Table 1: Comparison between the relative Gibbs energy ΔG (kJ/mol) for the monomer of *trans*-AI and its 1:1 and 1:2 complexes with DMSO-*d6*, calculated without (left column) and with (right column) dispersion correction.

	ΔG (kJ/mol)	
Monomer	B3LYP/6-311++G(d,p)	B3LYP-D3BJ/6-311++G(d,p)
eqg G	0.0	0.0
	1.9	2.4
	3.5	3.7
eqiG	4.3	4.1
eqg	5.1	5.0
	5.5	0:2
axg G	5.0	5.0
equ	6.2	6.0
1:1 complexes		
bi- eq g⁺ G⁻	0.0	0.0
mono _{oн} - eq g⁻G⁻	1.4	2.2
mono _{oн} - eq g⁻G⁺	2.0	5.7
mono _{oн} - eq tG	2.4	3.3
mono _{oн} - еq g⁻Т	3.4	3.6
noHB- eq g⁺G⁺	3.4	15.4
bi- eq g⁺T	4.1	3.0
mono _{oн} - ax g⁺T	4.7	10.2
mono _{oн} - eq tТ	6.8	6.3
mono _{NH} - eq g ⁺ G ⁺	10.8	14.3
mono _{oH} - eq g⁺G⁺	12.7	2.9
mono _{oн} - ax tG	13.7	2.4
mono _{oн} - ах tТ	16.2	7.1
mono _{NH} - eq tT	20.8	21.6
1:2 complexes		
dmso-bi- eq g⁺G⁻	0.0	1.1
dmso-mono _{oн} - eq g ⁻ G⁺	1.1	11.8
dmso-bi- eq g⁺T	1.6	6.1
dmso-mono _{он} - еq g ⁻ Т	2.3	7.6
dmso-mono _{oн} - eq tG ⁻	3.1	5.6
dmso-mono _{oн} - eq tT	5.5	0.0
dmso-mono _{oн} - аx g ⁻ G ⁻	6.0	20.7
dmso-mono _{он} - еq g ⁻ G ⁻	6.4	6.2
dmso-mono _{NH} - eq g ⁺ G ⁺	6.9	13.2
mono _{oн} -mono _№ - eq tG ⁺	8.1	15.4
mono _{oH} -mono _{NH} - eq g⁺G⁻	8.3	2.7
mono _{oH} -mono _{NH} - ax tT	15.7	10.5
dmso-mono _{oH} - ax g⁺T	16.9	8.2
dmso-mono _{NH} - ax tT	29.4	29.4



Scheme 1: Structure of trans-AI and atom numbering



 $\mathbf{eq} \, g^+ G^+$: 0.0 kJ·mol⁻¹



 $\mathbf{eq} \, g^+ G^-$: 1.9 kJ·mol⁻¹



 $\mathbf{eq} \ g^- G^+$: 3.5 kJ·mol⁻¹



 $eq tG^+$: 4.3 kJ·mol⁻¹



 $eq g^-T$: 5.1 kJ·mol⁻¹



 $\mathbf{eq} \, g^+T$: 5.5 kJ·mol⁻¹



Figure 1: Most stable structures of the *trans*-AI monomer calculated at the B3LYP/6-311G++(d,p) level in a DMSO continuum.





 mono_{OH} -eq g^-G^- : 1.4 kJ·mol⁻¹

bi-eq g^+G^- : 0.0 kJ·mol⁻¹







 mono_{NH} -eq g^+G^+ : 10.8 kJ·mol⁻¹

Figure 2: Most relevant stable structures of the *trans*-AI: (DMSO- d_6) 1:1 complex calculated at the B3LYP/6-311G++(d,p) level in a DMSO continuum.



Figure 3: Most relevant stable structures of the *trans*-AI: $(DMSO-d_6)_2$ 1:2 complex calculated at the B3LYP/6-311G++(d,p) level in a DMSO continuum



Figure 4: Contour plots of occurrence of O(*trans*-AI)-DMSO and N(*trans*-AI)-DMSO distances for each the five DMSO molecules in the 1:5 equatorial complex at 150 K, together with their superposition. The contour plots are divided in four regions labelled with the corresponding static 1:1 complexes.





Figure 5: Contour plots of occurrence of O(*trans*-AI)-DMSO and N(*trans*-AI)-DMSO distances for the 1:1 complex at 300 K in the FFMD simulations.



Figure 6: Dihedral angle C_1 - C_2 - C_3 - C_4 of the 5-membered ring of *trans*-AI during the simulations at 300 K with one, two and five DMSO molecules.



Figure 7: Contour plots of occurrence of O(*trans*-AI)-DMSO and N(*trans*-AI)-DMSO distances for both DMSO molecules (left and right) in the 1:2 complex at 300 K in the FFMD simulations.



Figure 8: Contour plots of occurrence of O(*trans*-AI)-DMSO and N(*trans*-AI)-DMSO distances for the 1:1 (top) and 1:2 complexes (bottom) in the FPMD simulations at the B3LYP level. Changer la figure.



Figure 9: a) Experimental IR absorption spectrum of (*S*,*S*)-*trans*-AI and simulated spectrum from the Boltzmann-weighted average for b) the monomer c) the 1:1 complex d) the 1:2 complex with DMSO-*d6*.



Figure 10: a) Experimental VCD spectrum of *(S,S)-trans*-AI and simulated spectrum from the Boltzmann-weighted average for b) the monomer c) the 1:1 complex d) the 1:2 complex with DMSO-*d6*.



Figure 11: a) Experimental VCD spectrum of (*S*,*S*)-*trans*-AI and simulated spectrum for the b) bieqg⁺G⁻c) mono_{OH}-eqg⁻G⁻d) mono_{OH}-eqtG⁻e) bi-eqg⁺T f)mono_{NH}-eqg⁺G⁺ and g) mono_{OH}-axtG⁻ conformers.



Figure 12: IR and VCD (left) spectra obtained from the FPMD simulations compared to the experiment. The BLYP-D3 and B3LYP-D3 results are shown in blue and red, respectively. Sampling clock (right), displaying how the conformational space of *trans*-AI is visited by the FPMD trajectory. The circle is divided in regions of OH orientation and sub-divided in regions of NH₂ orientation, using the notation of the static cluster analysis. The density of points is therefore proportional to the abundance of the corresponding conformation, whereas points in blue and red indicate equatorial and axial conformations, respectively.



Figure 13: FPMD study of non-local effects on the IR and VCD spectrum of *trans*-AI in DMSO solution by means of 1:1 clusters at the B3LYP-D3 level of theory; a) radially resolved spectra (top: IR, bottom: VCD) of the chiral solute with spatial regions marked as "local" and "solvent effect", respectively; b) IR (top) and VCD (bottom) spectrum of *trans*-AI without consideration of the solvent's polarisation (grey lines) and the difference spectrum as a consequence of the solvent (red lines).



Figure 14: a) Experimental VCD spectrum b) Simulated VCD spectrum obtained from the Bolzmann average of static 1:1 complex at the B3LYP/6-311G++(d,p) level c) VCD spectrum obtained from FPMD simulations using B3LYP-D3 trajectories. The VCD spectrum obtained from FPMD simulations has been shifted by -20 cm⁻¹ for better comparison with the experiment.