ORGANIC LETTERS

2012
Vol. 14, No. 10
2568–2571

Helicity Discrimination in Diaryl Dichalcogenides Generated by Inclusion Complexation with Chiral Hosts

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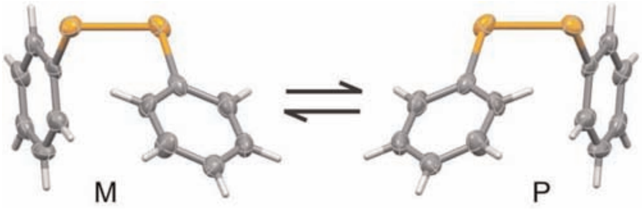
Received April 5, 2012

ABSTRACT



Inclusion complexation of diaryl dichalcogenides with either cholic acid or chiral diols results in their helicity discrimination and an induction of optical activity that can be detected by solid-state CD measurements.

Some molecules lacking stereogenic centers can adopt chiral conformations caused by internal rotation. They occasionally form optically active crystals with the component molecules frozen in a chiral conformation yielding conglomerates as a mixture of homochiral crystals.[1] Notable examples are diphenyl dichalcogenides **1**−**3** which crystallize in the Sohnke space group $P2_12_12_1$.[2] Due to a gauche effect caused by the interaction of adjacent electron lone pairs, they assume a skewed conformation with the torsional angle around the chalcogen−chalcogen bond being close to 90°.[3] Thus, dichalcogenides exist in chiral *P*- and *M*-helical forms. A low energy barrier to internal rotation (ranging from to 8.6 to 5.3 kcal/mol) going from diphenyl disulfide to ditelluride causes their rapid racemization in solution.[4] However, their optical activity should be detected in the solid state. Unfortunately, our attempts to measure their circular dichroism (CD) in KBr disks resulted only in very poor quality and noisy spectra. Similar noisy CD curves exhibiting extremely weak Cotton effects (CEs) have been reported by Kamigata and coworkers.[4] The spectra presented by these authors show monosignate CD in the region of two low energy n−σ^* electronic transitions. According to the theoretical predictions confirmed by several experimental results, typical CD curves of optically active dichalcogenides should consist of two oppositely signed CEs in the long-wavelength part of the spectra.[5,6]

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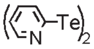
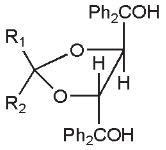
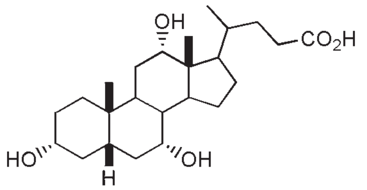
1, PhSSPh
2, PhSeSePh
3, PhTeTePh

4,


5,




6a, $R_1 = R_2 = (CH_2)_4$
6b, $R_1 = R_2 = (CH_2)_5$



CA

It is also known that upon replacement of the chalcogen with a heavier atom the n−σ* excitations are shifted to longer wavelengths,[5e] and therefore diphenyl disulfide (**1**), diphenyl diselenide (**2**) and diphenyl ditelluride (**3**) form colorless, yellow, and deeply red crystals, respectively. However, the reported CD maxima occurred at nearly the same wavelengths for all of these compounds.

Consequently, we developed an alternative method of detection for the optical activity of diaryl dichalcogenides. In recent years it has been shown that optical activity in symmetric molecules can be generated by inclusion complexation with chiral hosts.[7,8] Particularly, naturally occurring cholic acid (**CA**) appeared to be a versatile host for many aromatic compounds.[9] Since the guest molecules trapped in the crystal matrices of **CA** are frozen in a chiral conformation, it is now possible to measure their CD spectra in the solid state. Simultaneous X-ray crystallographic analysis of the inclusion crystals allows unequivocal assignment of the absolute configuration of the guest molecules. This method has been successfully applied for induction of CD in aromatic ketones, thioketones, azobenzene, and various *N*-nitrosamines.[8] By analogy, inclusion complexation should lead to helicity discrimination in diphenyl dichalcogenides, and indeed, cocrystallization of **CA** with **1** as well as **2** resulted in the smooth formation of the corresponding 2:1 inclusion complexes. X-ray diffraction analysis of the isostructural complexes **1**·**CA** and **2**·**CA** revealed features typical of the **CA** clathrates.[8,9] The host molecules self-assemble through intermolecular hydrogen bonds into corrugated bilayers, and the empty channels between the stacked bilayers are filled with the guest molecules organized into infinite columns (Figure 1).

