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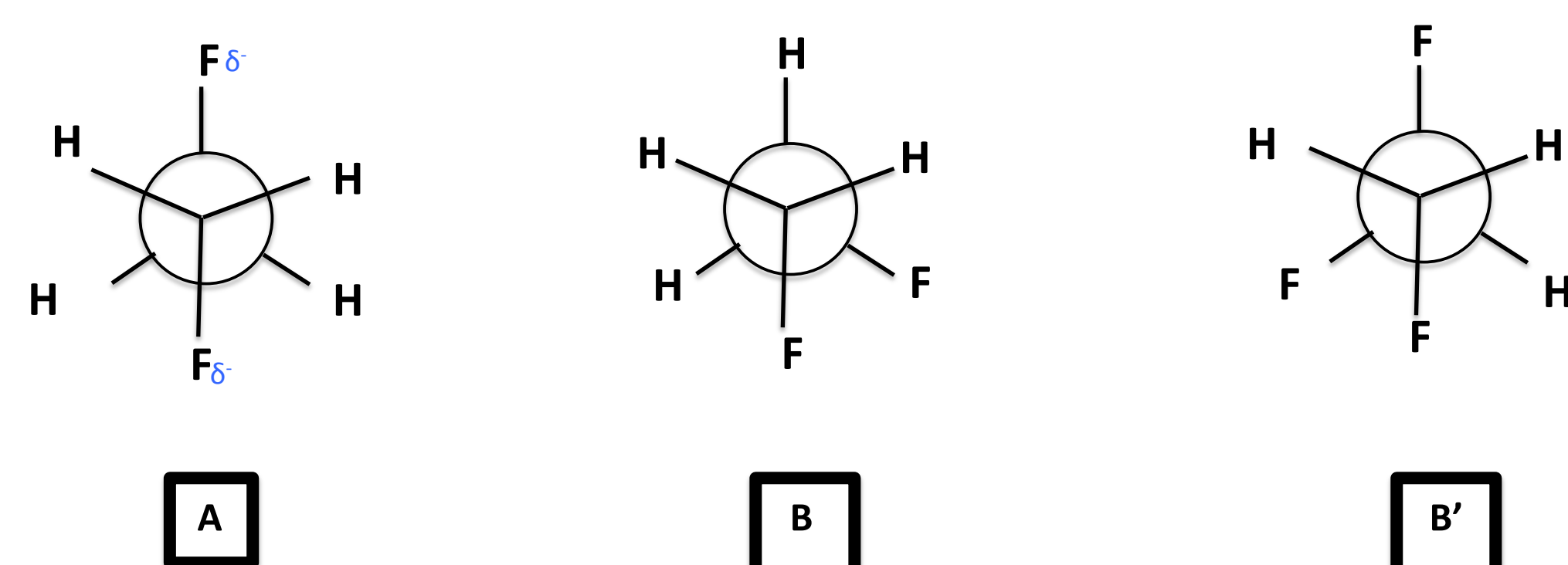
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Abstract

2R,3R-Butanediol is a simple polyol with two different isomers: the meso isomer and the racemic isomer. By examining different 2,3-Butanediol in different solvents, we investigate its conformational preferences to determine the conformational influences present in racemic-2,3-Butanediol. 2R,3R-Butanediol serves as a model molecule to understand the conformational influence in more complex compounds such as proteins. Some conformational influences we investigate are steric bulk, intramolecular hydrogen bonding, Coulombic attraction/repulsion, solvent effects, the polarity of conformer versus polarity of the solvent, and hyperconjugation. This project aims to understand the occurrence and effect of hyperconjugation between vicinal hydroxyl (OH) groups which are present in 2R, 3R-Butanediol. Hyperconjugation is an interaction between electrons in a sigma bond with a vicinal, coplanar anti-bonding sigma orbital which increases the stability of the system. The methodology employed is ¹H NMR and ¹³C NMR on 2R,3R-Butanediol in different solvents. Then, we simulate the experimental spectrum on gNMR to extract the J coupling values. We used the Altona equation in order to correlate the J-coupling constants dihedral angles there by determining the conformation of the compound.

