NMR Enantiodifferentiation Study of Spiroglycol Chirality

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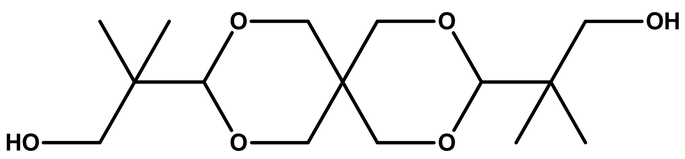
Introduction



Spiroglycol (SPG)

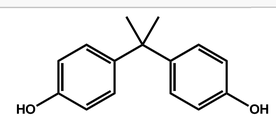
3,9-bis(1,1-dimethyl-2-hydroxyethyl)-2,4,8,10-tetraoxaspiro[5.5]undecane

Properties

- ✓ High molecular weight monomer
- ✓ Rigid alicyclic diol
- ✓ Not hazardous
- ✓ Not mutagenic

Applications

- ✓ Safe alternative to Bisphenol A
- ✓ Epoxy Resins
- ✓ Liquid Polyester Resins
- ✓ Radiation Curing Resins
- ✓ Polymer Films



Bisphenol A

NMR & Computational Study

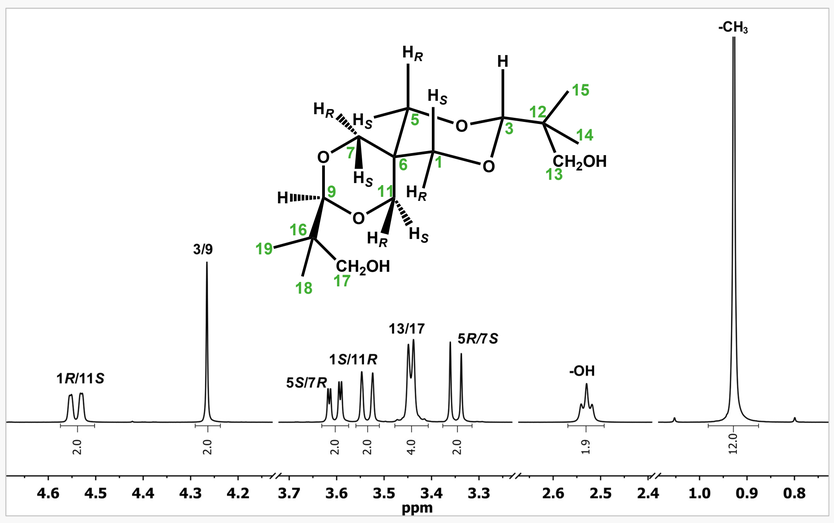


Figure 1. ^{1}H-NMR spectrum at 500 MHz of spiroglycol in $CDCl_3$. Both the axial and equatorial protons nearby the spirocarbon C6 are differentiated.

Herein, we perform for the first time a preliminary NMR and computational study of the spiroglycol structure. SPG is a highly symmetrical molecule but it should be chiral due to the presence of a chiral axis. The presence of two enantiomers was demonstrated performing NMR enantiodifferentiation experiments using α,α'-bis(trifluoromethyl)-9,10-anthracenedimethanol (ABTE) as chiral solvating agent (CSA).

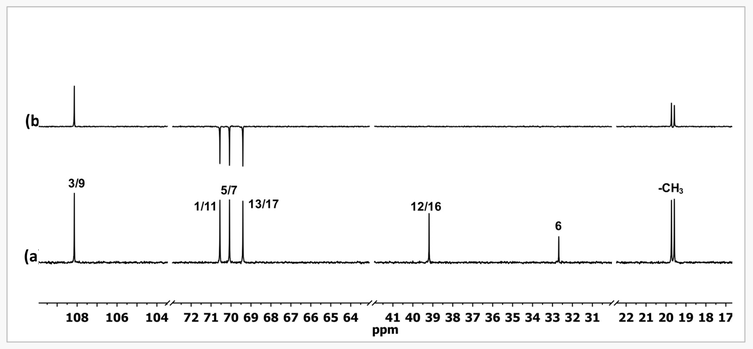


Figure 2. (a) ^{13}C-NMR spectrum at 125MHz and **(b)** DEPT135 spectrum at 125 MHz of spiroglycol in $CDCl_3$. No differentiation was observed in any signal.

