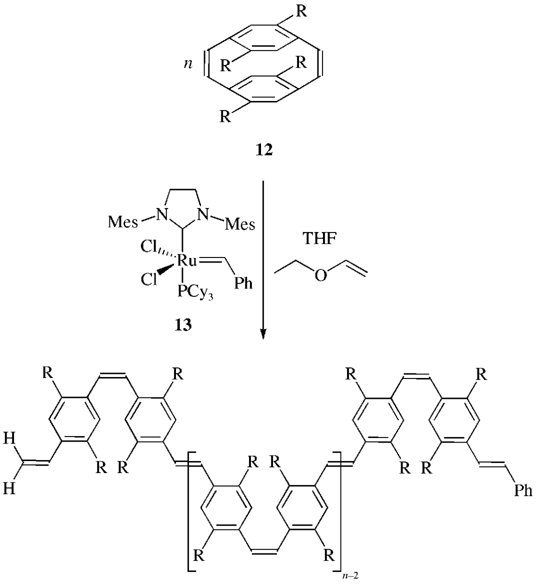


Scheme 3. Incorporation of metal crystals into Parylenes.

A different way of "destroying" the paracyclophane nucleus was followed in the case of the [2.2]paracyclophanediene derivatives **12** (Scheme 4).[15] Ring-opening metathesis polymerization (ROMP) of **12** in the presence of the second-generation Grubbs catalyst **13** in THF furnished the soluble polymer **14**, the molecular weight and structure of which were established by gel permeation chromatography and NMR spectroscopy. Depending on the **12**/**13** ratio the number-average molecular weight (M_n) varied between ca. 7000 and 24 000; the polydispersities of all polymer samples **14** were close to 1.2. The alternating *cis*/*trans* microstructure of the poly(*p*-phenylvinylene)s (PPVs, see below) was also established by NMR spectroscopy as well as by the corresponding out-of-plane vibrations in the FTIR spectra. Finally, the living nature of the ROMP process was demonstrated by controlled chain extension upon addition of further monomer.

In contrast to the above transformations in which the cyclophane nucleus is cleaved during the polymerization process, it is retained in the other large group of applications of cyclophanes in polymer chemistry and the transannular electronic interaction between the aromatic decks is deliberately introduced into the polymeric product. Linearly con-

Henning Hopf, born in 1940, studied chemistry at the Universities of Göttingen and Wisconsin (Madison), where he obtained his PhD degree in 1967. After his return to Germany he worked in Marburg and Karlsruhe (Habilitation, 1972), Würzburg, and Braunschweig, where he was Director of the Institute of Organic Chemistry from 1978 until his retirement in 2006. He has received numerous awards (including the Max-Planck-Forschungspreis, Adolf-von-Baeyer-Denkmünze, Gay-Lussac/Humboldt award) for his studies on unsaturated organic compounds. He served as vice-president of the German Chemical Society for two terms and as its President for one term (2004–2005).



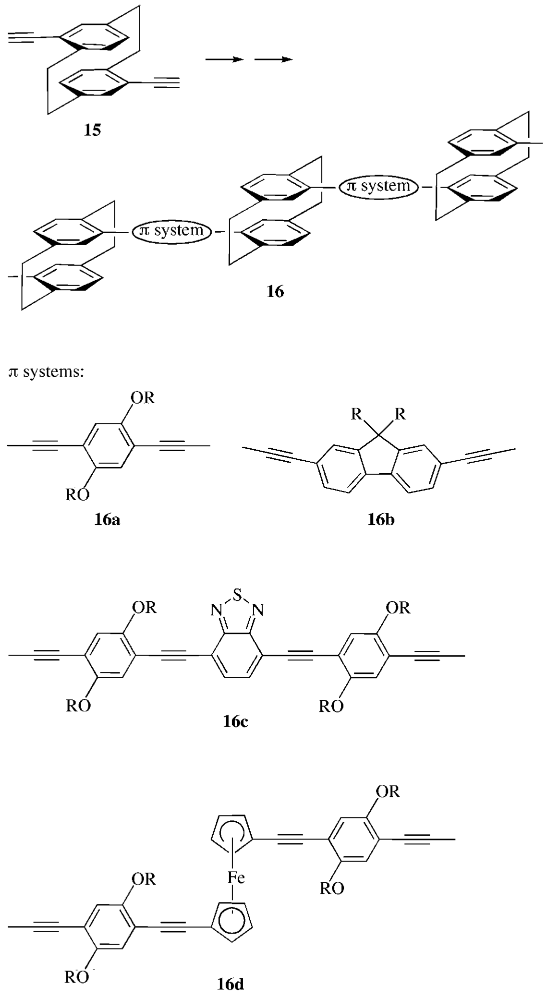
14 (R = OC_8H_{17})