Introduction

1,2-Difluoroethane Hyperconjugation study:



Gauche Effect describes gauche rotamers that are more stable than the anti-rotamer. In 1,2-difluoroethane the gauche effect with respect to hyperconjugation illustrates the donation of electron density from the C-H σ bonding orbital to the C-F σ^* anti-bonding orbital. In effect, the gauche isomer is considered the cause of stabilization. Since the electronegativity of fluorine is the highest, the C-F σ^* orbital is a better electron acceptor than the C-H σ orbital. On the other hand, the C-H σ orbital is a better electron donor than the C-F σ orbital. A good overlap among the better donor and the better acceptor is only conformation the gauche conformation provides.

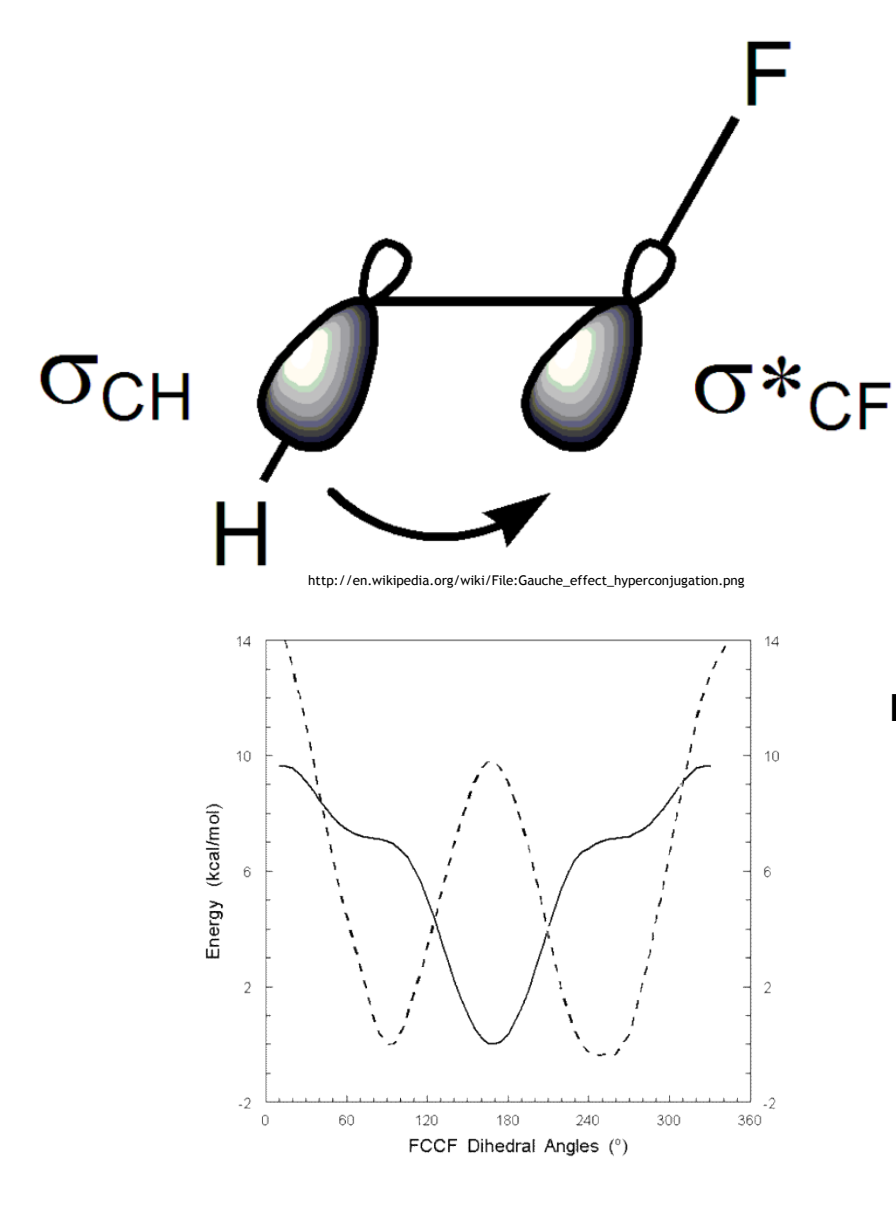
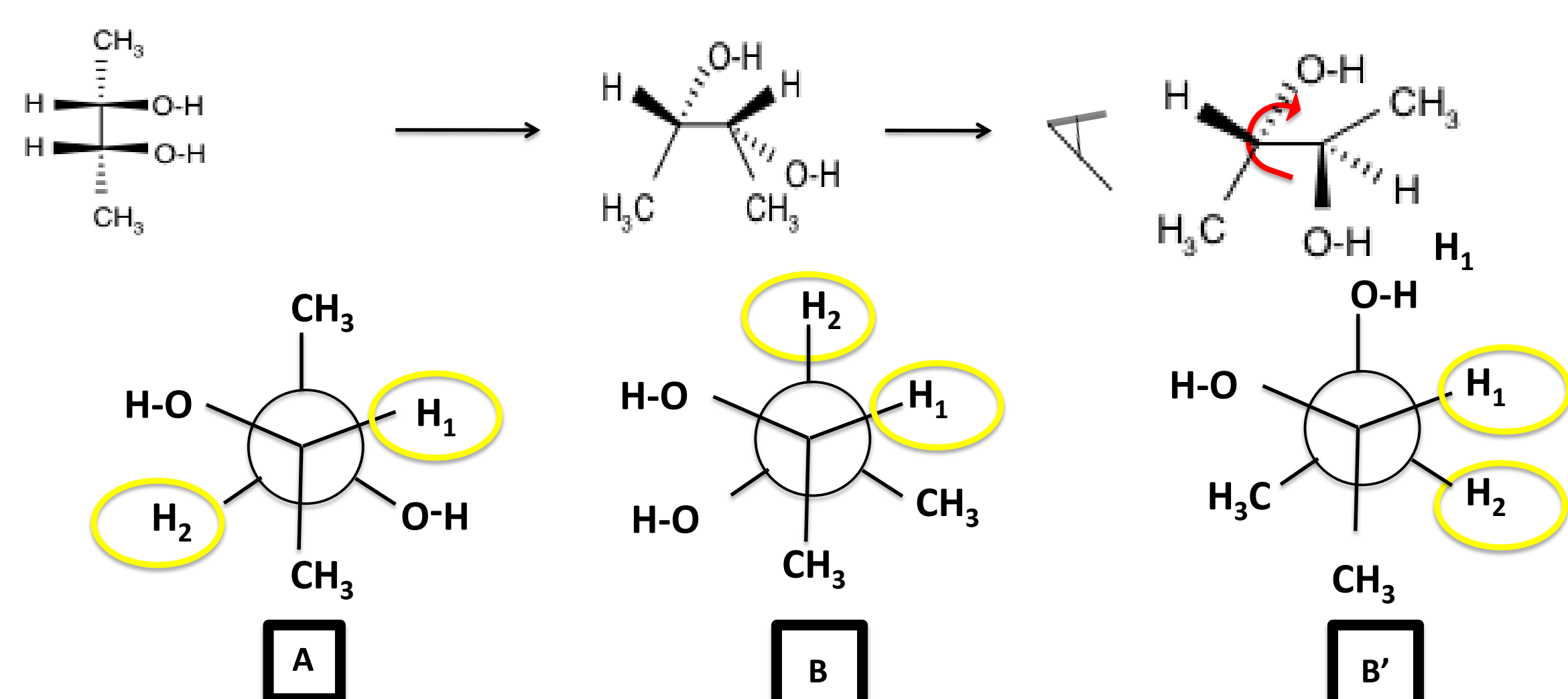


Figure 1: A model illustrating Hyperconjugation in 1,2-difluoroethane

Figure 2: It depicts the fully optimized potential curves obtained: when only the C₁-H/C₂-F* interactions are removed (---) when only the C₁-H/ C₂-F* interactions are retained with all other interactions expunged (---). Energy zero is arbitrarily taken at minimum of (---) curve.

