Electronic Supplementary Material (ESI) for RSC Advances.

Table 1: Dihedral parameters added for force field calculations

Dihedral	Kphi (kcal/mol)	θ_0 (degrees)	Mult
C-C-O-H	-0.34098948	0	1
C-C-O-H	0.3780115	180	2
C-C-O-H	0.3780115	0	3
C-O-C-H	0.2849904	0	1
C-O-C-H	0.1599904	180	2
C-O-C-H	0.2849904	0	3
H-C-C-H	0.1419933	0	1
H-C-C-H	-0.7166587	180	2
H-C-C-H	0.1570029	0	3
C-H-C-O	-0.327010038	0	1
C-H-C-O	0.5359943	180	2
C-H-C-O	0.1400096	0	3
C-C-O-C	-0.34098948	0	1
C-C-O-C	0.3780115	180	2
C-C-O-C	0.3780115	0	3
O-C-C-O	0.2039914	0	1
O-C-C-O	0.6989962	180	2
O-C-C-O	0.4799952	0	3
O-C-C-N	0.15	0	3
C-C-N-C	-0.22000478	0	1
C-C-N-C	0.3929971	180	2
C-C-N-C	0.1359943	0	3
H-C-C-N	-0.37198853	0	1

H-C-C-N	-0.61699331	180	2
H-C-C-N	0.169001	0	3
C-N-C-H	0.1969885	0	1
C-N-C-H	-0.19299713	180	2
C-N-C-H	0.280999	0	3

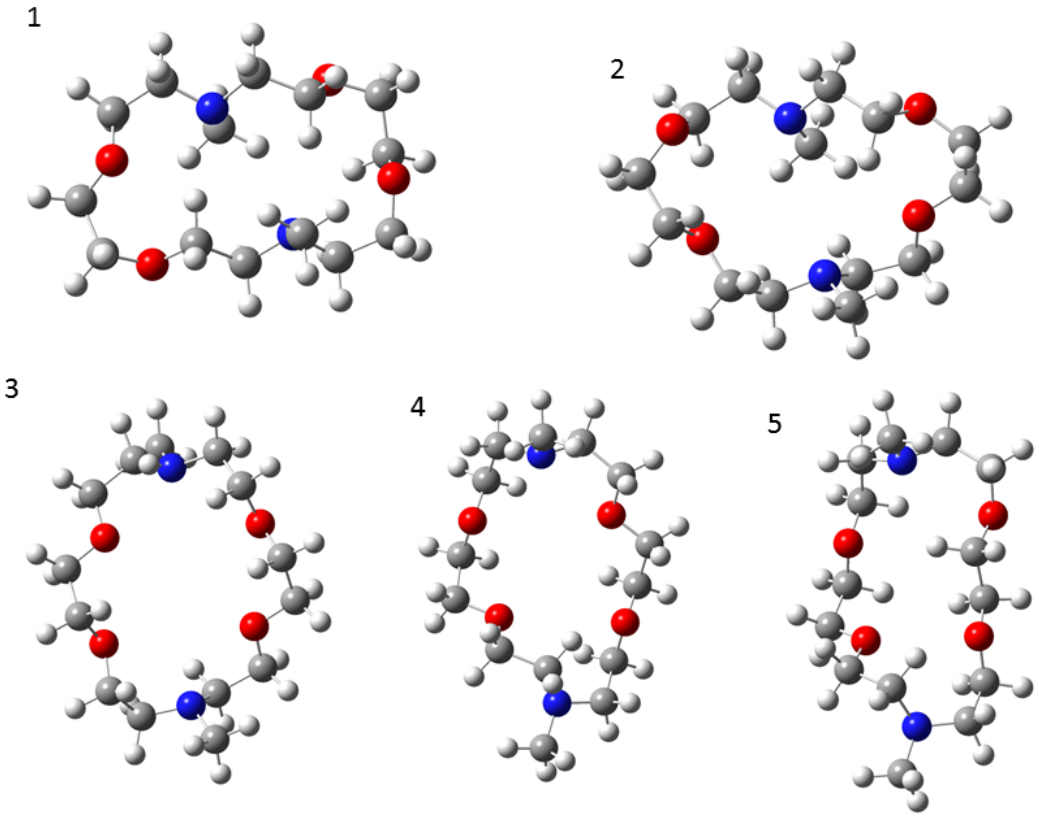


Figure S1 : Configurations related to the scans in Figure 3a (N-N scans).

