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Experimental and calculated circular dichroism spectra of monoaza[5]helicenes [☆]

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Abstract

Circular dichroism (CD) spectra have been measured in the range of 400–200 nm on CH₃OH solutions of both enantiomers for the almost complete series of monoaza[5]helicenes, namely the molecules where the hetero N atom occupies positions 1, 3, 4, 5, 6, and 7, respectively (the 2 isomer is missing due to difficulties in the synthesis). CD spectra recorded at controlled room temperature allow one to define precise racemization rates, that are nicely interpreted on the basis of DFT molecular orbital calculations. Time-dependent DFT methods provide us with calculated CD and UV spectra, that are compared with the corresponding experimental data. We discuss the role of the N atom in determining the height of the racemization barrier and in shaping the appearance of the CD spectra.

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1. Introduction

Helicenes are helicoidally shaped molecules, which exhibit unique chiroptical properties, e.g. large circular dichroism (CD) spectra and large optical rotations [1]: they have been long since studied as interesting compounds *per se*, both from the theoretical and experimental point of view [2–4]. However, recently they have received a lot of attention, for possible applications in the field of materials science, notably in photonics. Indeed, due to missing symmetry planes, third order nonlinear optical properties are expected and actually observed, to be used in photonics [5,6]. Also, due to the long lifetime of the triplet state and to the tendency to π – π^* stacking and the building of colum-

nar systems, these compounds may be the basis of materials for optoelectronic applications [7,8]. Through several years, we have developed some experience in the photochemical synthesis of several helicenes, with or without hetero atoms as well as with small or large numbers of fused aromatic rings [9–12]. We have also been able to characterize them spectroscopically [11], and to resolve the enantiomers thereof, so as to measure the CD spectra [13]. The present work is the extension of the work presented in Ref. [13]: indeed in Ref. [12] we accomplished and theoretically understood how to carry out the photochemical synthesis of some monoaza[5]helicenes, reacting benzo[*h*]quinoline based molecules and benzene based molecules, namely connecting together one- and three-membered ring systems, to give 9-styryl-benzo[*f*]isoquinolines, that were photochemically treated afterwards. The helicenes that we have been able to synthesize in Ref. [12] were not synthesized as efficiently, or were impossible to synthesize, by the alternative strategy that we had followed in Ref. [10]. Independently

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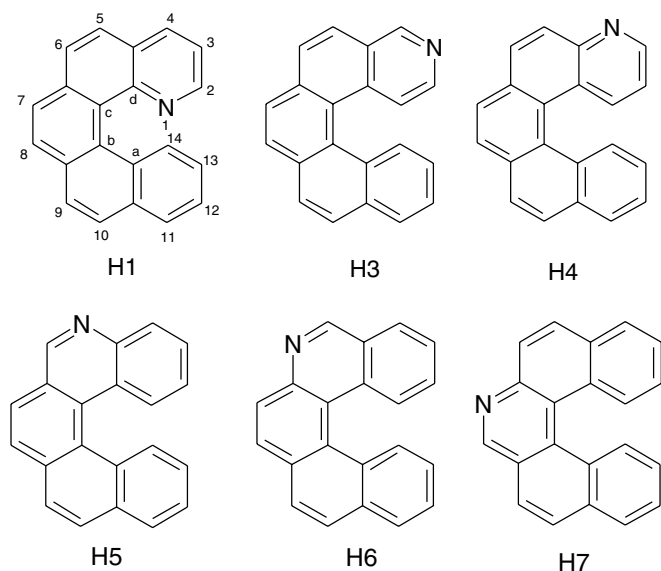


Chart 1.

from the synthetic ways, we were able to obtain the series of monoaza[5]helicenes presented in Chart 1, where N occupies positions 1, 3, 4, 5, 6 and 7. The enantiomeric resolution of the compounds has allowed us to measure CD spectra and, from comparison with DFT calculations, to understand the chiral stability of the enantiomers and to appreciate the role of the N-atom for that matter, as well as for determining the single electronic transitions.

