

Invited Review

Photochemical reactions applied to the synthesis of helicenes and helicene-like compounds



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ABSTRACT

Helicenes are composed of *ortho* annellated benzene moieties. Similar compounds contain heterocyclic or dihydrobenzene rings or smaller rings such as cyclopentadiene or cyclobutadiene (as part of benzocyclobutene units). The present article resumes photochemical reactions used for the preparation of these compounds. A very important and generally applicable reaction used for the synthesis of helicenes and helicene-like compounds is the photocyclization of stilbene subunits followed by oxidation. This reaction is often highly regioselective. The reaction can be conducted in the way that the formation of the helicene structure is favored. This selectivity is caused by the sum of the free valence numbers in the different positions of the stilbene precursor. Very fascinating structures are obtained with the cobalt catalyzed Vollhardt reaction which is photolytically supported. Helicenes are chiral and different methods of asymmetric synthesis were applied to the preparation of these compounds. A very convenient method is optical resolution using HPLC which is now currently used.

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Norbert Hoffmann studied chemistry at the Technical University (RWTH) Aachen, Germany and received his PhD degree in 1992 under the supervision of Hans-Dieter Scharf. In 1993, he obtained a permanent research position at the CNRS (Chargé de Recherche) in Reims, France. In 2004, he was appointed Research Director in the CNRS. His research interests are in the field of organic photochemistry: electron transfer, photoinduced radical reactions, cycloadditions of aromatic compounds, and application of these reactions to organic synthesis. Further research activities concern the production of fine chemicals from biomass and the synthesis of new organic semiconductor materials for microelectronics.

1. Introduction

Helicenes are carbon compounds which are constructed by *ortho* annellation of benzene. They are benzene analogs of phenanthrene [1,2]. When arranging benzene rings in this way, face-to-face overlapping necessarily occurs. A typical example is the heptahelicene or [7]helicene (Fig. 1) [3]. However, such steric interactions also occur in lower analogs such as [6] or [5]helicene derivatives. These interactions lead to the formation of typical helix structure and thus to chirality. One of the most characteristic properties of such compounds is their high optical activity [4]. For a recent theoretical treatments, see Ref. [5]. Recently, the vibrational circular dichroism (VCD) of helicenes has also been investigated [6]. The research interest in this field has been extended to helicene-like compounds incorporating heterocyclic moieties or smaller carbocycles such as cyclobutenes. Such compounds possess similar properties as the original helicenes. Helix structures with benzene moieties may also be generated by continuous *ortho* substitution with only one

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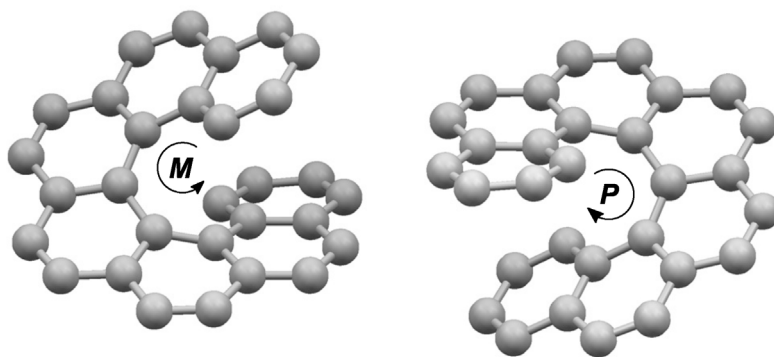


Fig. 1. Heptahelicene or [7]helicene (taken from X-ray structure analysis [3]).

C–C bond such as *ortho*-oligophenyl derivatives. For an interesting recent example of such compounds, see Ref. [7]. Meanwhile, a number of excellent reviews have been written on helicenes [8–20]. The fields of application of such compounds have also been extended [13,16]. The following article focuses on syntheses of helicenes and helicene-like compounds involving photochemical steps. These compounds may also be ranged among the exotic or fascinating molecules [1,21,22]. The synthesis of such compounds is often difficult using only conventional methods of organic synthesis. In such cases, photochemical reactions often provide solutions [23]. In combination with new reactor systems such as continuous flow- or microreactors and optimized light sources, these transformations are an efficient tool for the synthesis of complex molecular structures [24]. Application of these techniques often enables further optimization of photochemical reactions. Due to electronic excitation, the electronic configuration is changed and thus the chemical reactivity alters significantly [25–27]. Often, photochemical reactivity is even complementary to the chemical reactivity at the ground state. For this reason, a large variety of compounds becomes accessible which cannot or hardly be synthesized using thermal chemical reactions.

