

# Photochemical synthesis and structural properties of high membered thiohelicenes

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A general photochemical synthesis of large thiohelicenes containing nine and eleven rings is discussed along with the organisation of racemic thiohelicenes in crystals: heterochiral assembling is dominant except in the nine-ring system where interactions involving terminal ring S atoms favour the segregation of close-packed homochiral molecules in planes.

Helicenes are intrinsically chiral helical molecules structurally characterised by *ortho*-fusion of aromatic rings. Nonracemic, appropriately substituted systems exhibit a spontaneous organisation in macroscopic fibrous structures in the solid state, while in concentrated solutions and thin films a gigantic rotation of the plane of polarised light was evidenced.<sup>1–3</sup> The polyconjugated chiral structure of helicenes makes them interesting candidates for optoelectronic applications<sup>4</sup> and molecular devices.<sup>5</sup> Higher carbohelicenes are endowed with an inherent propensity to homochiral molecular recognition.<sup>6</sup>

Some studies on lower heterohelicenes containing thiophene rings were published long ago.<sup>7–9</sup> Here, we report on a general synthetic approach we used to prepare a series of heterohelicenes formed by alternate thiophene and benzene rings: trithia[5]heterohelicene **4**, tetrathia[7]heterohelicene **7** and, for the first time, large molecules such as pentathia[9]heterohelicene **10** and esathia[11]heterohelicene **13**. We also investigated the electronic and self assembling properties of these systems with the aim of establishing whether the preference for heterochiral molecular aggregation shown by the racemic five- and seven-member thiaheterohelicenes in crystals<sup>8,9</sup> persists in higher members of the series, specifically with reference to the crystal structure of **10**.

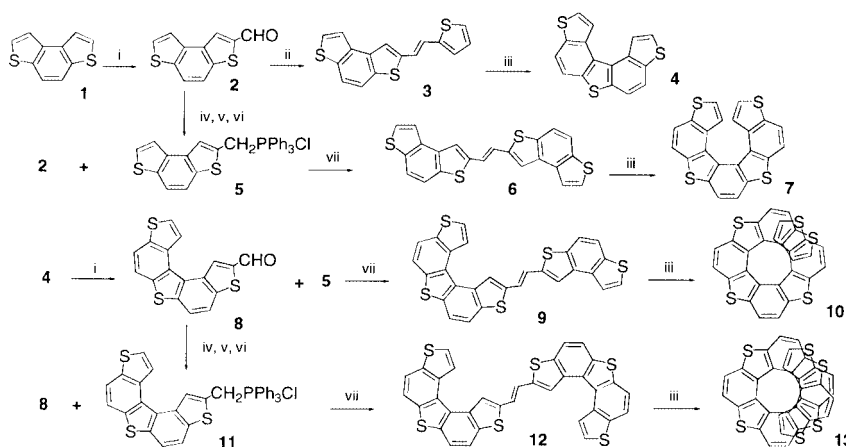
Substituted helicenes are obtained in good yield by chemical synthesis both in racemic or enantiomeric form.<sup>11,12</sup> We obtained a series of unsubstituted thiohelicenes using a general

procedure for the preparation of racemic molecules, shown in Scheme 1, where the photochemical cyclisation represents the final step. With this synthetic route it was possible to obtain molecules as large as the nine- and eleven-membered thiohelicenes.

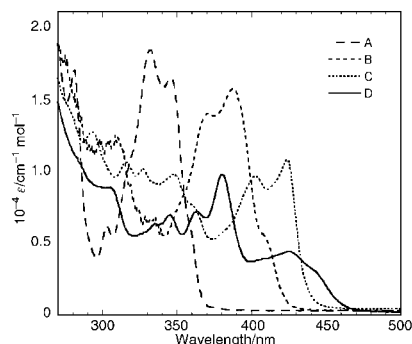
Two approaches were in principle possible to synthesise large condensed systems. The first consists of the double photochemical ring closure of a molecule containing two 1,2-disubstituted ethylenes. In this case the bis-ethylene molecule needs only to contain a heteroaryl moiety that does not exceed three members and can be easily prepared. The second possibility, preferable in the case of higher thiohelicenes, consists of a single photochemical cyclisation of a 1,2-diheteroarylethylene and larger heteroaryl substituents, such as thio[5]heterohelicenes, are necessary.