2. Experimental

The synthesis of molecules from H1 to H7 has been described in Refs. [11,12] and we do not comment on it further. The enantiomeric separation via HPLC of H4, H5, and H6 was described in Ref. [13]. The enantiomeric resolution of H1, H3, and H7 was performed using a HP 1090 system equipped with an analytical HPLC column (Chiralcel OD 250 4.6 mm, 20 μ m) at room temperature (approximately 20 °C). The eluent and the HPLC column were at room temperature. The room with the HP 1090 system was kept in the dark. The mobile phase was heptane–ethanol 98/2 v/v under isocratic conditions. The injection volume was 250 μ L. The run-time was 20 min at a flow rate of 1 mL/min. The detectors were a UV lamp at 254 nm and an online polarimetric detector at 653 nm. Retention times of the two enantiomers were: 10.13 min and 15.19 min for H1; 10.21 min and 15.13 min for H3; 8.31 min and 13.04 min for H7. The enantiomer exhibiting negative optical rotation (–) was always the first to be eluted. The fractions were kept in dry ice/acetone as soon as they were collected and the solvent was removed under vacuum, the flask being kept cold during evaporation; the fractions were stored in a freezer at –20 °C for a few hours before taking the CD spectra.

The CD spectra were recorded on a JASCO J500 instrument flushed with dry nitrogen. Each enantiomer fraction

that had been stored at –20 °C, was dissolved in CH₃OH. The spectra were taken in the 400–200 nm range using the following conditions: 100 nm/min scanning rate, 2 nm bandwidth, 1 s time constant and each single-scan CD spectrum was recorded every 2.5 min up to the racemic equilibration. For H1, H3, and H7, we used a 1 mm thermostated cell by running water at 23 °C from an external circuit (Haake K20 system). In Fig. 1 we provide the experimental CD spectra of both enantiomers of H1, H3, and H7 together with the previously measured CD spectra for H4, H5, and H6 [13], for sake of comparison. We do not superimpose all recorded CD spectra, but just four for the two enantiomers of each compound, and specify the times of data acquisition in the insets.

The DFT calculations have been carried out by the use of GAUSSIAN-03 package [14], the use of B3LYP functional and 6-31G** basis set. For all monoaza[5]helicenes in Chart 1, the equilibrium (eq) and transition state (TS) geometries, and the energy difference between TS and equilibrium, were determined by the method of quadratic synchronous transit (QST) [15,16], as described in Ref. [13]: a common racemization path was found for all molecules in Chart 1, namely racemization proceeds via a non-bond-breaking conformational path by a vibrational mode that is mostly due to out-of-plane motions mostly localized in the two most peripheral rings. The two out-of-plane modes are also out-of-phase and are depicted in Fig. 3 of Ref. [13]. The routine of GAUSSIAN-03 based on time-dependent (TD) DFT theory was used to calculate frequencies, dipole strengths and rotational strengths, and allowed us to generate calculated absorption and CD spectra with a homemade routine that assigns Gaussian band shapes to each calculated electronic transition with variable width $\Delta\nu$, with the rule proposed in Ref. [17]: $\Delta\nu = 7.5\nu^{1/2}$ (ν in cm^{-1}). In Fig. 2, we provide the results of the calculations for the CD spectra in black, and superimpose them to the experimental spectra in red and also to the bar representation of the calculated spectra.

3. Discussion of the results and conclusions

The spectra of Fig. 1 exhibit the same main features, namely the most intense CD band centered at ca. 305 nm, the sign of which is normally taken as diagnostic of the absolute configuration (AC) of the molecule, positive for P helicity and negative for M helicity [3,4,10]. Kinetic parameters of first-order kinetic process of racemization (kinetic constant k), and corresponding half-life times $t_{1/2} = \ln(2)/k$ are reported in Table 1. These values were derived, as done in Ref. [13], by least-squares averaging over plots of the logarithm of the absolute value of the CD signal of the most intense band versus time: often the plots for the M enantiomer do not coincide with those for the P enantiomer, bringing a maximum error of ca. 17% in the case of H3; in the other cases the errors are about 5%. One may see that $t_{1/2}$ values gently decrease from the H1 to H6 with a different behavior for H5 and H7 which have