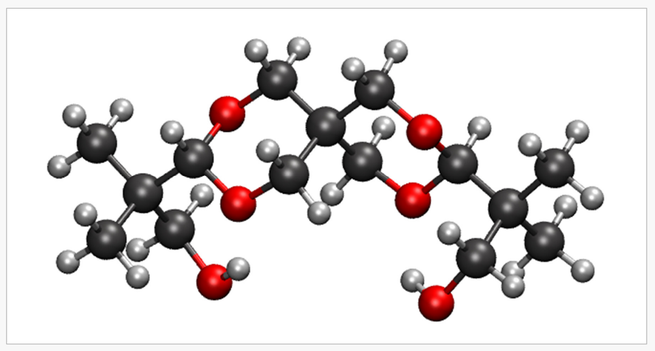
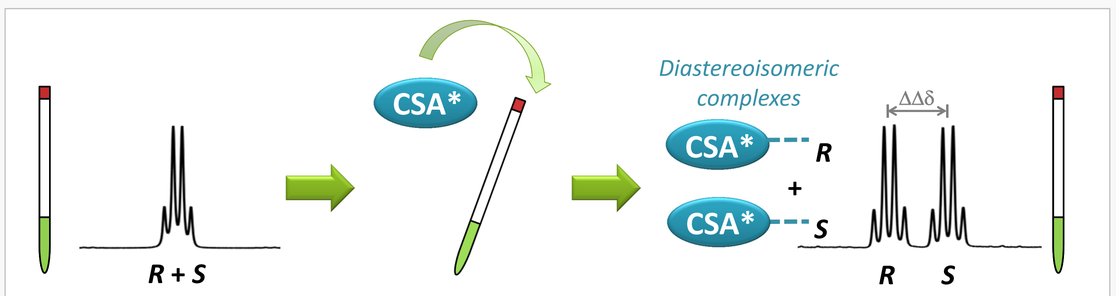


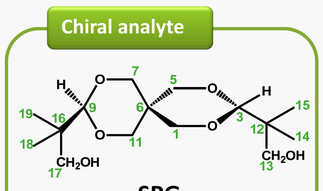
Figure 3. Lowest energy confomation of (*R*,*S*,*R*)-spiroglycol obtained by B3LYP/6-31G calculations. Two hidrogen bonds between the alcohol group and the cyclic acetal oxigen could be observed.

Enantiodifferentiation experiments



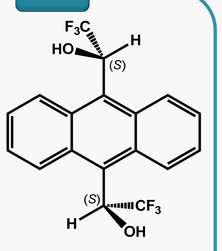
Example of enantiodifferentiation of a racemic mixture by ^{1}H NMR using a chiral solvating agent (CSA)

