Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

A Versatile Resolving Agent for Diffusion Edited Separation of Enantiomers, Complex Mixtures and Constitutional Isomers

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S1: Sample Preparation

S2: Experimental Details

S3: Chemical Structures of the molecules

S4: 400 MHz ^{19}F DOSY spectrum of 2-trifluoromethylaniline, 2-trifluoromethylphenol (sample consisted of 15 mg of analyte (each) in 0.5 ml of $CDCl_3$).

S5: 400 MHz ^{19}F DOSY spectrum of 2-trifluoromethylaniline, 2-trifluoromethylphenol after the addition of 180 mg of crown ether. (Sample consisted of 10 mg of analyte (each) in 0.5 ml of $CDCl_3$). Red, blue dotted lines represent 2-trifluoromethylaniline, 2-trifluoromethylphenol.

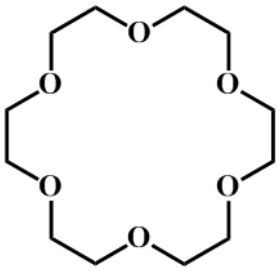
S6: Table of diffusion coefficients

Sample preparation

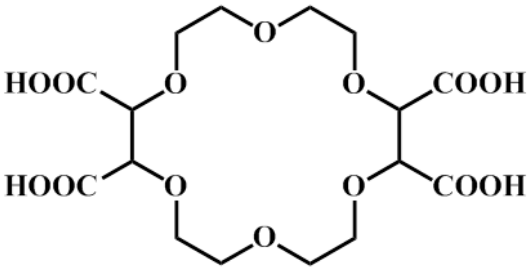
The stock solution of samples ortho-, meta- and para- chloroaniline was prepared by taking 10 mg of each isomer in 3 ml of $CDCl_3$ solution (sample1). The ^{1}H-DOSY spectrum was recorded at 298 K. To this solution the stepwise addition of 20 mg of crown ether was carried out and each time ^{1}H DOSY spectrum was recorded till the crown ether and solute attain 1:1 ratio. The best separation was achieved when 60 mg of crown ether was dissolved in 3 ml of $CDCl_3$ containing 10 mg of the solute (sample 2). The 10 mg mixture of 2-trifluoromethylaniline and 2-trifluoromethylphenol in 0.5 ml of $CDCl_3$ (sample 3). In the case of 2-trifluoromethylaniline and 2-trifluoromethylphenol, we have chosen 1:1 complex (Sample consisted of 10 mg of analyte (each) in 2 ml of $CDCl_3$) (sample 4). The 4 mg of 2-methylpiperidine, in 0.5 ml of $CDCl_3$ (sample 5). For the enantiomer discrimination in 2-methylpiperidine, incremental addition of 2 mg of Chiral crown ether in 2-methylpiperidine solution was carried out (sample 6). The best separation was achieved when the mixture pertains to 1mg of 2-methylpiperidine and 4.5 mg of crown ether. Nevertheless due to the high solubility of crown ether the solution was not viscous.

Experimental Details

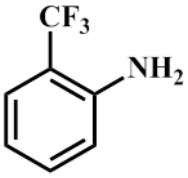
All the NMR experiments were carried out on 400 MHz using Bruker Avance-III NMR spectrometer with a total sample volume of nearly 500 µL taken in a 5 mm NMR tube. The sample temperature was maintained at 298 K using BVT-3000 temperature controller. The DOSY experiments were performed using the pulse sequence available in the Bruker library (ledbpgp2s), with stimulated echo, longitudinal eddy current compensation, bipolar gradient pulses, and two homo spoil gradients using 16 different gradient values varying from 2 to 95% of the maximum available gradient strength. Diffusion delay ranging from 100 to 1000 ms and bipolar gradient pulses from 1 to 5 ms were employed. The longitudinal eddy current delay was kept constant at 5 ms in all the experiments, whereas the gradient pulse recovery time was set to 200 µs. The gradient length was set to 2.2 ms for all the experiments. The data was processed using 65536 points in the F_2 dimension and 256 points in F_1 dimension. The line-width factor (LWF) set to 1 permitted the measurement of peak widths in the diffusion dimension



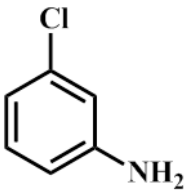
18-crown-6



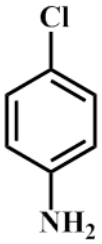
(18-Crown-6)-2,311,12-tetracarboxylic acid