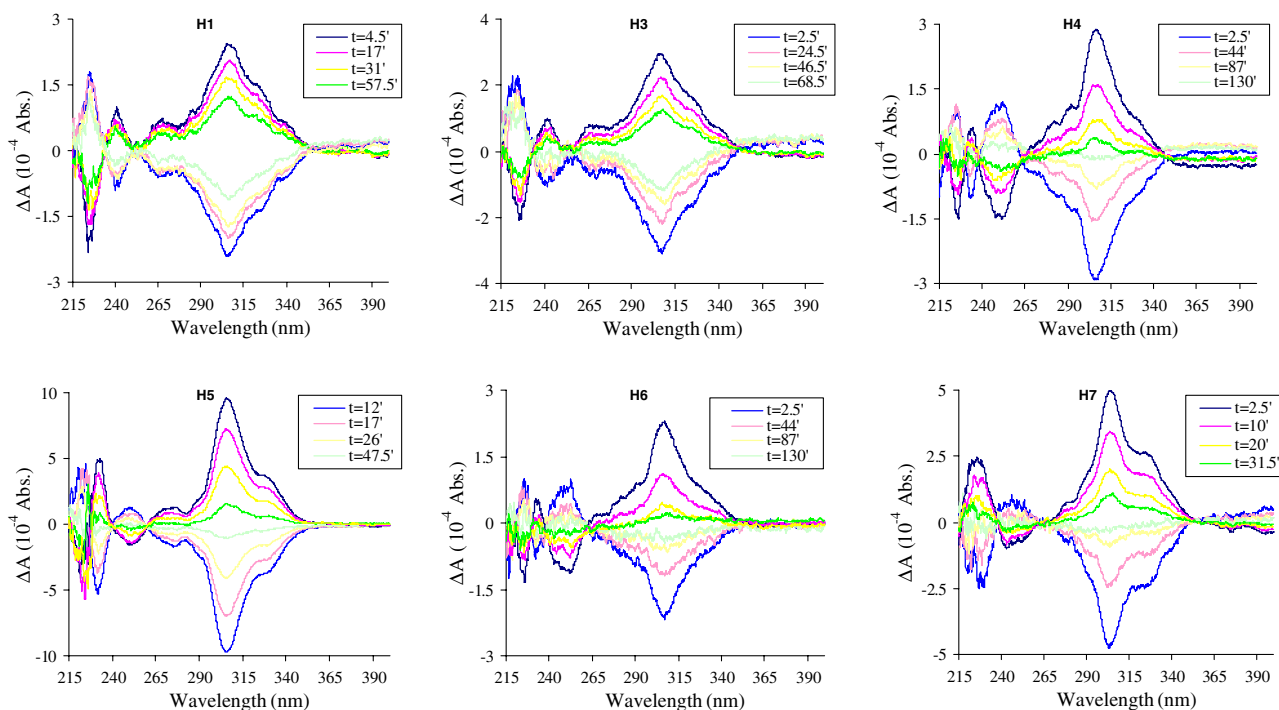


Fig. 1. CD spectra of both enantiomers of 1-aza[5]helicene (H1), 3-aza[5]helicene (H3), 4-aza[5]helicene (H4), 5-aza[5]helicene (H5), 6-aza[5]helicene (H6) and 7-aza[5]helicene (H7). Spectra were recorded in a thermostated quartz cell of 1 mm. For each enantiomer, four CD spectra are presented at four different times of racemization (see text for more details).