Chiral analyte



SPG

CSA



ABTE

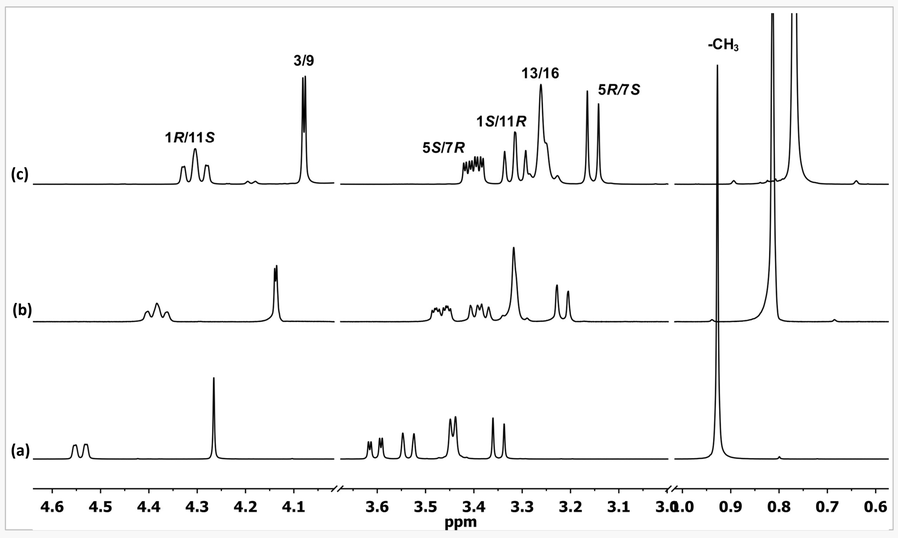
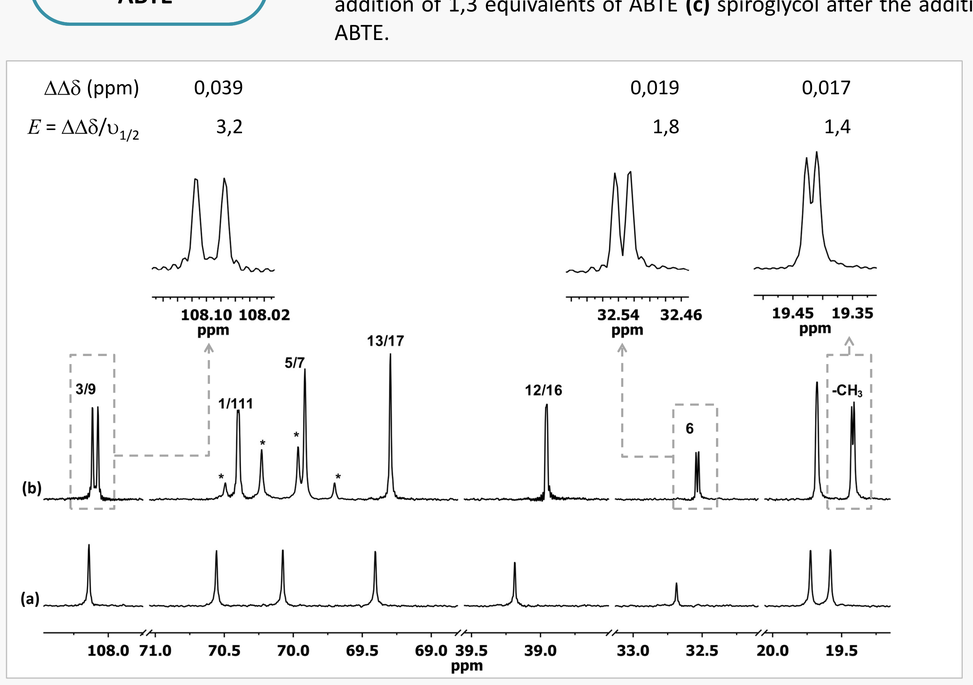


Figure 4. ^{1}H-NMR spectra at 500 MHz of **(a)** spiroglycol in $CDCl_3$ **(b)** spiroglycol after the addition of 1,3 equivalents of ABTE **(c)** spiroglycol after the addition of 3,0 equivalents of ABTE.



← **Figure 5.** ^{13}C-NMR spectra at 125 MHz of **(a)** spiroglycol in $CDCl_3$ **(b)** spiroglycol after the addition of 1,3 equivalents of ABTE. Asterisks denote signals corresponding to the chiral solvating agent (ABTE).

