



Synthesis, X-ray analysis and photophysical properties of a new N-containing pentacyclic helicene



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ABSTRACT

A new helically chiral pentacyclic system containing one pyrrole ring was prepared in a good yield and purity via a three-step sequence involving Heck coupling and classical oxidative photocyclization. X-ray crystal structure analysis indicated that the conformation resembled that of unsubstituted pentahelicene, the idealized symmetry of which is C_2 . The optical properties of the pentacyclic helicene were investigated and show interesting behaviour.

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Helicenes are polycyclic aromatic compounds formed from *ortho*-fused benzene or other aromatic rings that adopt a helical conformation to avoid overlapping of the terminal rings resulting in helically chiral structures. Their specific backbone, which combines electron delocalization and non-planarity of the π -electron network, makes them very stable towards acids and bases and relatively high temperatures.¹ These helically-shaped molecules have found applications as potentially useful components in chiral discotic liquid crystalline materials,² as building blocks for helical conjugated polymers³ and as rotors.⁴ In particular, functionalized helicenes are promising candidates for chiral catalysts⁵ and ligands⁶ in asymmetric syntheses because they have a rigid helical framework and possess high optical stability.

In recent years, the preparation of heterohelicenes has been studied extensively in order to exploit the unique properties of these chiral molecules.⁷ However, azahelicenes have not been elaborated sufficiently, and only a few reports have described the synthesis of nitrogen-containing helicenes, despite their possible applications in various branches of chemistry. Moreover, there are reports on only a few examples of azahelicene analogues with a pyrrole unit (pyrrolohelicenes), and methods with general applicability for the synthesis of such compounds are rare. The first representative of this family was pyrrolo[5]helicene **1** which was

synthesized by Meisenheimer and Witte in 1903 (Fig. 1).⁸ In an independent study, Fuchs and Niszel prepared the racemic pyrrolo[6]helicene **2**, in a two-step sequence.⁹ Following the same preparative pathway, Pischel et al.¹⁰ reported the synthesis of the corresponding tetramethyl derivative **3** in a low yield. Resolution of the latter was achieved only on analytical scale by chiral HPLC. Shi et al.¹¹ have described the synthesis of carbazole-based diaza[7]helicene **4**, and reported its use as a deep-blue dopant emitter in an organic light-emitting diode (OLED). Despite developments in helicene chemistry, it is still desirable to develop methods for easy access to pyrrolohelicenes via high yielding procedures for the examination of these compounds as ligands or for broader exploitation. Their delocalized π -electron system allows them to exhibit interesting opto- and photo-electronic

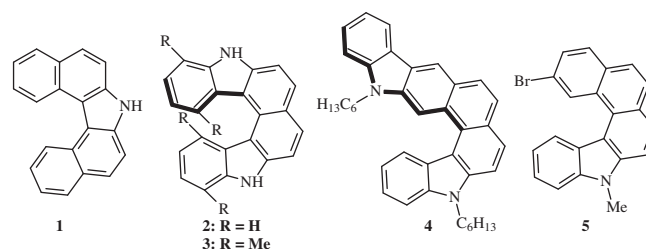


Figure 1. Structures of azahelicenes 1–5.

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properties. Thus, the development of new heterohelicenes and further studies of the underlying structure–property relationships represent an interesting challenge.

Thus, due to the small number of known azahelicenes and having in hand an alternative synthetic approach to helical compounds,¹² we have prepared nitrogen-containing helicene **5**.

The new helically chiral pentacyclic system **5**, containing one pyrrole unit, was prepared via a synthetic sequence relying on Mizoroki–Heck coupling and oxidative photodehydrocyclization reactions. Our procedure utilizes *N*-methylcarbazole (**6**) as the key building block for the synthesis of the helicene precursor **8**, which is then easily converted into the corresponding nitrogen-containing pentahelicene **5** by photocyclization. The nitrogen atom in this helically chiral compound could serve as a hydrogen acceptor as well as a metal-chelating agent for chirality recognition.

The synthetic route leading to the target helicene **5** began with the bromination of *N*-methylcarbazole (**6**) using *N*-bromosuccinimide (NBS) in chloroform, which provided monobrominated derivative **7** in 99% yield (Scheme 1). Compound **7** and 4-bromostyrene underwent a Mizoroki–Heck coupling reaction using 1% of Hermann's catalyst, sodium acetate as the base and with *N,N*-dimethylacetamide (DMA) as the solvent. The desired coupled product **8** was obtained in 75% yield by heating for two days at 140 °C. It was assumed to have *E*-stereochemistry at the double bond, based on a ¹H NMR study.¹³ The *Z*-isomer was neither isolated nor identified unambiguously as a minor product in the reaction mixture.