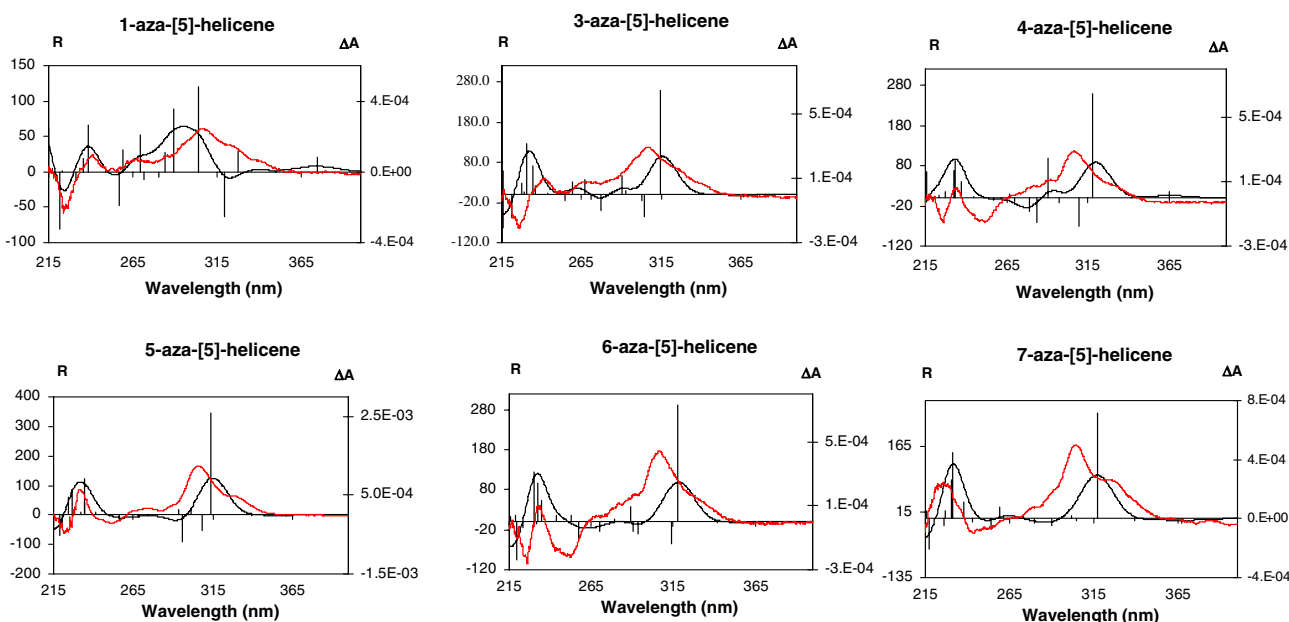


Fig. 2. Comparison of calculated and experimental CD spectra of the P enantiomers of 1-aza[5]helicene (H1), 3-aza[5]helicene (H3), 4-aza[5]helicene (H4), 5-aza[5]helicene (H5), 6-aza[5]helicene (H6) and 7-aza[5]helicene (H7). Rotational strengths, expressed in $\text{esu}^2 \text{cm}^2$ and multiplied by 10^{40} , are given as vertical bars, while the calculated spectra obtained by the application of Gaussian band shapes (as described in the text) in arbitrary units are given as black curves. Red curves are the experimental spectra in absorbance units, with the axis of values on the right-hand side.

much lower half-life time. We notice from Table 1 that there is a good agreement between experimental half-life times $t_{1/2}$ and calculated barrier heights $E = (E_{\text{TS}} - E_{\text{eq}})$ except for H1 (see discussion further on). The latter quantities have been derived by use of the QST approach, as described in Ref. [3]: this further supports that the mecha-

nism of interconversion is by way of a vibrational motion, that is mainly an out-of-plane motion of the outermost hydrogen and carbon atoms in the end benzene rings. Indeed, by taking a closer look at the atomic displacements for the vibrational mode bringing the molecules to racemization (as done in Ref. [13] for H4), one notices that at TS

Table 1
Measured kinetic constants (k) and half-life times ($t_{1/2}$) compared with calculated energy barriers (E)

| | k (min ⁻¹) ^a | $t_{1/2}$ (min) ^a | E (kcal/mol) ^b |
|----|---------------------------------------|------------------------------|-----------------------------|
| H1 | 0.014 | 49.5 | 11.7 |
| H3 | 0.016 | 44 | 23.3 |
| H4 | 0.015 | 47 | 23.2 |
| H5 | 0.061 | 12 | 22.2 |
| H6 | 0.020 | 35 | 22.9 |
| H7 | 0.105 | 6.6 | 21.7 |

Measurements made at 23 °C for H1, H3, and H7; at RT for H4, H5, and H6.

