Supporting Information Paragraph

Stereomutations of Atropoisomers of Sterically Hindered Salophen Ligands.

**Antonella Dalla Cort,^[a] Francesco Gasparrini,^[b] Lodovico Lunazzi,^[c] Luigi
Mandolini,^[a] Andrea Mazzanti,^[c] Chiara Pasquini,^[a] Marco Pierini,^[b]
Romina Rompietti^[b] and Luca Schiaffino^[a].**

^[a]Dipartimento di Chimica and IMC-CNR Sezione Meccanismi di Reazione, Università
La Sapienza, Box 34 Roma 62, 00185 Roma, Italy;

^[b]Dipartimento di Studi di Chimica e Tecnologia delle Sostanze Biologicamente Attive, Università
La Sapienza, Piazzale Aldo Moro 5, 00185 Roma, Italy;

^[c]Dipartimento di Chimica Organica “A Mangini”, Università di Bologna,
Viale Risorgimento 4, 40136 Bologna, Italy.

Index

Computational details of calculations on compound 2	S3
Temperature-dependent chromatographic profiles of 3	S4
HPLC resolution of the enantiomers of 3	S5
Temperature-dependent chromatographic profiles of 4	S6
HPLC separation of the distereoisomers of 4	S7
Temperature dependence of the ^1H signals of the imine hydrogen of 4	S8

Compound 2

Conformational searches on **2** were carried out at dielectric constant values of 47 and 3 to simulate the effects of DMSO and C₆H₆, respectively, on the stability of *trans* and *cis* conformations. Calculations were performed by Montecarlo stochastic algorithm with 3000 generated structures, using MMFFs Force Field as implemented in Macromodel v. 7.2. All the rotatable bonds were explored. Low energy structures found within 3 kcal mol⁻¹ were selected and analyzed by a thermodynamic statistical approach. In table 1s are reported the calculated thermodynamic quantities ΔH , ΔS and ΔG as a function of the dielectric constant for both isomers.

Table 1s. Molecular mechanics calculated values of the steric enthalpy (ΔH in kcal mol⁻¹), steric entropy (ΔS in cal mol⁻¹ K⁻¹), steric free energy (ΔG in kcal mol⁻¹) and of the Boltzmann populations ratios of the *cis* and *trans* stereoisomers of **2** at 298 K as a function of the dielectric constant (ϵ).

		TRANS ISOMER	CIS ISOMER	% Population TRANS:CIS
		[<i>a</i> _{1,8} <i>P</i> (<i>M</i>); <i>a</i> _{6,7} <i>P</i> (<i>M</i>)]	[<i>a</i> _{1,8} <i>P</i> (<i>M</i>); <i>a</i> _{6,7} <i>M</i> (<i>P</i>)]	
$\epsilon = 47$	ΔH	131.9	132.7	91:9
	ΔS	6.7	4.7	
	ΔG	129.9	131.3	
$\epsilon = 3$	ΔH	136.5	138.8	99:1
	ΔS	3.9	2.7	
	ΔG	135.4	138.0	

Compound 3

Figure 1s. Temperature-dependent chromatographic profiles of **3** on Chiralcel-OD column. Experimental chromatogram (eluent: n-hexane/2-propanol/methanol 95/3.5/1.5, flow rate 1 ml/min, UV detection at 254 nm) as function of temperature (left). Computer simulated profiles obtained with the given rate constants for the on-column enantiomerization process (right).

Figure 2s. Top: HPLC resolution of the enantiomers of **3** at 10 °C on Chiralcel-OD column (eluent: n-hexane/2-propanol/methanol 95/3.5/1.5, flow rate 1 ml/min, UV (trace a) and CD (trace b) detection at 254 nm). Bottom: corresponding CD spectra.

Compound 4

Figure 3s. Temperature-dependent chromatographic profiles of **4** on Chiralcel-OD column. Left: experimental chromatogram (eluent: n-hexane/2-propanol/methanol 95/3.5/1.5, flow rate 1 ml/min, UV detection at 254 nm) as function of temperature. Right: computer simulated profiles obtained with the given rate constants for the on-column diastereomerization process.

Figure 4s. Top: HPLC separation of the distereoisomers of **4** at 5 °C on Chiralcel-OD column (eluent: n-hexane/2-propanol/methanol 95/3.5/1.5, flow rate 1 ml/min, UV (trace a) and CD (trace b) detection at 254 nm). Bottom: corresponding CD spectra.

Figure 5s. Temperature dependence of the ¹H signals (600 MHz) of the N=CH hydrogen of **4** in nitrobenzene-*d*₅ (left), and spectral simulation based on the given rate constants (right).