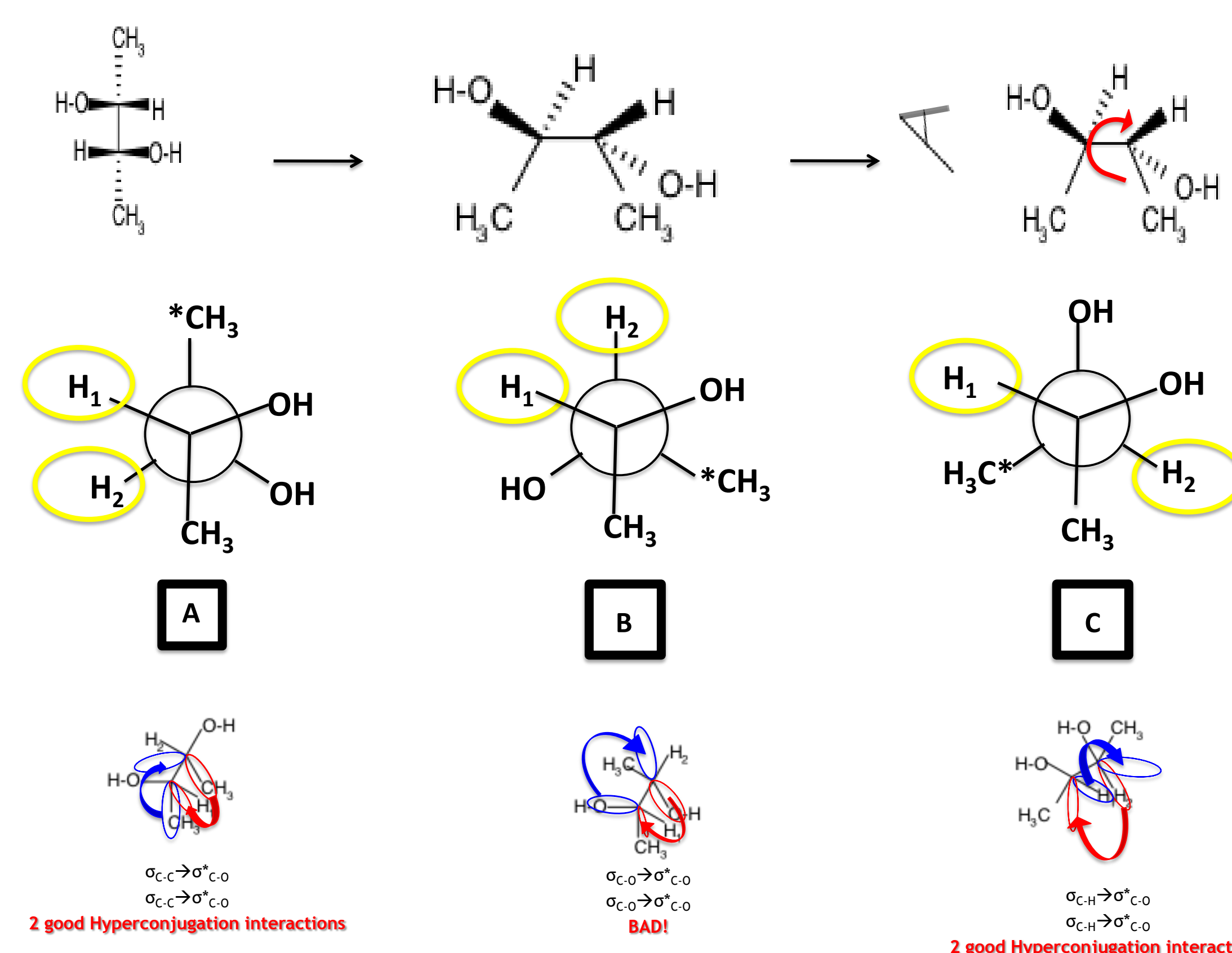
Two Isomers:



Meso-2,3-Butanediol

Unknown: $F_A, F_B, F_{B'}$
 $J_{12} = (F_A)(J_{12A}) + (F_B)(J_{12B}) + (F_{B'})(J_{12B'})$
 $F_A + F_B + F_{B'} = 1$
 $F_B = F_{B'}$

Introduction (Cont'd)



