The absolute configuration of heptahelicene: a VCD spectroscopy study†

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The comparison between experimental and calculated VCD spectra allowed the unequivocal assignment of the absolute configuration of heptahelicene $C_{30}H_{18}$ as *P*(+).

Molecules with helical structures have fascinated chemists for many years. Helicenes possess an inherent chiral chromophore and exhibit outstanding linear and nonlinear optical activity.[1] The absolute configuration of all-carbon helicenes and heterohelicenes is believed to be such that *P*-helicenes are dextrorotatory at wavelengths longer than those of the UV/VIS absorption bands. This assignment is based on two anomalous X-ray scattering studies, the so-called Bijvoet method[2] performed on (−)-2-bromohexahelicene with subsequent debromation to (−)-hexahelicene[3] and for a (−)-sulfur heterohelicene.[4] However, the determination of absolute configuration *via* the Bijvoet method has been challenged by Tanaka *et al.* in 1973, who came to opposite conclusions based on chiroptical methods.[5] Furthermore, much criticism has been expressed on how the determination of absolute configuration has been carried out.[6] With the exception of the early study by Moscowitz,[7] the *P*-(+) assignment was supported by theoretical calculations predicting the optical rotation and the electronic CD spectra of helicenes.[8]

More recently Furche and coworkers demonstrated the potential of time-dependent density functional theory for the calculation of electronic CD spectra of several helicenes, including heptahelicene.[9] Comparison with experimental CD spectra revealed reasonable agreement in most cases, allowing the assignment of the absolute configuration of the helicenes with relatively high confidence. Time-dependent density functional theory was also applied to calculate optical rotations of several small to medium-sized molecules,[10] of which heptahelicene was the largest, again showing reasonable agreement with experiment.

On the other hand, optical activity associated with molecular vibrations contains detailed structural information. Vibrational circular dichroism spectroscopy (VCD) and Raman optical activity (ROA) have been found to be reliable techniques for the determination of the absolute configuration of chiral molecules in solution.[11] Below we demonstrate that the absolute configuration of heptahelicene ($C_{30}H_{18}$, Fig. 1) can be assigned with a very high level of confidence by comparison of experimental and calculated VCD spectra.

The structure of the heptahelicene molecule is largely determined by repulsive forces between the two ends of the helix. The C1–C21, C1–C23 and H1–C23 distances (see Fig. 1) were calculated to be 3.02, 3.12 and 2.49 Å at the B3LYP/6-31G(d,p) level of theory. This compares well with the crystal structure since the corresponding distances were reported as 2.89–2.91, 3.04–3.08 and 2.36–2.51 Å, depending on the crystal modification and the molecule within the unit cell.[12] The intramolecular repulsion gives the molecule a pronounced rigidity and therefore large VCD signals can be expected.

Fig. 2 shows the VCD spectra of both enantiomers of heptahelicene in CH_2Cl_2. The black (grey) trace corresponds to the enantiomer that we labelled H1 (H2), since it elutes first (second) from the chromatographic column. The reliability of the measurements is confirmed by the mirror-image-like VCD spectra of the H1 and H2 enantiomers. The strongest VCD band in the spectral range covered in Fig. 2 at 950 cm^{-1} exhibits a rather large anisotropy ratio of about $\Delta A/A = 10^{-3}$, indicating a large magnetic dipole contribution. This band is associated with a vibration of *b* symmetry within the C_2 point group and has prominent C–H out-of-plane bending character at the terminal rings (see ESI). Interestingly the VCD spectrum of another helical molecule, a heptathiophene that was very recently reported,[13] did not show unusually large anisotropy ratios in the experimental spectra. The latter molecule, however, does not contain hydrogen atoms within the helix.