Scheme 4. Preparation of poly(*p*-phenylvinylene)s by ROMP of [2.2]paracyclophanedienes. Cy = cyclohexyl, Mes = 2,4,6-trimethyl phenyl.

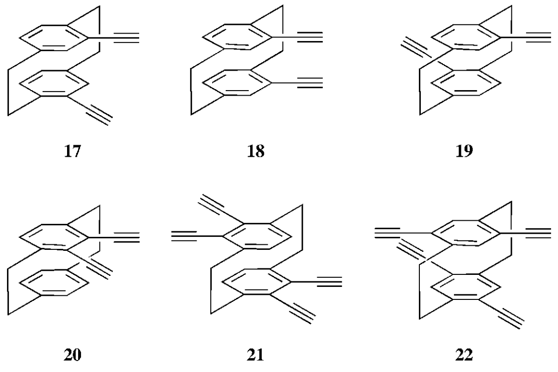
jugated macromolecules have been investigated extensively (polyacetylene, poly(arylenevinylene)s (PAVs, the most prominent example being poly(*p*-phenylenevinylene), PPV), poly(arylene–ethynylene)s (PAEs)[16,17]). In contrast, relatively little is known about the electronic and chemical properties of extended π systems containing unsaturated subunits that interact through space. To prepare these compounds appropriate cyclophane building blocks are coupled together using electrochemical and transition-metal-catalyzed polymerization processes, as well as by polycondensation with butyllithium. Since this area has been reviewed in this journal in 2006,[18] a few examples suffice to illustrate the types of polymers that have been prepared. Most of these polymers have been synthesized from *pseudo-para*-diethynyl[2.2]paracyclophane (**15**) and hence possess the general structure **16** (Scheme 5).

An impression of the structural variety that has been achieved is given by examples **16a–d**. The cyclophane-containing polymers can be processed into thin films by casting or spin-coating from toluene; they possess good thermal stability and show photoluminescence. For example, the fluorene derivative **16b** displays a strong emission of blue light in solution and in the solid state,[19] whereas the benzothiodiazole **16c** exhibits strong orange photoluminescence.[20] Although further optimization of these novel polymers will presumably be required, their application in optoelectronic materials and molecular devices seems likely.

One possible way of influencing the electronic properties of such compounds could involve changes in the substitution pattern of, for example, **15**. Recently the synthesis of isomers of this building block has been described, such as the diethynyl derivatives **17–20**,[13,21,22] as well as of higher ethynylated cyclophanes like the *anti*-configurated tetraethynyl hydrocarbon **21**[23] and its “crossed” isomer **22** (Scheme 6).[21] First coupling experiments with these hydrocarbons have already been carried out. With **18**, for example, derivatives could be prepared in which two extended unsaturated substituents are located directly over each other,[24] allowing the study of their intramolecular interaction.[25]



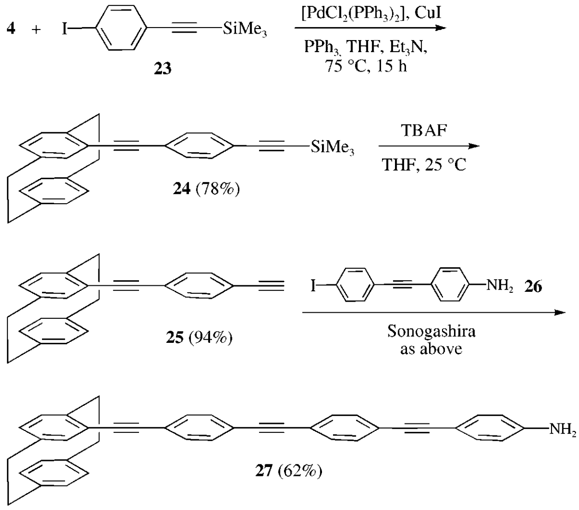
Scheme 5. Novel polymers containing [2.2]paracyclophane subunits.