A lot of applications of helicenes have been reported [16]. Only some of them are mentioned here. Due their chiral properties (see below), helicenes were applied to asymmetric synthesis. Different phosphine ligands carrying a helicene moiety have been prepared [28]. Such compounds were, for instance, used for asymmetric hydrogenation. Helicenes carrying a nitrile group [29] have been used for asymmetric epoxidations [30]. These compounds may also be used as electron transfer sensitizers [31]. Helicenes were applied to asymmetric organocatalysis [32]. Optically enriched helicene samples added to the reaction mixture of an asymmetric autocatalytic Soai reaction are able to induce very efficiently chirality [33]. Due to high chiral amplification in this reaction, the chiral information is only needed in low amounts [34]. In the present case, this means that efficient chiral induction is possible with helicene samples possessing a low enantiomeric excess. A helicene moiety can also be incorporated in a crown ether [35]. Such compounds may be applied to chiral recognition [36,37]. Helicenes are used as chiral auxiliary in asymmetric synthesis [38]. Helicene structures are found in chemosensors [36,39]. Some foldamer structures with helicene moieties have been synthesized [37,40]. Helicenes are also incorporated into supramolecular structures [19]. For example, they have been used to induce chirality in liquid crystals by twisting a nematic phase [41]. Applications in material science have also been reported. Thus, capto/dative substituted helicenes have been tested in OLEDs [42]. Helicene interaction with DNA [37,43] or enzymes such as telomerase [44] or topoisomerase I [45] may be used for medicinal purposes. It must be pointed out that although the number of application fields is high, many applications are only superficially or occasionally investigated. In such cases, more

profound studies are necessary in order to develop the whole potential of helicenes in the corresponding application domains. In this context, new and efficient synthetic approaches to helicenes are also particularly needed.

2. Synthesis of carbohelicenes

Carbohelicenes are composed only of a benzene skeleton with a delocalized π -system (for example compare references [10,13,14]). In such systems, only the hydrogen atoms may be substituted. Among the photochemical methods used for the synthesis of helicenes, the photocyclization of stilbene moieties followed by dehydrogenation is the most important one. Thus the typical phenanthrene subunit is built up [46–50]. This reaction sequence was first reported in this context in the late 1960s. It marks a breakthrough in the synthesis of helicenes [9]. The stilbene derivative **1** undergoes photochemical *cis/trans* isomerization which yields compound **2** (Scheme 1) [51,52]. In most cases of such syntheses, photochemical *cis/trans* isomerization is involved. So, no particular effort is needed to prepare selectively the *cis* isomer of a starting compound. In a pericyclic reaction, compound **3** is formed. The conrotatory cyclization mode of the photochemical procedure favors a distant arrangement of the terminal arene moieties [53]. The irradiation was carried out in the presence of iodine which enables the oxidation of compound **3** to [7]helicene **4**. The photocyclization of conformer **5** to the corresponding regioisomer **6** is not observed. Simple Hückel calculations and the determination of the sum of the free valence numbers for the excited state enable the prediction of the regioselectivity of such reactions [10,47,52,54,55]. Of course, this parameter may also be calculated on higher level. The sum of the free valence numbers for the excited state $\Sigma F_{r,s}^*$ for two positions *r* and *s* is defined as: $F_r^* + F_s^* = (\sqrt{3 - \Sigma P_r^*}) + (\sqrt{3 - \Sigma P_s^*})$. ΣP^* is the sum of the bond orders at the excited state in a particular position. The following tendencies are observed. The photocyclization does not occur when $\Sigma F_{r,s}^* < 1$. When two reactions are in competition, only one of them is observed when $\Delta(\Sigma F_{r,s}^*) \geq 0.1$ between the two positions. Furthermore, in the case when $\Sigma F_{r,s}^* > 1$ and when the formation of planar product is in competition with the formation of a non planar product, the first one is favored. In the case of compound **1**, $\Sigma F_{2,2'}^* = 0.927$. For the formation of compound **6** via conformer **5** $\Sigma F_{4,2'}^* = 1.027$. Compound **6** is non-planar. The formation of compound **4** is favored since $\Sigma F_{4,4'}^* = 1.126$.

As a consequence of this relationship, the strategies of the syntheses may be optimized when the substitution at the alkene double bond is chosen in the right way. When compound **7** is irradiated, the [6]helicene **8** is only obtained in low yields while compound **9** is isolated as major product (Scheme 2) [10,52]. The helicene **8** resulted from C–C bond formation in positions 4 and 1' while **9** is generated by the formation of a C–C bond

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