^a Experimental.

^b Calculated.

the atoms that are vibrating the most are at the two extreme outer rings, while at equilibrium also the atoms in the 2nd outermost ring in the arm not containing the N-atom exhibit significant displacements; for H7 the mode is more symmetrical in the two arms. This mechanism was first established by Grimme and Peyerimhoff [18] on [n]carbohelicenes ($n = 3-6, 8$) on the basis of SCF ab initio methods. The N-atoms are seen to affect little the vibrational motions taking the helicenes to TS, whereby one benzene end moves out of phase with respect to the other benzene end. On the other hand, we observe that the insertion of an N-atom decreases the enantiomeric stability of the helicene, since the parent molecule [5]helicenes are reported in the literature to possess a half-life time $t_{1/2} = 62.7$ min at 57 °C [1,19]. For H1, the calculated ΔE is by far too low and does not bear any interpretation of the present experimental results; we observe that at least the value $\Delta E = 11.7$ kcal/mol, much smaller than the other aza[5]helicenes, is still higher than the value $\Delta E = 3.5$ kcal/mol, that Grimme and Peyerimhoff had calculated for [4]helicene [18].

Some further clues into the understanding of the non-monotonic behavior of $E = (E_{TS} - E_{eq})$ with the position of N from the outer benzene ends to the joining ones may come from considering in Table 2 some geometrical characteristics of the equilibrium geometry. Dihedral angles are shown in the first three rows: C–C–C–C (**center**)

Table 2
Geometrical parameters resulting from DFT calculations

| | H1 | H3 | H4 | H5 | H6 | H7 | Carbo |
|--|-------------------|------|------|------|------|------|-------|
| C–C–C–C (center) | 28.6 | 29.6 | 29.1 | 28.4 | 29.9 | 27.8 | 29.8 |
| C–C–C–C (N side) | 12.1 | 16.5 | 18 | 16.6 | 16 | 18.5 | 17.8 |
| C–C–C–C | 18.7 | 18.2 | 18.2 | 18.2 | 17.8 | 16.8 | 17.8 |
| CC int | 1.43 ^a | 1.44 | 1.44 | 1.44 | 1.44 | 1.44 | 1.44 |
| CC front | 1.36 | 1.36 | 1.37 | 1.37 | 1.37 | 1.34 | 1.37 |
| CC others | 1.41 | 1.41 | 1.42 | 1.42 | 1.42 | 1.41 | 1.42 |
| CN | 1.32 | 1.32 | 1.32 | 1.3 | 1.3 | 1.31 | |
| CN' | 1.36 | 1.36 | 1.36 | 1.38 | 1.38 | 1.37 | |
| Pitch-internal C (10 ⁻² Å/°) | 0.67 | 0.72 | 0.72 | 0.71 | 0.71 | 0.71 | 0.73 |
| Pitch-remaining C (10 ⁻² Å/°) | 0.95 | 1 | 0.98 | 0.98 | 0.99 | 0.98 | 1.01 |
| $z_2 - z_{13}$ (Å) | 3.13 | 3.35 | 3.35 | 3.30 | 3.34 | 3.29 | 3.4 |

The meaning of the quantities listed in the first column is explained in the text.

^a This averaged length has been evaluated, including also the CN-length.