For heptahelicene very large VCD signals were also observed (and calculated) for some C–H out-of-plane bending vibrations in the spectral region between 800–860 cm^{-1} (not shown). Calculations show that the strongest band in both

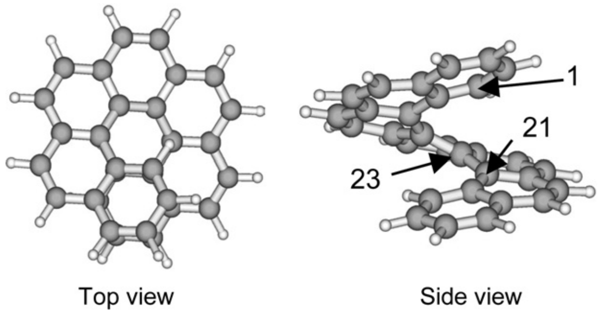

Fig. 1 Calculated structure of *P*-heptahelicene.

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† Electronic supplementary information (ESI) available: two calculated normal modes and CD spectra of the heptahelicene enantiomers. See http://www.rsc.org/suppdata/nj/b3/b312877f/

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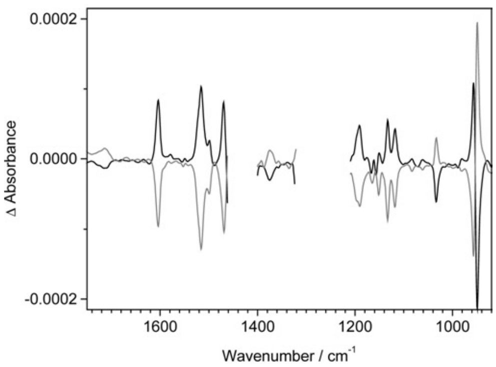

Fig. 2 VCD spectra of the two enantiomers of heptahelicene. The black trace corresponds to the enantiomer H1 that elutes first from the chromatography column. Solutions of 9 mg in 400 µl CH_2Cl_2 were used. Path length: 1 mm. About 3600 scans were averaged for each spectrum and a VCD spectrum of the solvent was subtracted. The missing parts of the spectra correspond to regions of strong solvent absorption.

the absorption and VCD spectra in this region is associated with a normal mode characterized by in-phase, out-of-plane hydrogen deformation (see ESI). Strong VCD signals were recently also reported for a highly configurationally stable [4]heterohelicenium cation,[14] which indicates that strong VCD activity is a common property of rigid helical molecules.

In Fig. 3 calculated and experimental absorbance and VCD spectra are compared. For the calculations the *P* enantiomer shown in Fig. 1 was chosen, whereas the experiment corresponds to H2. The comparison allows the unequivocal assignment of H1 (H2) to the *M* (*P*) enantiomer. In particular, in the spectral regions with a relatively low density of fundamental modes at 900–1170 cm^{-1} and 1450–1700 cm^{-1} the calculated and experimental spectra match very well. The broad band at around 1700 cm^{-1} also shows significant VCD activity (see Fig. 2). This signal has to be assigned to overtone and combination bands since no fundamentals are expected in this region. The frequency is consistent with overtone and combination bands of C–H out-of-plane bending modes. Their appearance shows the high VCD activity of heptahelicene. On the other hand the corresponding signals are missing in the calculated absorption and VCD spectra because a normal modes analysis only accounts for fundamentals.

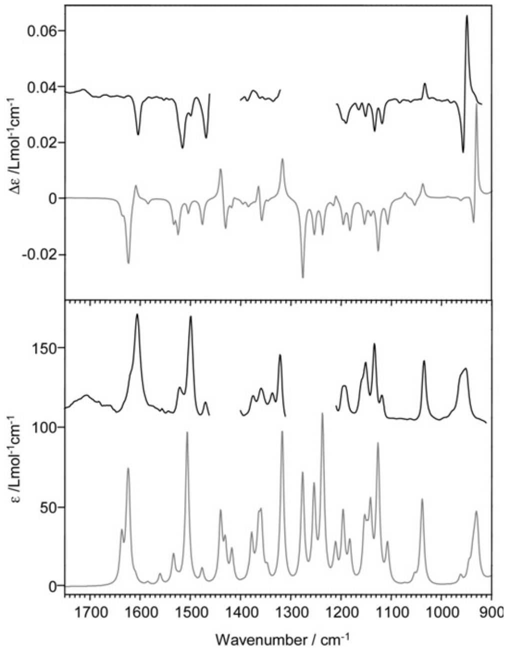

Fig. 3 Comparison between calculated (grey) and experimental (black) absorption (bottom) and VCD spectra. The experimental spectrum corresponds to the enantiomer that elutes second from the chromatography column (H2). For experimental conditions see Fig. 2. The calculations were performed at the B3LYP/6-31G(d,p) level of theory and were performed on the *P* enantiomer shown in Fig. 1. The calculated frequencies were scaled by a factor of 0.97.