Derivatization

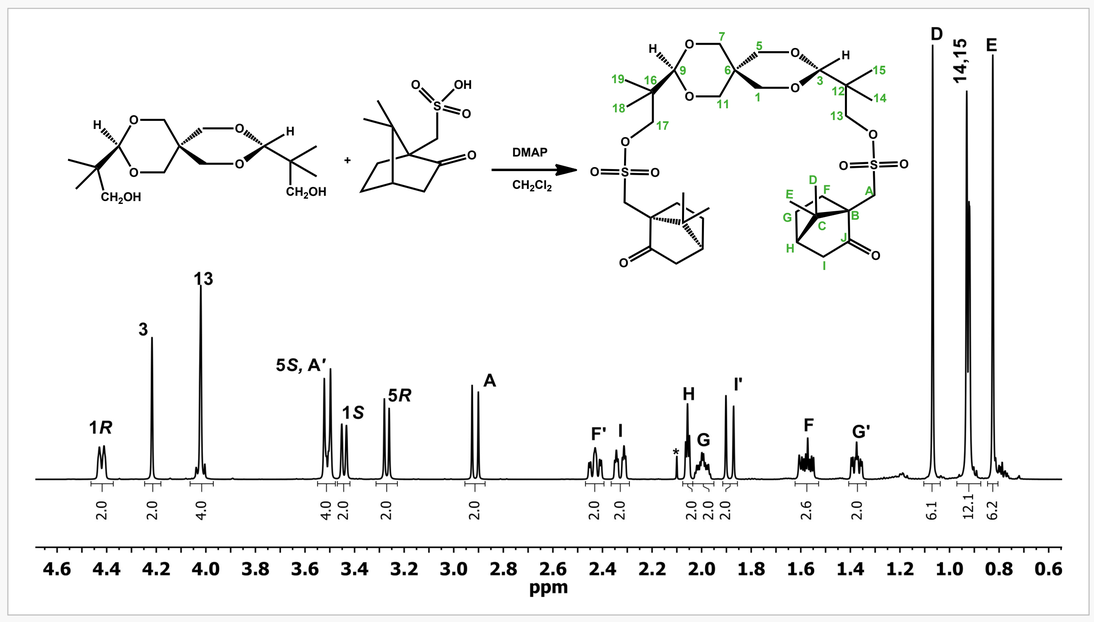


Figure 6. ^{1}H-NMR spectrum at 600 MHz of spiroglycol derivative of camphorsulfonic acid in $CDCl_3$. Asterisks denote impurities.

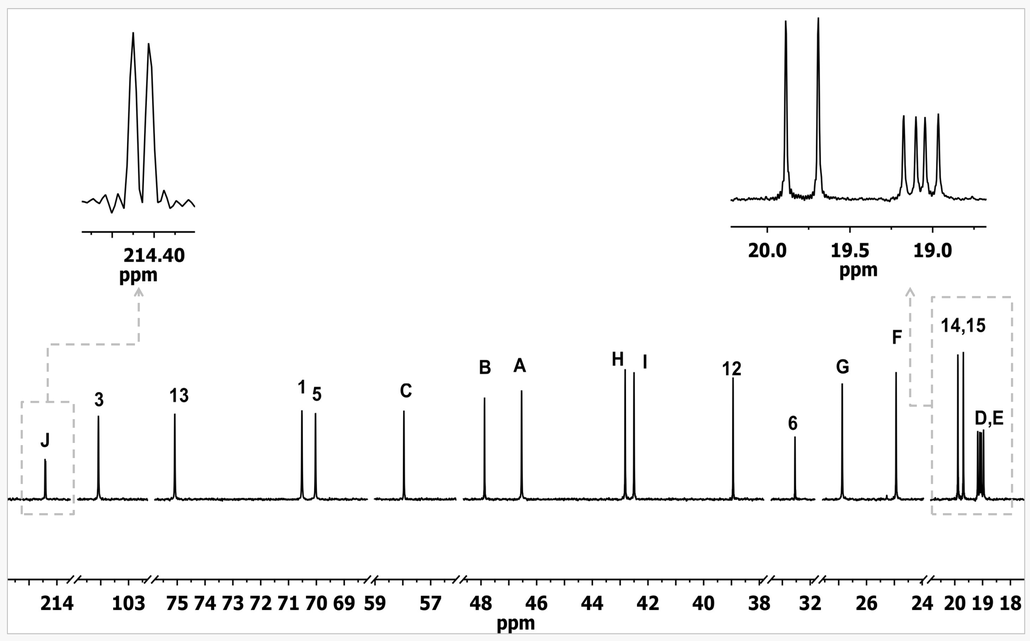


Figure 7. ^{13}C-NMR spectrum at 125 MHz of spiroglycol derivative of camphorsulfonic acid in $CDCl_3$.

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