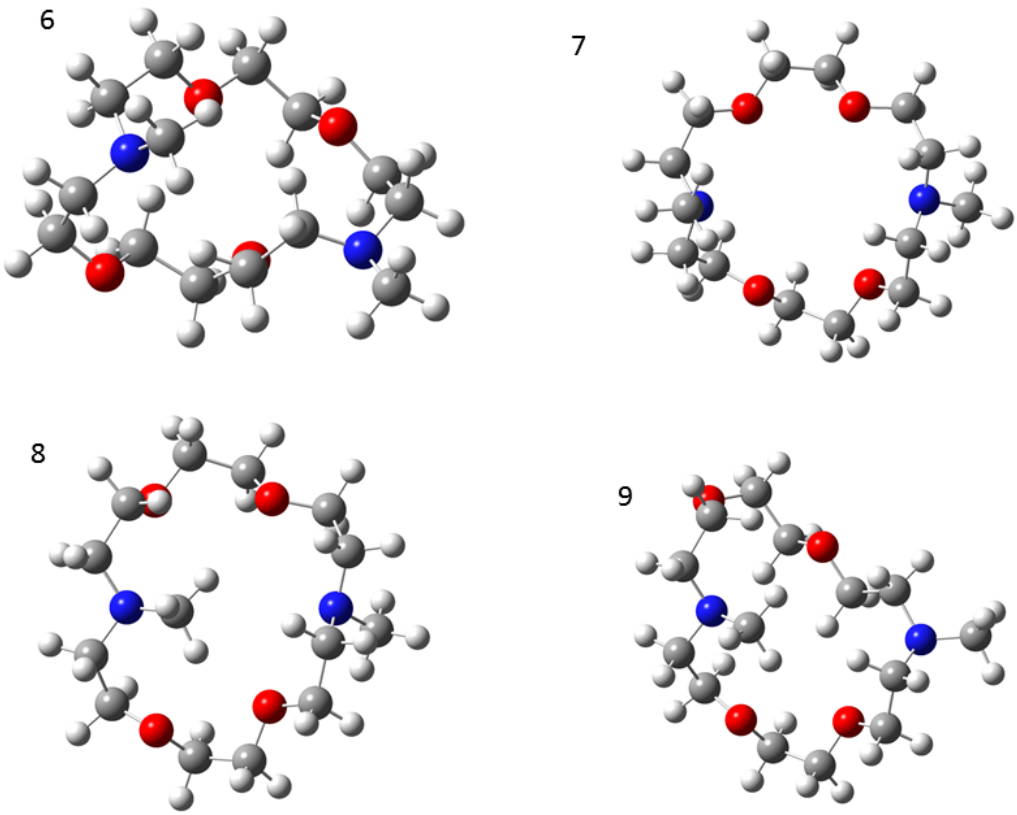


Figure S2 : Configurations related to the scans in Figure 3a (O-O scans).

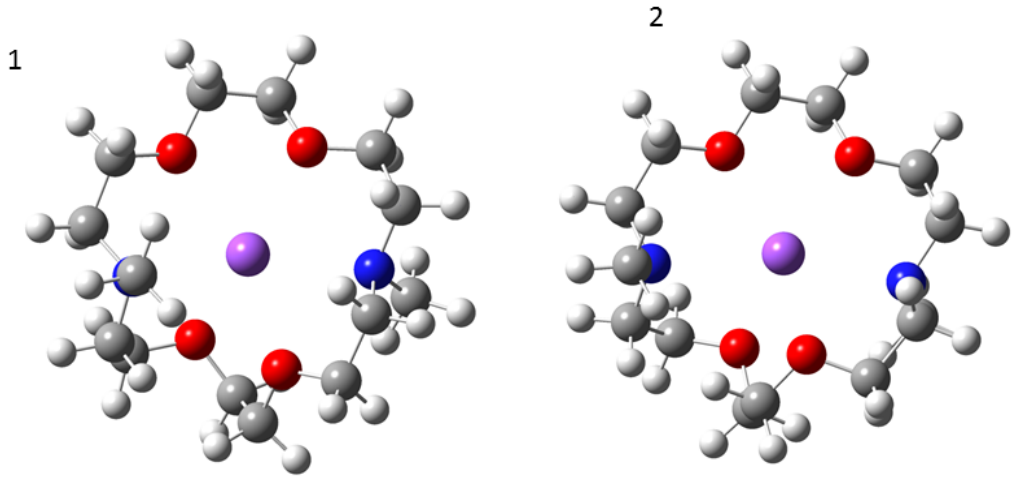


Figure S3 : Configurations related to the scans in Figure 3 b).