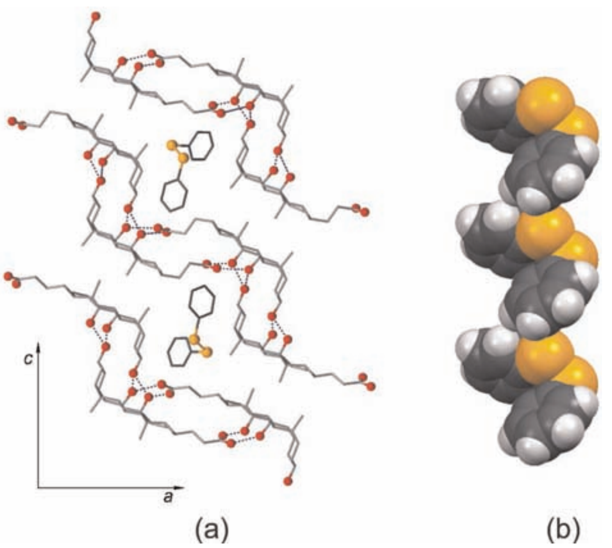


Figure 1. Crystal structure of **2**·**CA** showing (a) the guest molecules accommodated in two symmetry independent channels (view along the *b* axis) and (b) arrangement of the guest molecules within the channels (view perpendicular to the *b* axis).

In both cases the guest molecules assume chiral conformations with the dichalcogenide unit twisted in the *M* sense; the C−S−S−C torsional angle in two symmetry independent guest molecules is −88.3(2)° and −91.0(2)° in the case of **1**, and the C−Se−Se−C torsional angle is −88.1(2)° and −90.9(2)° in **2**. Unfortunately, several attempts to prepare a diphenyl ditelluride (**3**) complex with **CA** failed. This was probably due to the molecular parameters of **3**, particularly the long Te−Te bond of 2.71 Å, causing the molecule to not fit into the empty channels of the **CA** crystal lattice. To overcome this difficulty we tried to use chiral diols (*R,R*)-**6a** and (*R,R*)-**6b** known as TADDOLs ($\alpha,\alpha,\alpha',\alpha'$-tetraphenyl-1,3-dioxolane-4,5-dimethanols).[10] Again, we were not able to achieve a complexation. Since TADDOLs are known to bind host molecules with the use of intermolecular hydrogen bonds,[11] we prepared bis-(2-pyridyl)diselenide (**4**)[12] and bis(2-pyridyl)ditelluride (**5**),[13] which appeared to easily form 2:1 host−guest complexes with **6a**. The crystal structures of these complexes confirmed that the host molecules bind guest units by the strong O−H···N hydrogen bonds (Figure 2), thus preventing the intramolecular chalcogen·pyridine nitrogen[14]

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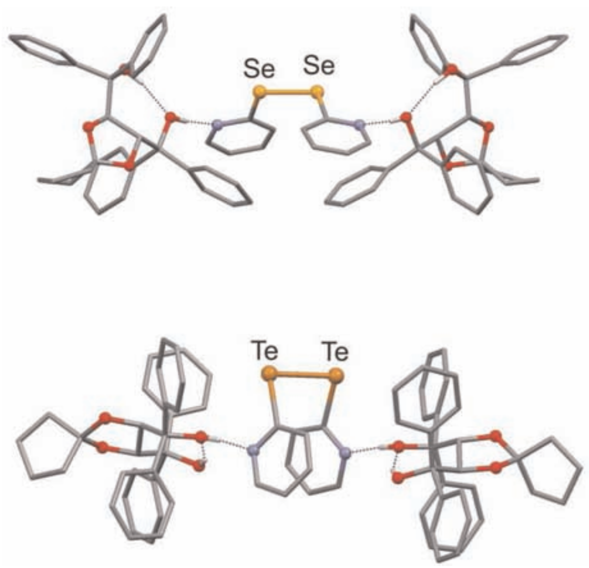

Figure 2. Heterotrimers formed *via* hydrogen bonds in **4·6a** (top) and **5·6a** (bottom).

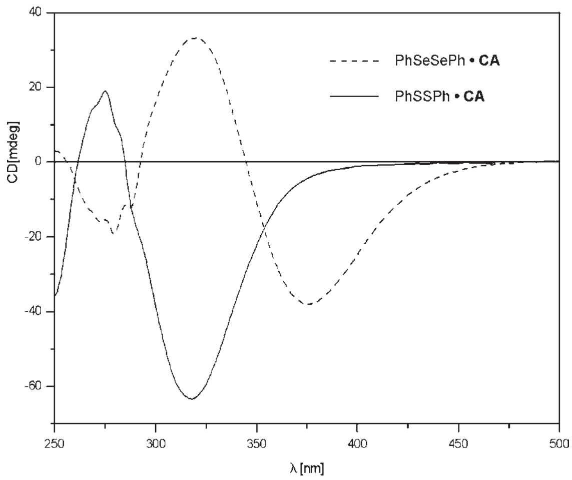

Figure 3. CD spectra of **1·CA** and **2·CA** measured in KBr disks.

