Organic & Biomolecular Chemistry

RSC Publishing

PAPER

View Article Online
View Journal | View Issue

Cite this: *Org. Biomol. Chem.*, 2013, **11**, 7522

Helicity discrimination in *N,N'*-dibenzoyl-1,2,3,4,7,8,9,10-octahydro-1,10-phenanthrolines and their thiono- and selenocarbonyl analogues by inclusion complexation with chiral diols†

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Received 12th June 2013,
Accepted 10th September 2013

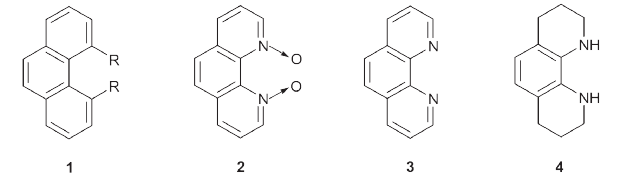
DOI: 10.1039/c3ob41216d

www.rsc.org/obc

X-ray crystallographic analysis of the title compounds revealed that they assume a folded helical conformation of an approximate C_2 symmetry in the solid state. Dithioamide **5b**, diselenoamide **5c** and monoselenoamide **5d** were resolved to enantiomers by inclusion crystallization with optically active diols (TADDOLs). The absolute configuration of the guest molecules in the complexes **5b·6a**, **5c·6a** and **5d·6a** was assigned as *P*. The optical activity of the resolved compounds is manifested by their CD spectra showing relatively strong Cotton effects in the region of thionoamide and selenoamide n–π* transition. The optically active thiono- and selenoamides are configurationally labile compounds and gradually racemize in solution but they are stable in the form of the inclusion complexes. The first-order kinetics of the racemization in solution allowed us to assign the racemization barriers by the spectropolarimetric measurements.

Introduction

Molecules that adopt helical conformation attract a lot of attention due to their biological functions as well as their relevance to material science, supramolecular chemistry and asymmetric catalysis.[1] A helical structural motif has been observed primarily in biopolymers such as polypeptides and polynucleotides[2] or synthetic foldamers of the aryl oligoamide,[3] oligoarene,[1b,4] oligoresorcine[5] or *m*-phenylene–acetylene[6] structure. Other examples can be found among smaller molecular systems like famous [*n*]helicenes,[1a,b,7] cyclooctapyrroles,[8] "Geländer" molecules[9] and polynuclear transition metal complexes.[10] The helical topology can be induced by steric effects in [*n*]helicenes, hydrogen bonding in protein α-helix, aromatic–aromatic interactions in DNA or oligoanthranilamides, metal coordination in many double or triple stranded helicates and guest inclusion in oligo(*m*-ethynylpyridines).



Steric strain in 4,5-disubstituted phenanthrenes (**1**)[11] or in 9,10-phenanthroline *N,N'*-dioxide (**2**)[12] is responsible for helical distortion of the molecular skeletons that results in the C_2 symmetry chiral structures. In some derivatives of **1** the steric hindrance is large enough for enantiomer separation, however,[11] in the case of **2** a rapid equilibration between two enantiomeric forms occurs in solution.[12] We focused our attention on 1,2,3,4,7,8,9,10-octahydro-1,10-phenanthroline (**4**), prepared by the reduction of the pyridyl rings of 1,10-phenanthroline (**3**),[13] which seems to be a potentially useful template

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† Electronic supplementary information (ESI) available: NMR (^{1}H, ^{13}C, ^{77}Se) data for all products (compounds **5a–d** and **7**). CCDC 927852–927859. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ob41216d