Racemic-2,3-Butanediol

Unknown: F_A, F_B, F_C
 $J_{12} = (F_A)(J_{12A}) + (F_B)(J_{12B}) + (F_C)(J_{12C})$
 $F_A + F_B + F_C = 1$
 $J_{H_1C_{obs}} = (F_A)(J_{12C}) + (F_B)(J_{12H_C}) + (F_C)(J_{12H_C})$

Methodology

¹³C NMR spectroscopy, we simulated the experimental spectra on gNMR to extract coupling constants

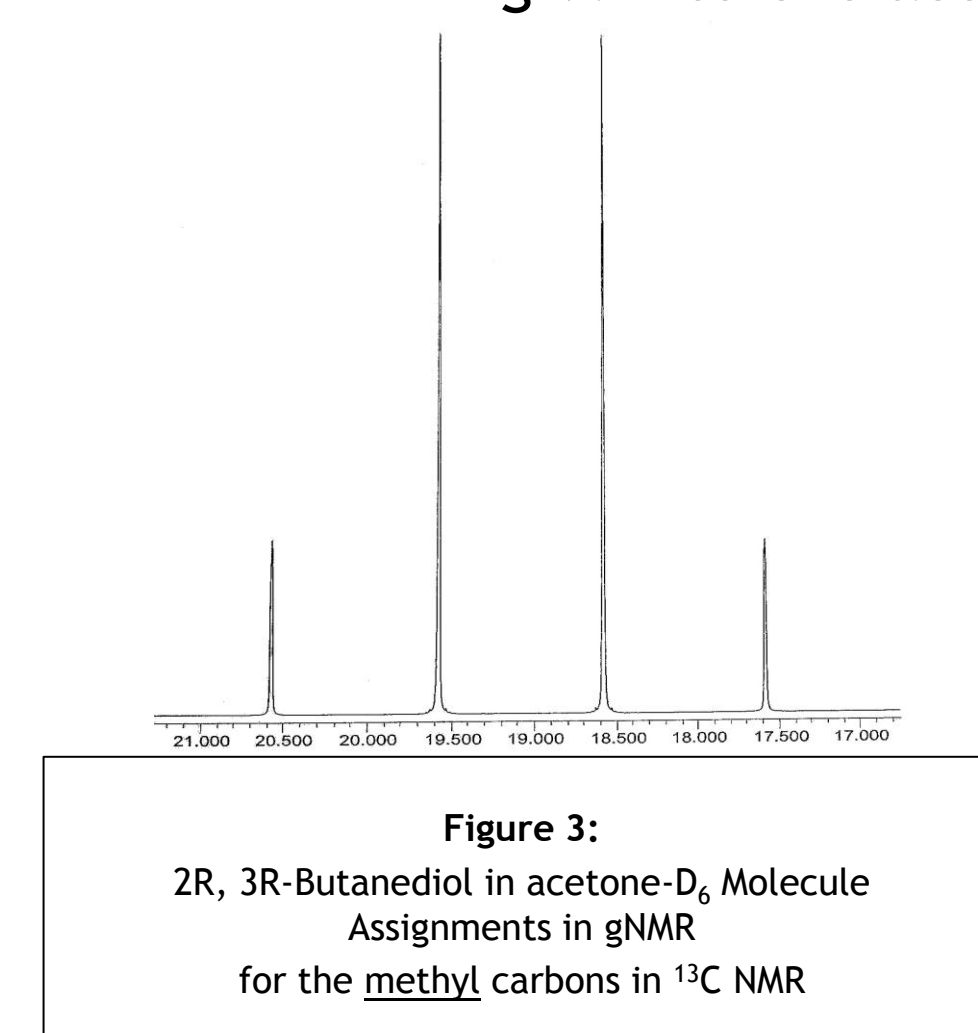


Figure 3: 2R, 3R-Butanediol in acetone-D₆ Molecule Assignments in gNMR for the methyl carbons in ¹³C NMR