Scheme 6. Ethynyl[2.2]paracyclophanes as building blocks for new molecular scaffolds.

Building blocks such as those summarized in Scheme 6 are useful substrates not only for the preparation of novel polymers but can also be employed for the deliberate construction of novel three-dimensional π systems by "molecular scaffolding". Phanes are very suitable for this purpose not only because of their rigid structure, but also since they may be regarded as polyvalent "superatoms". [2.2]Paracyclophane (**1**), for example, possesses 16 positions to which functional groups may be attached that then point in clearly defined directions in three-dimensional space and also have a fixed orientation towards each other. Furthermore, unlike other polyvalent superatoms—cubane, adamantane, even C_{60}—**1** can undergo two completely different types of reactions on its aromatic and aliphatic portions, resulting in the extraordinarily rich chemistry of the cyclophane system.[2–7]

Recent applications of [2.2]paracyclophane in materials science exploit this possibility of deliberately constructing three-dimensional π systems that not only show the usual overlap of *p* orbitals in benzene rings and $C{=}C$ and $C{\equiv}C$ bonds, but also the cofacial electronic overlap between the decks of a cyclophane.[26] An interesting example is the monosubstituted [2.2]paracyclophane **27** recently prepared by Taticchi and co-workers.[27] This cyclophane carries an extended side arm and displays all three types of conjugation (Scheme 7). To synthesize **27** the monoacetylene **4** was first coupled under Sonogashira conditions with the iodophenylacetylene **23** to provide the diyne **24**. This was desilylated to give **25** to allow a second chain-extension step, this time with the tolane derivative **26** to provide the target molecule **27**. A similar protocol has been used to prepare analogous cyclophane derivatives in which some of the benzene rings in the side arm are replaced by heteroaromatic systems[28] or anthracene units.[29] Derivatives of this type modify the electrochemical and optical properties of polymers in an interesting and varied fashion. For example, when **27** was incorporated as an electroactive component into a conductive polymer such as poly(3-butylthiophene), the blend showed a photoelectric response higher than that of the neat polymer.[27] Furthermore, a derivative of **27** in which the central benzene ring of the side arm is replaced by an anthracene moiety, has been employed as an active layer in solar cells.[29] The presence of both the anthracene unit and the terminal amino group is essential in this application: when the amino group was absent no photovoltaic behavior was observed.



Scheme 7. Modular approach for the construction of novel extended π systems. TBAF = tetrabutylammonium fluoride.

For the fabrication of devices based on molecular materials the patterning of surfaces with functional structures is of great importance. This type of patterning was possible with **27** by a multistep thin-film technology. A fluorine-doped tin oxide (FTO) surface was treated with CF_4 plasma through a mask, the mask was removed, and **27** was then drop-cast. The plasma-exposed surface displayed preferential wetting of **27** which displayed a nanometer-sized rodlike morphology on the surface. The photoresponse of this structured surface was much larger than that of **27** as a bulk compound.[30,31]

In yet another recent application of **27** the aminocyclophane was reacted with carboxy-functionalized single-walled carbon nanotubes (C-SWNTs) resulting in the formation of [2.2]paracyclophane-modified nanotubes. By the above mask-assisted deposition method these could then be selectively positioned on FTO/glass substrates, a prerequisite for their integration into optoelectronic devices.[32]

As this selection of recent applications shows, [2.2]paracyclophanes have long lost the status of more or less esoteric compounds of interest to only hydrocarbon chemists. Research on these compounds has been revitalized in numerous academic as well as industrial applications where the first recognized intriguing features of the cyclophanes, that is, their deformed benzene rings, are of secondary importance.

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