A comparison between CD and optical rotation, which were also measured, and VCD spectra of heptahelicene results in the following correlation: the *P* (H2) enantiomer is dextrorotatory at 590 nm, that is at longer wavelengths than the absorption bands in the visible. The CD spectrum that we measured for the *P* enantiomer (as determined by VCD) is identical with the spectrum of the enantiomer, which was also assigned as *P*, based on calculated CD spectra.[9]

In conclusion we have found that heptahelicene exhibits strong VCD activity. Absorption and VCD spectra of this relatively large molecule calculated from hybrid density functional methods in combination with a medium-sized basis set are in good agreement with experimental spectra and allow a definite assignment of the absolute configuration. The procedure followed to determine the absolute configuration of heptahelicene, that is the comparison between experimental and calculated VCD spectra, is analogous to the one recently reported for absolute configuration determination from electronic CD spectra.[9] Both approaches have advantages and disadvantages. CD spectra are more easily measured, mainly due to the larger cross sections associated with electronic as compared to vibrational transitions. On the other hand VCD is more easily treated theoretically than CD. In CD spectroscopy electronically excited states are involved, whereas in VCD usually only the electronic ground state plays a role. An inherent disadvantage of CD with respect to VCD spectroscopy is the fact that the spectral information is usually less separated. Electronic transitions tend to be broad at room temperature such that a CD spectrum exhibits typically only a handful of bands, composed of overlapping transitions.

Experimental and theoretical methods

Heptahelicene (benzo[*c*]phenanthro[4,3-*g*]phenanthrene) was synthesized as described previously.[15] After separation of the enantiomers on a preparative HPLC system with a Daicel Chiralcel OD column (21 mm diameter, 250 mm length, mobile phase 9:1 hexane–2-propanol) the enantiomeric purity of the different fractions was determined on an analytical HPLC system with a Daicel Chiralcel OD-H column (4.6 mm diameter, 250 mm length). The chromatograms showed exclusively one peak. An enantiomeric excess of ee $>99\%$ was estimated from the maximum signal of the opposite enantiomer, which could possibly be hidden in the noise. CD spectra of both enantiomers were identical to those reported previously.[9,16] IR and VCD spectra were measured using a Bruker PMA 37 accessory coupled to a VECTOR/33 Fourier transform infrared spectrometer as described in detail elsewhere.[17] A photoelastic modulator (Hinds PEM 90) set at l/4 retardation was used to modulate the handedness of the circular polarized light and demodulation was performed by a lock-in amplifier (SR830 DSP). In order to enhance the signal-to-noise ratio an optical low-pass filter (<1800 cm^{-1}) was put before the photoelastic modulator. A transmission cell equipped with KBr windows and a 1 mm teflon spacer was used. A single beam spectrum of the neat solvent served as the reference for the absorption spectrum and a spectrum of the neat solvent recorded in VCD mode was subtracted from the VCD spectrum of the dissolved molecules. The data are presented without smoothing or further data processing.

VCD spectra were calculated using GAUSSIAN98.[18] Complete optimization of all internal coordinates of the molecule was performed at the density functional B3LYP and B3PW91 levels of theory using 6-31G(d,p) and cc-pvdz basis sets. For the minimized structures a normal coordinate analysis was performed. Rotational and dipole strengths associated with the normal modes were calculated and spectra were simulated by convolution with a Lorentzian line shape as described elsewhere.[17] In general the calculated absorption and VCD spectra were very similar for the density functionals and basis sets considered.

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