The synthesis of thio[*n*]helicene (*n* = 7, 9 condensed rings) starts by reacting thio[*n* – 4]helicene with Vilsmeier reagent [POCl<sub>3</sub> and PhN(Me)CHO in boiling toluene] in order to obtain the corresponding 2-carbaldehyde. The phosphonium salt **5** is produced from the 2-carbaldehyde **2** with a sequence of reactions illustrated in Scheme 1 and described elsewhere.<sup>13</sup> The Wittig reaction between the phosphonium salt and the 2-carbaldehyde of the thio[*n* – 4]helicene gives a 1,2-diheteroarylethylene. The racemic thio[*n*]helicene can be easily obtained in high yield by the photoinduced cyclodehydrogenation of appropriate 1,2-diheteroarylethylenes.<sup>†</sup> The synthesis of the larger esathia[11]helicene **13** begins with the reaction between the 2-carbaldehyde-thio[5]helicene **8** and the phosphonium salt of the thio[5]helicene **11**, followed by photocyclisation of the 1,2-diheteroarylethylenes **12**.<sup>†</sup>

Electronic absorption spectra of the thiohelicene series in solution are shown in Fig. 1. Upon increasing the number of condensed rings, the absorption bands shift to lower energy owing to the lengthening of the  $\pi$ -conjugation in the helical



**Scheme 1** Reagents and conditions: i, POCl<sub>3</sub>, PhN(Me)CHO, toluene; ii, (C<sub>4</sub>H<sub>5</sub>S)CH<sub>2</sub>PPh<sub>3</sub>Br, NaOMe, anhydrous MeOH; iii, hv: 350 nm or visible light; iv, NaBH<sub>4</sub>, EtOH–THF; v, SOCl<sub>2</sub>, benzene–Py; vi, PPh<sub>3</sub>, benzene; vii, NaOMe, anhydrous MeOH.

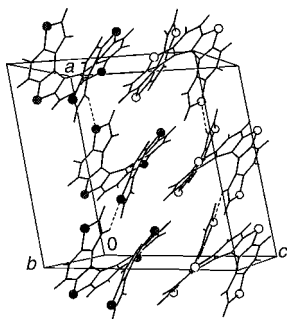


**Fig. 1** Electronic molar absorption spectra of molecules in chloroform solution: A trithia[5]heterohelicene, B tetrathia[7]heterohelicene, C pentathia[9]heterohelicene and D esathia[11]heterohelicene.

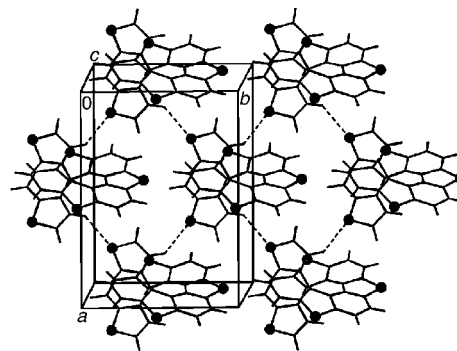
system. The photoluminescence spectra show a similar behaviour, with emissions that are red-shifted increasing the molecular size.<sup>‡</sup>