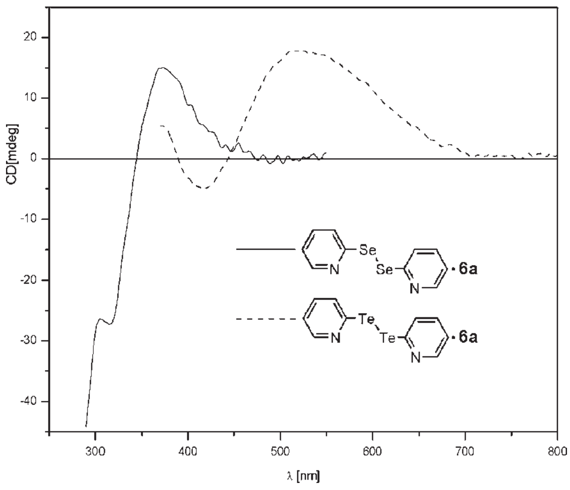

Figure 4. CD spectra of **4·6a** and **5·6a** measured in KBr disks.

interaction that might lead to the frequently observed planar dichalcogenide structures.[15]

The guest dichalcogenide **4** and **5** molecules assume skewed conformations of *M* and *P* helicity as indicated by the C–Se–Se–C and C–Te–Te–C torsional angles −109.7(3)° and 52.1(3)° respectively. The CD spectra of complexes **1·CA** and **2·CA** (Figure 3) as well as **4·6a** and **5·6a** (Figure 4) measured in KBr disks show two strong and oppositely signed CEs of moderate to strong intensity in the long wavelength part of the spectrum. They can be assigned to the $n_s-\sigma^*$ and $n_a-\sigma^*$ electronic transitions of the dichalcogenide chromophore[5e] where n_s and n_a represent the symmetric and antisymmetric combinations of the chalcogenide p orbitals. According to theoretical predictions, the first CE at longer wavelength is diagnostic for the helicity of the chromophore. The sign is positive for *P* helicity and negative for *M* helicity if the absolute value of the dichalcogenide torsional angle is from 0° to 90°, whereas the opposite signs are expected when the angles exceed 90°.[5] On the other hand, torsional angles with an absolute value close to 90° should result in degeneration of the two $n-\sigma^*$ excitations and low CD intensity. Then the sign should depend on the perturbations exerted by a chiral surrounding.

Thus, the helicity rule explains the observed positive CE signs at 370 and 520 nm for **4·6a** and **5·6a**, respectively. Similarly, the negative CD bands at 320 and 375 nm for **1·CA** and **2·CA** remain in accordance with the chromophore helicity assuming that the contribution from the guest molecules with the acute dichalcogenide torsionals are responsible for the signs of the CE. However, in this case the observed CEs show strong intensity despite the fact that S–S and Se–Se torsional angles approach 90°.

In summary, inclusion complexation of diaryl dichalcogenides with either cholic acid or chiral diols results in their helicity discrimination and leads to the induction of optical activity. Solid state CD measurements of the inclusion complexes allowed us to observe two oppositely signed and relatively strong Cotton effects in the region of the two

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(16) The reasons for the extremely low intensity of the CEs exhibited by pure diphenyl dichalcogenides is not clear. One of the possible reasons might be a low melting point, which for **1**–**3** remains below 70 °C, that may result in partial melting of the sample during formation of KBr disks used for CD measurements. Another possiblity might be racemic twinning of the crystals.

n$-\sigma^*$ electronic transitions. In contrast, single crystals of pure diphenyl dichalcogenides **1**−**3** show only negligible CD in the solid state.[16]

Acknowledgment. We are indebted to Prof. J. Frelek (IChO PAN, Warsaw) for CD measurements with use of her Jasco J-715 dichrograph. We also thank Dr. Christopher Boucher (Piramal Health Care, Canada Ltd.) for critical reading of the manuscript. This work was supported by the Ministry of Science and Higher Education, Grant No. NN 204 1820 36.

Supporting Information Available. Experimental details of the inclusion complexes preparation, crystallographic analyses, and X-ray crystallographic file. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.