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-otpmized structures of **sty-2** and **sty-5** (Table ESI1). Calculated and experimental ${}^3J_{\mathrm{Me8,H9a}}$ and ${}^3J_{\mathrm{Me8,H9b}}$ values (in Hz) for **sty-2** and **sty-5** (Table ESI2). UV absorption spectrum of 7-hydroxy-4-methylcoumarin in CH_3CN (Figure ESI1). Description of the procedure for estimating transition dipole moment positions from excited-states calculations.

sty-2					**sty-5**				
Conformer	$d_{8,9}$	$d_{8,10}$	E (kcal/mol)	Pop$^{(a)}$%	Conformer	$d_{8,9}$	$d_{8,10}$	E (kcal/mol)	Pop$^{(a)}$%
ax_0	+17	−1	0	36	eq_0	−11	−5	0	37
eq_0	−11	0	0.13	29	ax_0	+13	−5	0.01	37
ax_1	+17	+120	0.32	21	eq_1	−12	+118	0.78	10
ax_2	+3	−147	1.14	5	eq_2	−15	−152	1.00	7
eq_1	−11	+121	1.33	4	ax_2	+6	−153	1.09	6
eq_2	−13	−142	1.31	4	ax_1	+5	+148	1.47	3

Table ESI1.

Relative energies and relevant dihedral angles (in deg; see Figure 4) of DFT$^{(b)}$ optimized structures of (*S*)-**sty-2** and (*S*)-**sty-5**.

$^{(a)}$ Relative Boltzmann population at 300K.

$^{(b)}$ B3LYP/6-31G** level, in $CHCl_3$ (GB/SA solvation model).

		sty-2		**sty-5**	
		$^3J_{\mathrm{Me8,H9a}}$	$^3J_{\mathrm{Me8,H9b}}$	$^3J_{\mathrm{Me8,H9a}}$	$^3J_{\mathrm{Me8,H9b}}$
Calculated$^{(a)}$	Overall$^{(b)}$	6.2	3.3	6.3	4.2
	$eq_0$$^{(c)}$	6.3	5.4	6.2	5.4
	$ax_0$$^{(c)}$	6.2	1.5	6.6	2.3
Experimental		6.1	4.8	6.7	5.8

Table ESI2.

Calculated and experimental $^3J_{\mathrm{Me8,H9a}}$ and $^3J_{\mathrm{Me8,H9b}}$ values (in Hz) for **sty-2** and **sty-5**.

$^{(a)}$ Using the Karplus equation $^3J_{\mathrm{C,H}} = 3.6\cos 2\varphi - \cos\varphi + 4.3$, where φ is $\varphi_{\mathrm{Me8–C8–C9–H9a}}$ or $\varphi_{\mathrm{Me8–C8–C9–H9b}}$ dihedral angle measured for the DFT-computed structures.

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

$^{(c)}$ Values calculated for the two lowest energy conformers ax_0 and eq_0 (see Table ESI1).

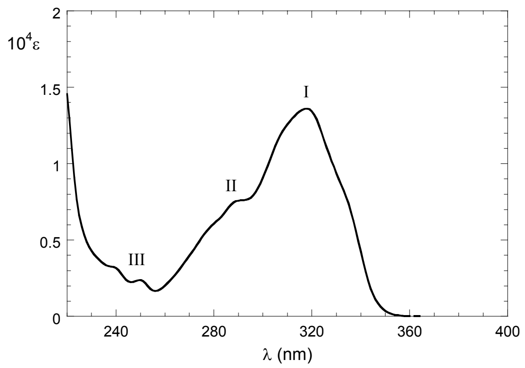

Figure ESI1.

UV absorption spectrum of 7-hydroxy-4-methylcoumarin $4.58 \cdot 10^{-5}$ M in acetonitrile.

Procedure for the calculation of transition dipole moment position.

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

$$\rho_{\nu}^{i\to j} = C_{\nu}^{i} C_{\nu}^{j}$$

$$p_{\nu,\mu}^{i\to j} = \left(C_{\mu}^{i} C_{\nu}^{j} - C_{\nu}^{i} C_{\mu}^{j} \right) < \nabla_{\mu-\nu} >$$

where C_{ν}^{i} is the amplitude coefficient of the atomic orbital (AO) ν in the molecular orbital (MO) i, and $<\nabla_{\mu-\nu}>$ 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 π-π* transition, C_{ν}^{i} 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

$$C_{\nu}^{i} C_{\mu}^{j} = \sum_{\lambda} c_{\nu}^{i(\lambda)} c_{\mu}^{j(\lambda)}$$

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

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[1] S. F. Mason, *Molecular Optical Activity and the Chiral Discrimination*, Cambridge University Press, Cambridge, 1982; p. 66-69.

[2] W. H. Inskeep, D. W. Miles, and H. Eyring, *J. Am. Chem. Soc.*, 1970, **92**, 3866-3872.