Absolute stereochemistry of dihydrofuroangelicines bearing C-8 substituted double bonds: a combined chemical/exciton chirality protocol

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Electronic Supplementary Information

Relative energies and relevant geometrical parameters of DFT-optimized structures of sty-2 and sty-5 (Table ESI1). Calculated and experimental $^3J_{Me8,H9a}$ and $^3J_{Me8,H9b}$ values (in Hz) for sty-2 and sty-5 (Table ESI2). UV absorption spectrum of 7-hydroxy-4-methylcoumarin in CH$_3$CN (Figure ESI1). Description of the procedure for estimating transition dipole moment positions from excited-states calculations.
Table ESI1.
Relative energies and relevant dihedral angles (in deg; see Figure 4) of DFT\textsuperscript{(b)} optimized structures of (S)-\textit{sty-2} and (S)-\textit{sty-5}.

\begin{table}
\begin{tabular}{llllll}
\hline
 & Conformer & \(d_{8,9}\) & \(d_{8,10}\) & E (kcal/mol) & Pop\textsuperscript{(a)}
\hline
\textit{sty-2} & ax\textsubscript{0} & +17 & -1 & 0 & 36
 & eq\textsubscript{0} & -11 & 0 & 0.13 & 29
 & ax\textsubscript{1} & +17 & +120 & 0.32 & 21
 & ax\textsubscript{2} & +3 & -147 & 1.14 & 5
 & eq\textsubscript{1} & -11 & +121 & 1.33 & 4
 & eq\textsubscript{2} & -13 & -142 & 1.31 & 4
\hline
\textit{sty-5} & eq\textsubscript{0} & -11 & -5 & 0 & 37
 & ax\textsubscript{0} & +13 & -5 & 0.01 & 37
 & eq\textsubscript{1} & -12 & +118 & 0.78 & 10
 & eq\textsubscript{2} & -15 & -152 & 1.00 & 7
 & ax\textsubscript{2} & +6 & -153 & 1.09 & 6
 & ax\textsubscript{1} & +5 & +148 & 1.47 & 3
\hline
\end{tabular}
\end{table}

\textsuperscript{(a)} Relative Boltzmann population at 300K.
\textsuperscript{(b)} B3LYP/6-31G** level, in CHCl\textsubscript{3} (GB/SA solvation model).

Table ESI2.
Calculated and experimental \(3^J\text{Me8,H9a}\) and \(3^J\text{Me8,H9b}\) values (in Hz) for \textit{sty-2} and \textit{sty-5}.

\begin{table}
\begin{tabular}{llllll}
\hline
 & \textit{sty-2} & \textit{sty-5}
\hline
 & \(3^J\text{Me8,H9a}\) & \(3^J\text{Me8,H9b}\) & \(3^J\text{Me8,H9a}\) & \(3^J\text{Me8,H9b}\)
\hline
Overall\textsuperscript{(b)} & 6.2 & 3.3 & 6.3 & 4.2
Calculated\textsuperscript{(a)} & eq\textsubscript{0}\textsuperscript{(c)} & 6.3 & 5.4 & 6.2 & 5.4
ax\textsubscript{0}\textsuperscript{(c)} & 6.2 & 1.5 & 6.6 & 2.3

Experimental & 6.1 & 4.8 & 6.7 & 5.8
\hline
\end{tabular}
\end{table}

\textsuperscript{(a)} Using the Karplus equation \(3^J_{\text{C,H}} = 3.6 \cos 2\phi - \cos \phi + 4.3\), where \(\phi\) is \(\phi_{\text{Me8-C8-C9-H9a}}\) or \(\phi_{\text{Me8-C8-C9-H9b}}\) dihedral angle measured for the DFT-computed structures.

\textsuperscript{(b)} Boltzmann-weighted average values at 300K for all the six DFT-computed minima (see Table ESI1).

\textsuperscript{(c)} Values calculated for the two lowest energy conformers ax\textsubscript{0} and eq\textsubscript{0} (see Table ESI1).
Procedure for the calculation of transition dipole moment position.

In the point-dipole approximation for a transition dipole moment allied to a one-electron $i \rightarrow j$ transition, its position may be calculated as the center-of-mass of atom-centered transition monopoles $\rho_{i \rightarrow j}^{\nu \rho}$ (in the dipole length formulation, DL) or of the bond-centered transitional bond-order vectors $p_{i \rightarrow j}^{\nu \rho}$ (in the dipole velocity formulation, DV).\(^1\) The above quantities are defined as follows:

$$\rho_{i \rightarrow j}^{\nu \rho} = C_i^{\nu} C_j^{\rho}$$
$$p_{i \rightarrow j}^{\nu \rho} = \left(C_i^{\mu} C_j^{\nu} - C_i^{\nu} C_j^{\mu}\right) <\nabla_{\mu \nu}^{\rho}>$$

where $C_i^{\nu}$ is the amplitude coefficient of the atomic orbital (AO) $\nu$ in the molecular orbital (MO) $i$, and $<\nabla_{\mu \nu}^{\rho}>$ the average expectation values of the dipole-velocity element, tabulated for different bond-types with various lengths.\(^2\)

In the case of ZINDO computed MOs for a $\pi-\pi^*$ transition, $C_i^{\nu}$ represents the coefficient of a $2p_{\pi}$ AO (on carbon or oxygen atoms for 7-hydroxycoumarin, and on carbon atoms only for styrene). In the case of TDDFT computed MOs, it may be defined

$$C_i^{\nu} C_{\mu}^{\rho} = \sum_{\lambda} c_{\nu}^{(\lambda)} c_{\lambda}^{(\mu)}$$

where $c_{\nu}^{(\lambda)}$ is the coefficient of the AO $\lambda$ centered on $\nu$ in the MO $i$.


Figure ESII.

UV absorption spectrum of 7-hydroxy-4-methylecoumarin 4.58·10^{-5} M in acetonitrile.