Finally, the resulting diarylethene **8** was subjected to photocyclization in toluene under irradiation with a Hanovia high-pressure mercury lamp, on a 200 mg scale per run, for about 2 h. The irradiation was carried out in the presence of a stoichiometric amount of iodine as oxidizing agent and an excess of tetrahydrofuran as a hydrogen iodide scavenger,¹⁴ to give the target aza[5]helicene **5** in 76% yield, after purification by column chromatography (Scheme 1).¹⁵

No other isomer was isolated from the reaction mixture, indicating that the ring closure of alkene **8** had occurred from the opposite side of the tricyclic moiety. Importantly, the anthracene-like derivative **9** (Fig. 2) was not formed during the cyclization step, as this regioisomer would be expected to display characteristic signals for both H-6 and H-13 at low field in the ¹H NMR spectrum.¹⁶

The helicene obtained was fully characterized by NMR spectroscopy and by HRMS, and was found to have good solubility in common organic solvents including dichloromethane, chloroform,

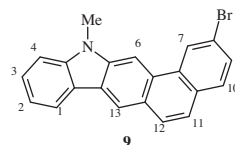


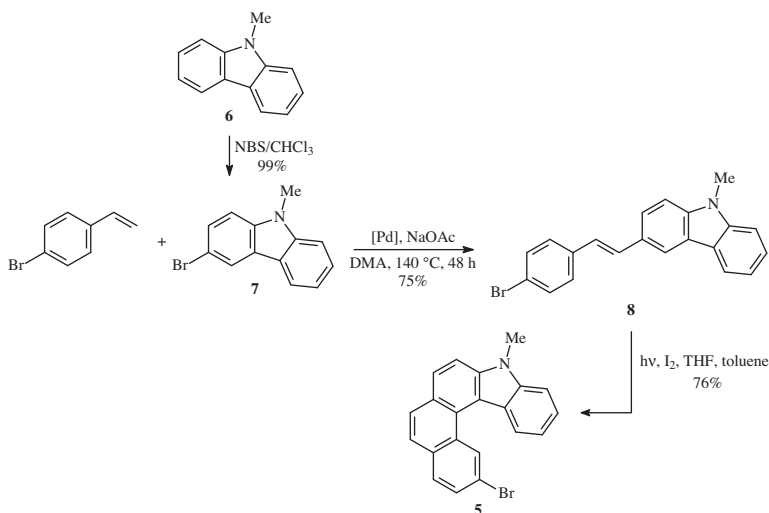
Figure 2. Chemical structure of the anthracene-like derivative **9**.

toluene, ethyl acetate and tetrahydrofuran. The product was highly stable in air and to light.

Suitable crystals of pentacyclic helicene **5** were obtained as pale yellow plates by slow evaporation of a dichloromethane solution at room temperature. X-ray analysis of the helicene was carried out on a single crystal obtained from the racemic form as shown in Figure 3. This compound did not undergo spontaneous resolution, though its space group was *P*bca. Some of the inner and outer bond lengths are given in Table 1. It was found that the pyrrole ring of the helicene molecule did not affect appreciably the outer bond lengths. The outer bonds C(5)–C(6), C(10)–C(11), C(13)–C(14) and C(16)–C(17) were shortened to 1.34–1.37 Å with respect to the average bond length in benzene (1.39 Å), whereas the inner bond distances C(1)–C(2), C(2)–C(3), C(1)–C(21), C(20)–C(21) and C(19)–C(20) were lengthened to 1.40–1.45 Å (Table 1). The distance between the hydrogen atoms H(3...H(19)) was found to be 2.098 Å and these H atoms point away from each other.

The torsion angles along the inner helical rim ($\varphi_1 = \text{C3–C2–C1–C21}$; $\varphi_2 = \text{C2–C1–C21–C20}$; $\varphi_3 = \text{C1–C21–C20–C19}$), which varied from 8.72° to 19.93°, were also a convenient measure of the helicity and were in accord with those observed in pentahelicene (Table 2). The terminal inner helical torsion angles (C3–C2–C1–C21 and C1–C21–C20–C19) were not equal and were relatively small angles of 8.72° and 17.41°, respectively. The distortion of the molecular structure (46.07°) is defined by the sum of the three dihedral angles (C3–C2–C1–C21, C2–C1–C21–C20 and C1–C21–C20–C19). The repulsion of the facing terminal benzene rings leads to an interplanar angle of 35.69° between the terminal benzene rings. The angles between the least-squares planes of neighbouring rings were between 7.39° and 10.74°.

The thermal behaviour of compound **5** was investigated by differential scanning calorimetry (DSC), with a heating rate of 10 °C/min from 25 to 300 °C, under a nitrogen atmosphere (Fig. 4). DSC indicated that compound **5** has a melting point of



Scheme 1. The synthesis of the helical pentacyclic system **5**.

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