Fig. 2 and 3 show views of the packing of the nine ring helicene **10** as obtained by single crystal X-ray diffraction.<sup>§</sup> The structure of the eleven ring system **13** will be presented elsewhere.<sup>14</sup> The tendency to stacking of antipodes<sup>9</sup> in interdigitated columnar structures is apparent (Fig. 2) for all of the thiohelicene racemic structures including **10**. The stacking interactions involve especially the third and/or the fourth rings (from the molecular ends) of enantiomeric pairs, and vary depending upon the particular molecule. In all the systems investigated specific interactions engaging sulfur<sup>15,16</sup> and hydrogen atoms at distances slightly shorter than the sum of the van der Waals radii (1.80 Å for S and 1.20 Å for H) were found. They always involve atoms of terminal rings and are quite probably attractive playing a role in molecular recognition and self assembly. The contacts are S...S 3.544 Å and S...H 2.89 Å in the case of the five- and seven-ring systems respectively. In the case of **10** S...H interactions<sup>§</sup> at 2.87 Å appear a key feature of the microsegregation of homochiral, tubular molecules in planes parallel to the *ab* lattice plane (ca. Fig. 3). The helical axes of all molecules within a plane are parallel and form an angle of ca. 40° with *c*, while the twofold intramolecular axes are all parallel to *b*. The adopted *C2/c* space group corresponds to that predicted to yield best packing for racemic molecules preserving their *C2* symmetry in the crystal.<sup>17</sup>

We can conclude that for larger oligomers of thiohelicenes homochiral lateral aggregation of helices becomes more favourable. Interactions between terminal units are still important in the recognition pattern also for the nine- and eleven-ring systems. In the supermolecular tubular structures formed in racemic systems the two enantiomers alternate along a tube (Fig. 2). The role played by sulfur in the intermolecular interactions allows rationalisation of the different behaviour as



**Fig. 2** Crystal packing of pentathia[9]heterohelicene evidencing both the stacking of enantiomers along the *c* axis direction and planes of isochiral molecules parallel to the *ab* plane. The molecular chirality is made apparent by the graphic codes of the sulfur atoms.



**Fig. 3** Packing of pentathia[9]heterohelicene showing the arrangement of isochiral molecules in quasi-hexagonal planar assemblies parallel to the *ab* plane. Short S...H interactions are evidenced.

compared to carbohelicenes. Attempts at optically resolving **10** and **13** are in progress to determine their chiroptical properties and characterise the self assembling properties of large homochiral thiohelicenes.

## Notes and references

<sup>†</sup> Tetrathia[7]heterohelicene: photochemical cyclisation yield 85%; *m/z* 402;  $\delta$  6.76 for the  $\alpha$  hydrogen of thiophene. Pentathia[9]heterohelicene: photochemical reaction quantitative; *m/z* 508;  $\delta$  5.52 for the  $\alpha$  hydrogens. Esathia[11]heterohelicene: photochemical reaction yield 60%; *m/z* 614;  $\delta$  5.25 for the  $\alpha$  hydrogens.

<sup>‡</sup> Emission spectra of chloroform solutions: tetrathia[5]heterohelicene emission maximum 360 nm; tetrathia[7]heterohelicene 410 nm; pentathia[9]heterohelicene 440 nm; esathia[11]heterohelicene 480 nm.

<sup>§</sup> Crystal data for **10**:  $C_{28}H_{12}S_5$ ,  $M_r = 508.68$ , monoclinic, space group *C2/c* (no. 15),  $a = 14.655(1)$ ,  $b = 10.656(1)$ ,  $c = 13.976(1)$  Å,  $\beta = 100.25(1)^\circ$ ,  $V = 2147.7(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.57$  g cm<sup>-3</sup>,  $\mu = 5.098$  mm<sup>-1</sup>, 3662 reflections (1875 unique,  $R_{int} = 0.078$ ) were collected on a Siemens P4 diffractometer. The structure was solved by direct methods using the SIR97 program and refined by full-matrix least squares with SHELXL97. The final stage converged to  $wR(F^2) = 0.048$  ( $R_w = 0.123$ ). To better evaluate intermolecular contacts standard neutron C–H distances of 1.08 Å were used. CCDC 182/1649. See <http://www.rsc.org/suppdata/cc/b0/b002581j/> for crystallographic files in .cif format.

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