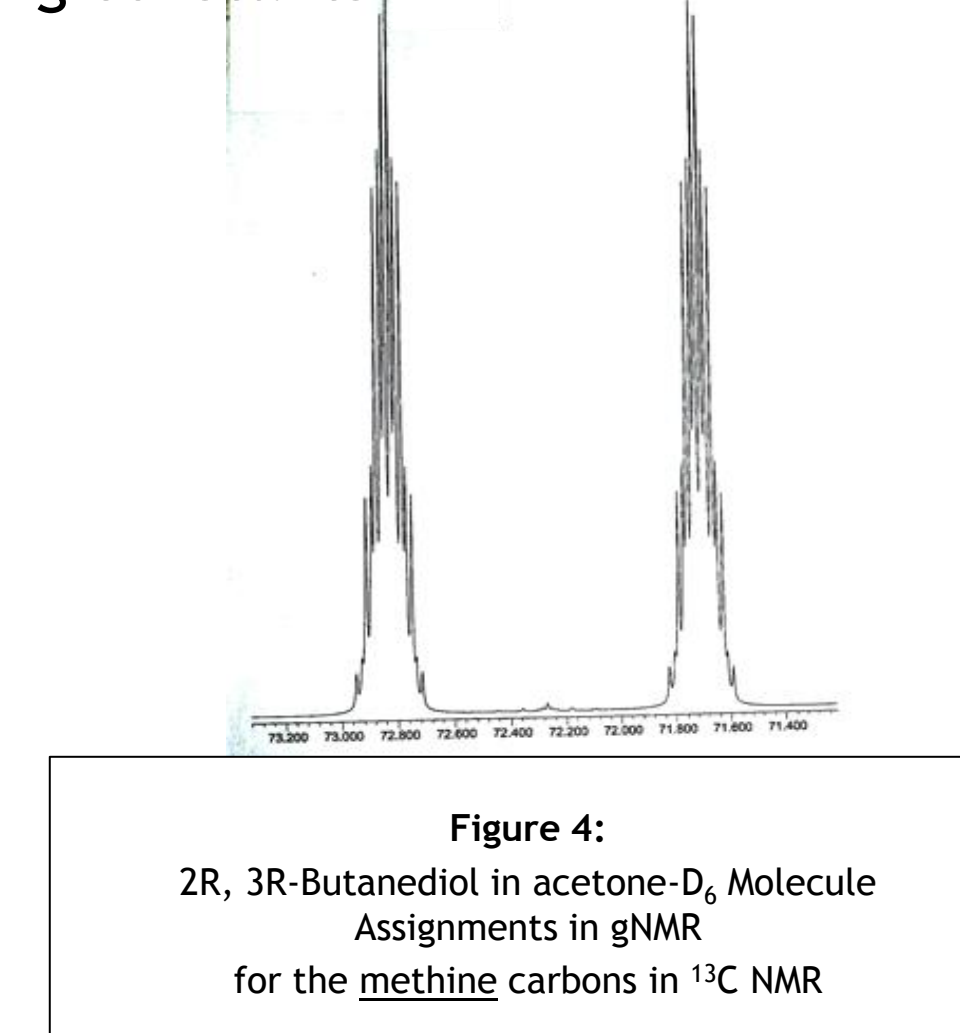


Figure 4: 2R, 3R-Butanediol in acetone-D₆ Molecule Assignments in gNMR for the methine carbons in ¹³C NMR