corresponds to atoms a-b-c-d in the schemes in Chart 1; C–C–C–C (**N-side**) corresponds to atoms b-c-d-1; C–C–C–C corresponds to atoms c-b-a-14. In the next three rows, some average lengths of C–C bonds are presented: **CC int** is the average over the internal bond lengths, involving the pairs of atoms 14-a, a-b, b-c, c-d and d-1; **CC front** is the average over the bond lengths of the pairs of atoms in front of the previous ones, that is 5–6, 7–8 and 9–10; **CC-others** is the average over the remaining C–C bond lengths. In the subsequent two rows, **CN** and **CN'** are the lengths of the two bonds involving the N atom. The pitch [20,13] is defined as the quantity p such that for each atom i , the relation $z_i = p\phi_i$ holds, where $\phi_i = y_i/(x_i^2 + y_i^2)$. The reference frame is centered in the point determined by the average position of all carbon and nitrogen atoms, with an X axis intersecting the middle point between atoms 7 and 8 and with Y axis parallel to the C–C bond joining these two atoms. One may observe that while the dihedral angle C–C–C–C (**center**) and $z_2 - z_{13}$ (z being the coordinate of the screw axis of the helix, Chart 1) gradually decreases in moving from H3 to H5, they go back to higher values for H6 (close to the carbohelicene value), and then they decrease again in H7. This may mean that the higher value of $E = (E_{TS} - E_{eq})$ is due to a more rigid structure at equilibrium for H6, like in carbohelicene. We have verified that indeed there is a linear dependence between experimental $t_{1/2}$ and calculated $z_2 - z_{13}$ for all compounds except for H1. The anomalous value of $E = (E_{TS} - E_{eq})$, together with the singular behavior of the calculated CD spectra (see next), places H1 in a special position, possibly because this helicene is the only one bearing the nitrogen in an inner position. So far we have no convincing explanation for it, but we only observed that the same kinds of difficulties were encountered by one of us in justifying by TDDFT methods, the experimentally observed fluorescence times. The interpretation of CD spectra is not an easy task, even though the gross characteristics are easily predicted by the TDDFT calculations: for H4, H5, and H6 this had been done in Ref. [13] and for carbohelicene in the seminal paper on TDDFT by the German school [20]. The CD bands for the P enantiomers are observed more or less to be the same

for all helicenes and their signs and wavelengths are presented in the scheme below:

We are indebted to Markus Juza for the helpful suggestions.

| 224 | 232 | 236 | 240 | 248 | 265 | 272 | 278 | 289 | 305 | 323 | 330 | 339 | λ (nm) |
|-----|---------|-----|-----|-----|-----|-----|-----|-----|-----|-------|-----|-----|----------------|
| – | | | + | | + | | | | + | + | | + | H1 |
| – | | | + | | + | | | | + | + | | + | H3 |
| – | + | | | – | | | + | + | + | | + | | H4 |
| – | + | | | – | | | + | + | + | | + | | H6 |
| + | | | | – | | | + | + | + | + | | | H5 |
| + | | | | – | | | + | + | + | + | | | H7 |
| | – (229) | + | | | – | – | | | + | (310) | | + | CARBO |

As one may see, the main differences in the various [5]helicenes are mostly at low wavelengths.

The main feature at ca. 305 nm is predicted with a right sign and magnitude by calculations (Fig. 2) even if at higher wavelengths: this is a notorious defect of TDDFT calculations [20]. Due to this, we have decided also to run semiempirical ZINDO calculations (not reported): we still got an acceptable correspondence with the experiment, though with fairly different rotational strengths and wavelengths from the DFT method. In the case of H1 instead, the main positive calculated band is at lower wavelength with respect to the experiment, but we think that this is one of the inconsistencies of the calculations versus the experiments that we have hinted above. The fact that at higher wavelengths no electronic transition is predicted leads us, in accord with Grimme et al. [20], to assign the observed features at ca. 339 and 323 nm to vibronic ones. In all cases, a positive large band at ca. 230 nm, due to a convolution of several transition with positive rotational trends, is calculated that correlates with the strongest positive CD signal observed at low wavelengths. However, the (–, +) doublet in order of increasing wavelengths observed between 215 and 230 nm for H1, H3, H4, H5, H6 is not found in the calculations for H3, H4, and H6. The intermediate region, from 240 to 305 nm, which comprises features of alternating signs in all monoazahelicenes (see the above scheme) is predicted to receive contributions from several transitions with varying sign and is hard to rationalize.

We would like finally to spend a word for H1. We see that the most intense CD band is calculated at lower wavelengths than other monoaza[5]helicenes, which may be tied to several facts regarding H1, that are under study: the different geometries (see Table 2), the possible change in conjugation, the different role of the N-atom, etc. A study of the solvent effect on the CD spectra of H1 may add useful data to clarify the discrepancy between calculations and experiments.

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