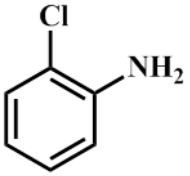
2-Chloroaniline



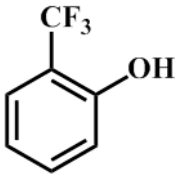
3-Chloroaniline



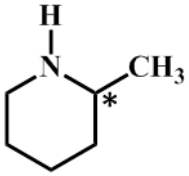
4-Chloroaniline



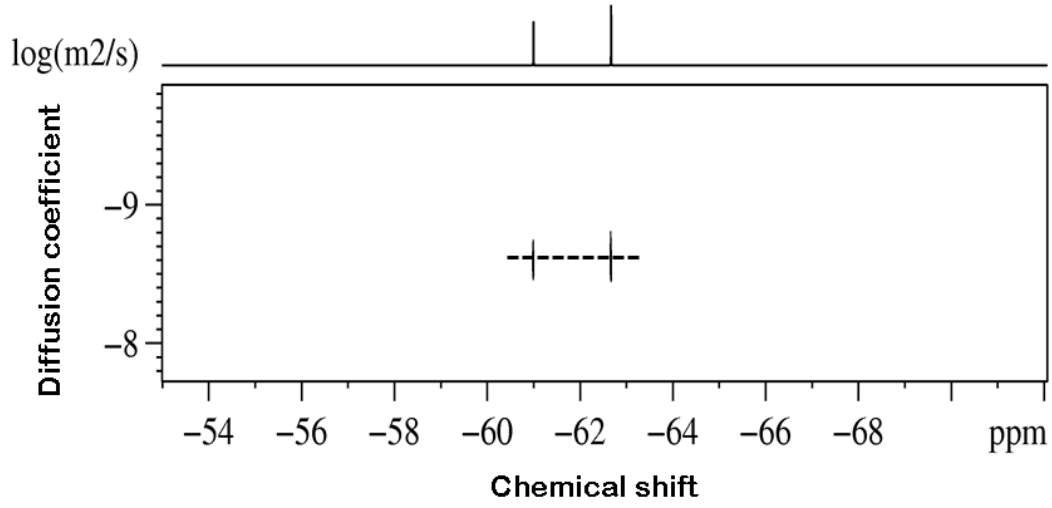
2-Trifluoromethylaniline



2-Trifluoromethylphenol



2-methylpiperidine



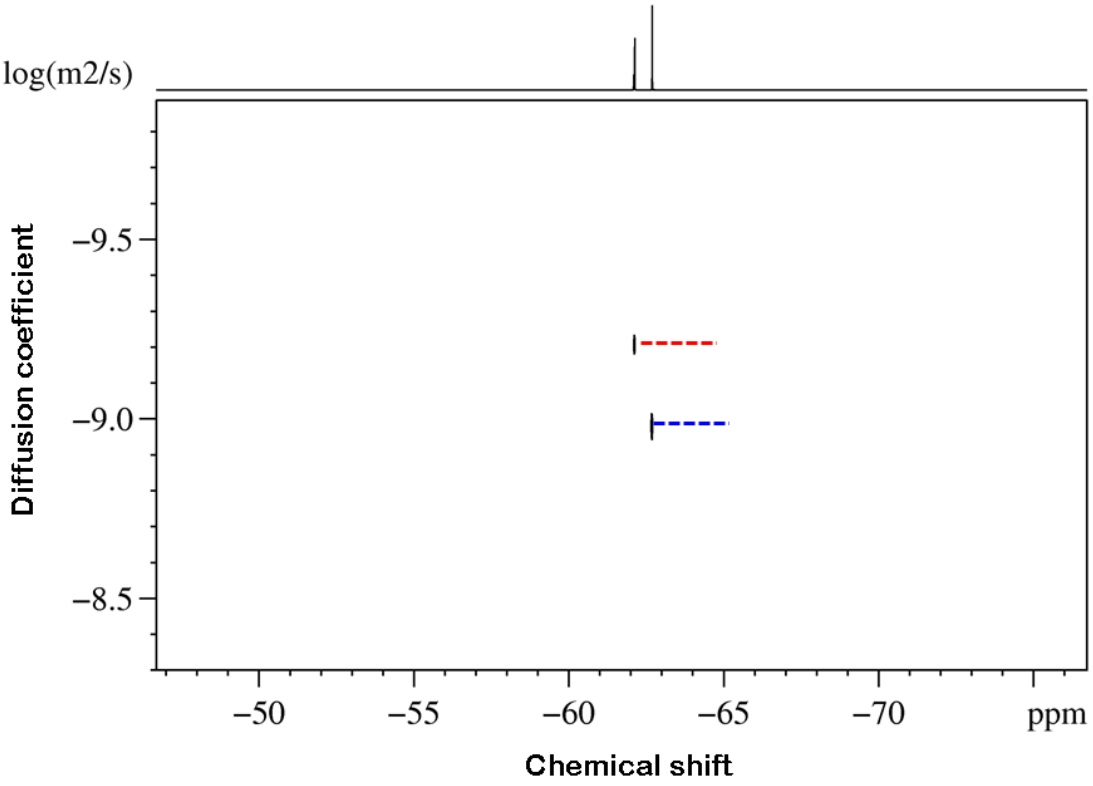


Table 1: The measured diffusion coefficients for investigated molecules in the free and complexed stated with crown-ether. The errors are given in parenthesis.

Molecule	**Diffusion Coefficient *10^{-9} (m^2/s)**	
	Free state	Complexed state with crown ether
o-chloroaniline	2.36 (3%)	1.68(1.5%)
m-chloroaniline		1.60(1.3%)
p-chloroaniline		1.49(2.4%)
2-Trifluoromethylaniline	2.80(2.2%)	0.80 (6.2%)
2-Trifluoromethylphenol		1.28 (2.6%)
2-methyl piperidine	1.50 (1.7 %)	R/S-1.25 (1%)
		S/R-1.16 (0.9 %)