# COMPUTATIONALLY HANDLING ION PAIRS

Comparing S_N2 and S_N1 reactions using computational methods is often quite difficult. The problem is that the heterolytic cleavage in the S_N1 reaction leads to an ion pair, and in the gas phase this is a highly endothermic process. Optimization of the ion pair in the gas phase invariably leads to recombination. This is disturbingly the result even when one uses PCM to mimic the solvent, which one might have hoped would be sufficient to stabilize the ions.

The computational study of the glycoside cleavage by Hosoya and colleagues offers some guidance towards dealing with this problem.[1] They examined the cleavage of triflate from 2,3,4,6-tetra-O-methyl-α-D-glucopyranosyl triflate **1**.

1
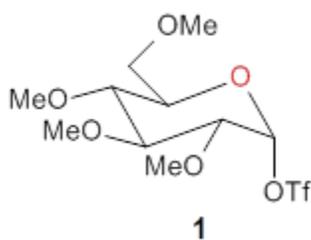
Benchmarking the dissociation energy for the cleavage of **1** and considering computational performance, they settled on M06-2X/BS-III//M06-2X/BS-I, where BS-III is aug-cc-pVTZ basis set for O, F, and Cl and cc-pVTZ for H, C, and S and

BS-I is 6-31G(d,p) basis sets were employed for H, C, and S, and 6-31+G(d) for O, F, and Cl. Solvent (dichloromethane) was included through PCM.

Attempted optimization of the contact ion pair formed from cleavage of **1** invariably led back to the covalent bound **1**. PCM is not capable of properly stabilizing these types of ions in proximity. To solve this problem, they incorporated four explicit dichloromethane molecules. A minor drawback to their approach is that they did not sample much of configuration space and so their best geometries may not be the lowest energy configurations. Nonetheless, with four solvent molecules, they were able to locate contact ion pairs and solvent-separated ion pairs. Representative examples are shown in Figure 1. This method of explicit incorporation of a few solvent molecules seems to be the direction we must take to treat ions or even highly polar molecules in solution.
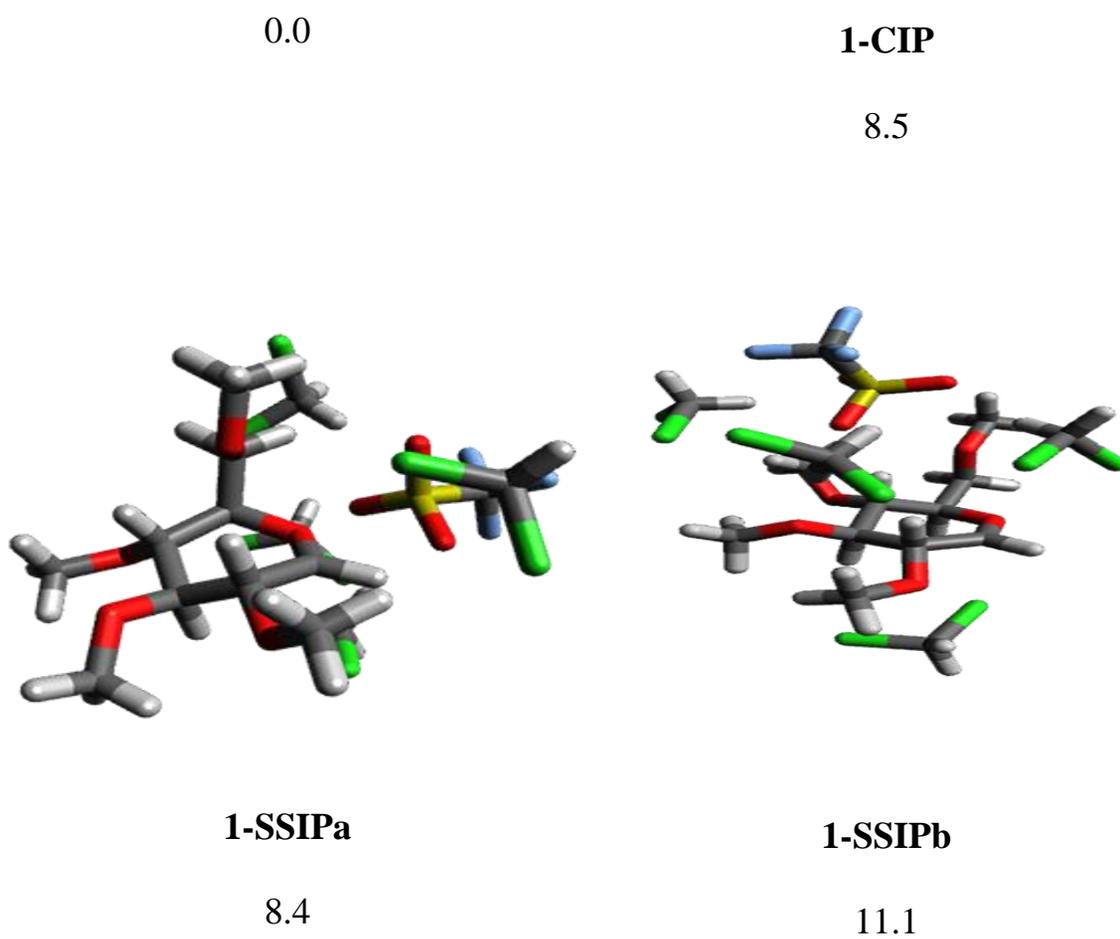

1

0.0

1-CIP

8.5

1-SSIPa

8.4

1-SSIPb

11.1
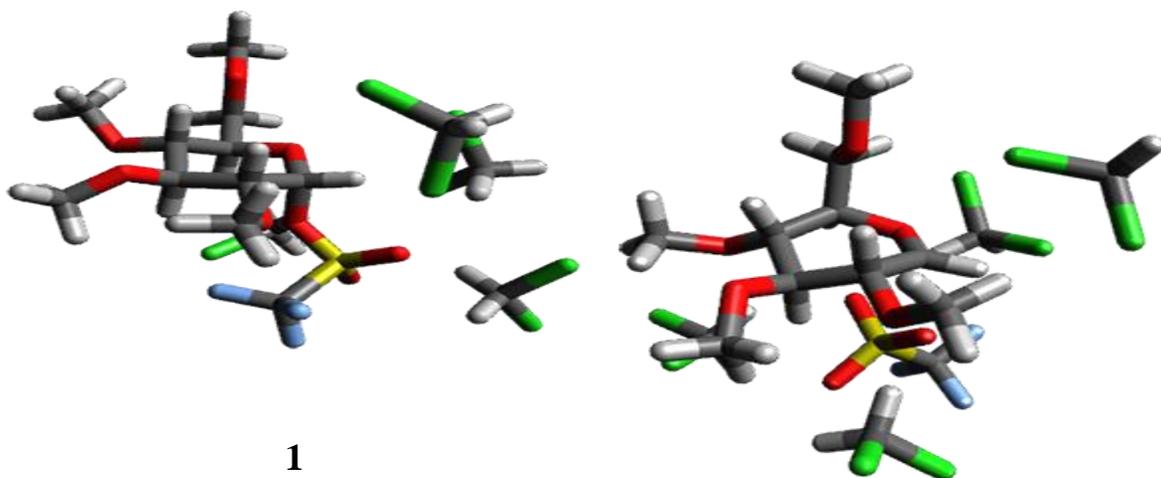
Figure 1. Representative examples of microsolvated **1**, its contact ion pair (CIP) and solvent separated ion pair (SSIP) computed at M06-2X/BS-III//M06-2X/BS-I, and relative energies (kcal mol^{-1})