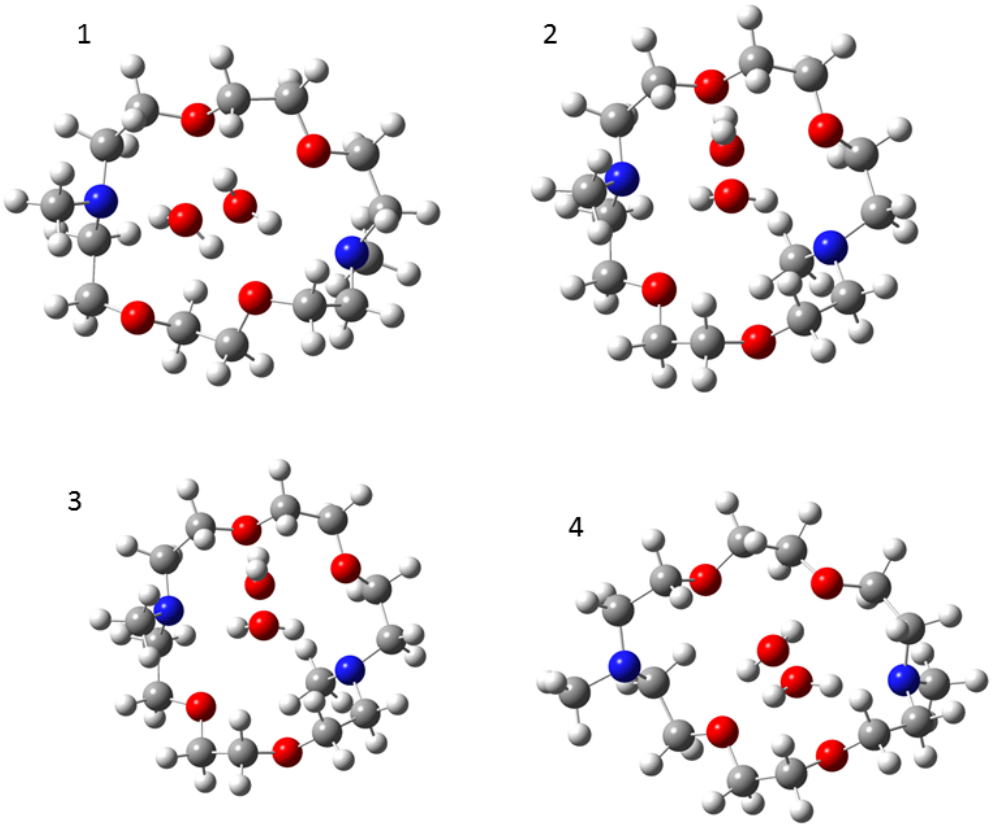
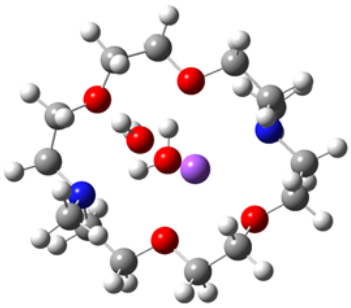


Figure S4: Configurations related to the scans in Figure 3c (N-N scans).

1



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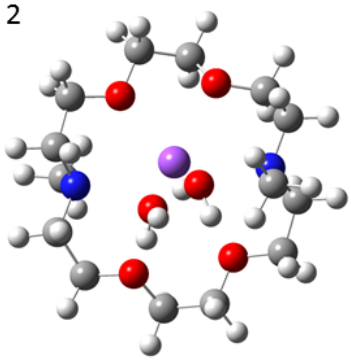

3

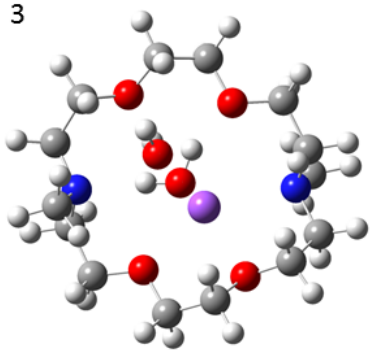

Figure S5: Configurations related to the scans in Figure 3d

Table S2: Relative, Enthaphy, Entropy and free energy

	Enthalpy (kcal/mol)	Entropy (cal/mol/k)	Free energy(kcal/mol)
D_{3d}	8.13	7.76	5.81
C_i	0	0	0
Mixed	1.91	3.50	0.87