Projected Methodology

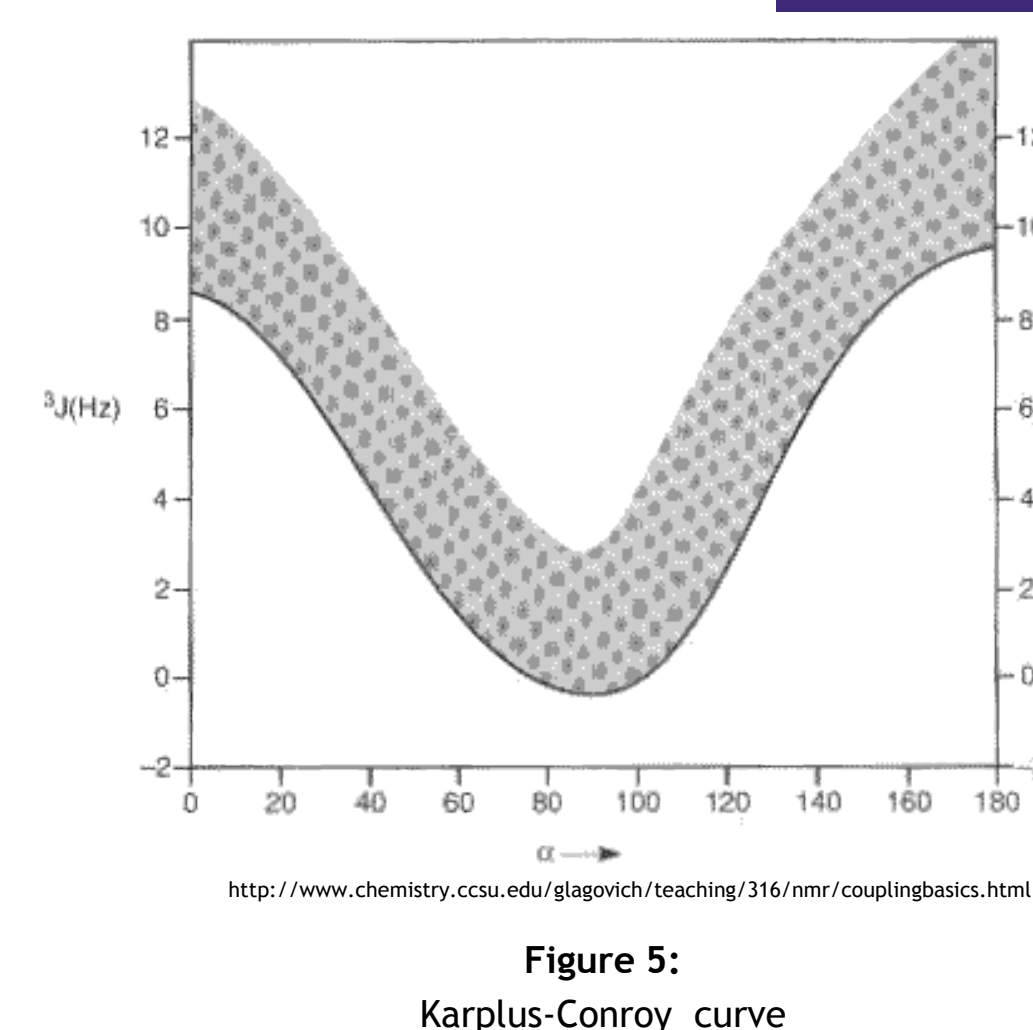


Figure 5: Karplus-Conroy curve

We project in using the Altona equation for our conformational analysis. The Altona equations for vicinal ³J_{HH} (H-Csp³-sp³C-H) are: $^3J = p_1 \cos^2(\phi) + p_2 \cos(\phi) + p_3 + S_1 I_1 (p_4 + p_5 \cos^2(e_i \phi + p_6 |I_1|))$

In which the sum is over the four substituents. The order of substitution around each carbon makes a difference. The direction coefficient, e_i , is +1 for S₁ and S₃ and -1 for S₂ and S₄. The "beta effect" is the electronegativity of the substituents includes and is provided as:

$$I_i = (C_i - C_H) + p_7 S (C_i - C_H)$$

where C_i is the Huggin's electronegativity of the directly attached a atom, C_H is the electronegativity of hydrogen, and the sum is over the b atoms that are attached to the a atom. The substituent electronegativity for each attached group is listed under the substituent name. The coefficients have also been modified to use empirical chemical group substituent constants.

Results

The coupling constants gathered from gNMR after simulation of the experimental spectra for 2R, 3R-Butanediol in diverse solvents through ¹H NMR and ¹³C NMR.

