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Synthesis, enantiomeric resolution and optical properties of 8-cyanohexahelicene

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Abstract: A novel hexahelicene bearing a cyano group at a selected position on a middle aromatic ring has been synthesized, in good yield, through a short synthetic strategy involving the preparation of 2-bromo-5-cyanobenzo[*c*]phenanthrene as a synthetic intermediate. The racemate was resolved by HPLC on a chiral stationary phase providing both (+)- and (-)-**3** enantiomers with high optical purity. The absolute configurations of (+)- and (-)-**3** were assigned as *P* and *M*, respectively, by circular dichroism spectroscopy. The optical properties of the hexacyclic helicene were investigated and showed interesting behaviour.

Keywords: Photocyclization, Helicene, Enantiomeric resolution, Chiroptical properties.

Helicenes are polycyclic aromatic compounds in which the aromatic ring systems are *ortho* annulated leading to nonplanar screw-shaped skeletons. They exhibit helicoidal chirality even though they have no asymmetric carbon atoms or other chiral centres. The chirality arises from the steric hindrance between the terminal aromatic rings, which locks the system in either the clockwise and counterclockwise direction.[1] Both enantiomers can be isolated owing to their stability and rigid helical framework. These helically-shaped molecules exhibit unique electronic and chiroptical properties, such as strong circular dichroism (CD) and large optical rotations.[2] Those features are highly desirable in many fields of material sciences including optoelectric materials,[3] molecular machines,[4] molecular recognition[5] and self-assembly.[6] Furthermore, enantiomerically enriched helicenes have proved successful as chiral catalysts[7] and ligands[8] in asymmetric synthesis because of their rigid framework, high optical stability and resistance to isomerisation.