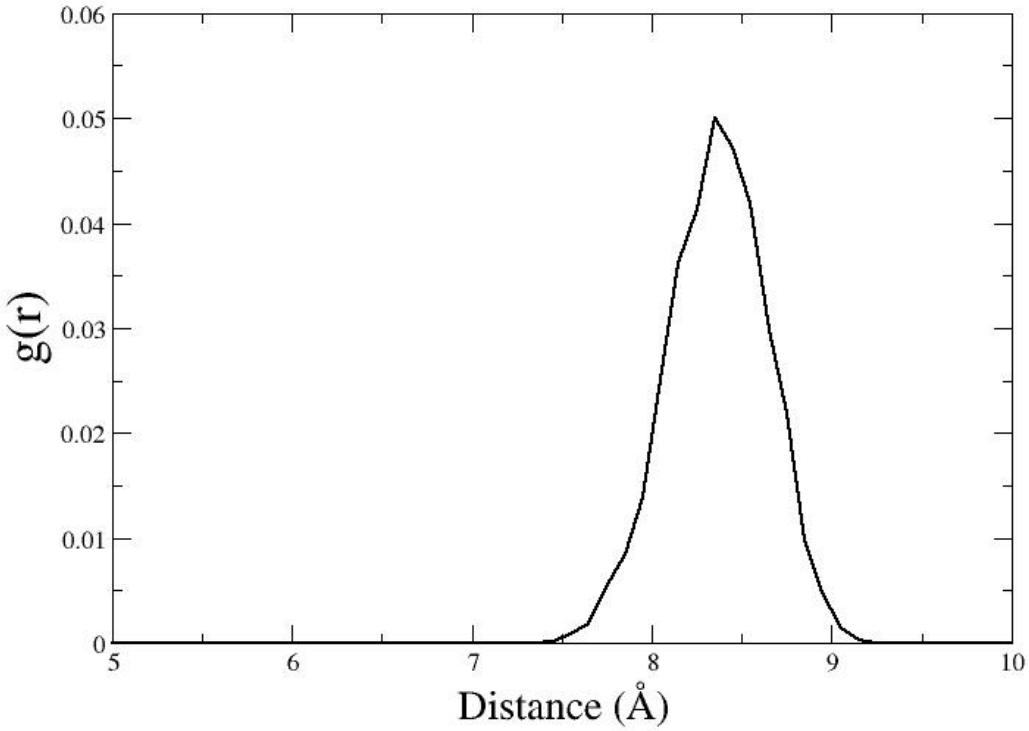

Figure S6: Diazacrown-N-N distances from the molecular dynamics simulation of hydraphile complexed to Na^+ as it is being pulled through a lipid bilayer.

Effect of Solvation model on intermolecular distances

The distances are affected by using the solvation model but most drastically are those involving explicit water molecules. For the diazacrown/water system, the water becomes bound to only two atoms, the nitrogen and one oxygen rather than two oxygen atoms; it moves farther from one oxygen atom and closer to the nitrogen and oxygen. For the Na^+-water system, the distance is considerably greater for the PCM model than in the gas phase. For the diazacrown-Na^+ cluster the Na^+ to crown oxygen and Na^+ to crown nitrogen atom distances becomes greater. The distances for the Diazacrown-Na^+-water system showed similar trends where the main difference between the solvation model and gas phase was in the Na^+-water distance, which incresed due to solvation, in line with the Na^+-water system.

Water mediated charge-transfer for Configuration 3 of diazacrown-Na^+-water cluster

There is electron transfer from both water molecules to the Na^+ (stabilization energies of water-O, 11.80 and water O-N, 10.65 kcal/mol). There is also electron transfer from the diazacrown to the two water molecules, which is part of the water mediated electron transfer. For Water O-N, there is transfer from both the crown oxygen (4.58 kcal/mol) and nitrogen (9.71 kcal/mol) lone pairs to water O-H anti-bonding orbitals. For Water O, there is only electron transfer (11.70 kcal/mol) from the crown oxygen lone pair to the water antibonding orbitals (no nitrogen to water transfer).