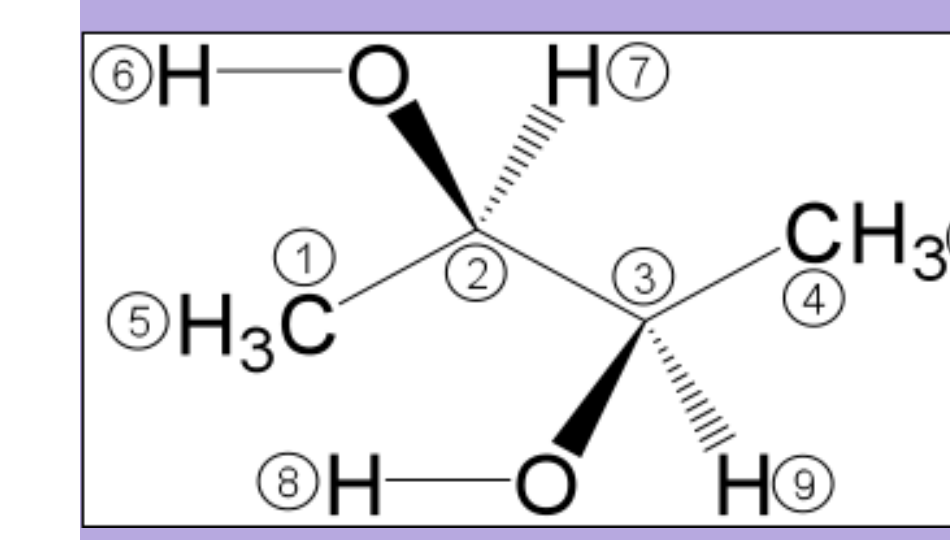


Figure 6: 2R, 3R-Butanediol molecule that correspond to the coupling constants below.

solvent	chemical shifts (ppm)		coupling constants (Hz)																				
	¹ H	¹³ C	carbon-proton							proton-proton													
D ₂ O	19.422	73.146	1.129	not obs.	3.610	126.14	-1.99	1.99	0.28	not obs.	not obs.	142.15	-4.50	not obs.	not obs.	-2.29	4.40	6.45	not obs.	-0.30	not obs.	5.94	
methanol-d ₄	18.924	72.895	1.112	not obs.	3.511	125.60	-1.29	2.35	0.21	not obs.	not obs.	141.02	-4.40	not obs.	not obs.	-2.02	4.40	6.41	not obs.	-0.29	not obs.	5.84	
ethanol-d ₄			1.101	not obs.	3.522													6.41	not obs.	-0.32	not obs.	5.87	
isopropyl alcohol-d ₆			1.106	not obs.	3.514													6.36	not obs.	-0.31	not obs.	6.04	
t-butyl alcohol-d ₈			1.108	not obs.	3.496													6.55	not obs.	-0.21	not obs.	6.39	
DMSO-d ₆	18.255	70.510	0.962	4.294	3.379	125.16	-0.19	1.36	0.00	not obs.	not obs.	139.94	-4.34	not obs.	not obs.	-2.37	4.34	6.31	0.01	-0.65	-4.73	-0.29	5.53
acetone-d ₆	19.086	72.272	1.073	3.538	3.437	125.34	-1.24	0.67	0.00	not obs.	not obs.	140.96	-4.47	not obs.	not obs.	-2.26	4.47	6.41	-0.03	-0.27	4.15	-0.27	6.02
acetonitrile-d ₃	19.888	73.152	1.052	2.859	3.437													6.15	-0.03	-0.44	-4.25	-0.24	5.94
p-dioxane-d ₁₀			1.038	3.212	3.341																		

References

Contribution to the Study of the Gauche Effect. The Complete Structure of the Anti Rotamer of 1,2-Difluoroethane Norman C. Craig, Anthony Chen, Ki Hwan Suh, Stefan Klee, Georg C. Mellau, Brenda P. Winnewisser, and Manfred Winnewisser. *J. AM.Chem.Soc.* 1997; 119(20) pp 4789-4790; (communicate)

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Acknowledgements



MCNAIR
SCHOLARS PROGRAM
UC Merced • CSU Stanislaus

- Dr. Michael D. Drake, for the opportunity, supervision, funding, and mentorship in his project.
- Mr. Yacoub, Ms. Lalimar, Ms. Ayaee for their past contributions in this project.
- Funded in part by Ronald E. McNair Post Baccalaureate Achievement Program as a research scholar.
- Mr. Jorge Camarena, Ms. Marsha Bond-Nelson, Ms. Michelle Greenwood, Mr. Jesus Cisneros, and my fellow McNair Scholars cohort for being supportive and helpful in the McNair Scholars Program.