Theoretical insights into the structure of the Aminotris(methylenephosphonic acid) (ATMP) anion: a possible partner for conducting ionic media.

Henry Adenusi[1], Gregory Chass[2,3,4], Enrico Bodo[1*]

1 Chemistry Department, University of Rome "La Sapienza", Piazzale Aldo Moro 5, 00185, Rome Italy
2 School of Biological and Chemical Science, Queen Mary, University of London, London, UK
3 Department of Chemistry, McMaster University, Hamilton, Canada
4 Department of Chemistry, The University of Hong Kong, Hong Kong, China
* Correspondence: enrico.bodo@uniroma1.it

Supporting Information

S1 Validation of DFTB approach vs DFT (B3LYP)

Global minima search was conducted by extracting random snapshots from the MD simulations and isolating the various dimeric structures. Starting from these geometries we have generated the various charge variants by removing or adding protons to the structures when needed. For each possible dimer variants, four different initial geometries were generated. Each of them has been used as a starting point for an optimization using B3LYP/6-311+G(d,p) [1-2]] in both the gas phase and the PCM [3] model solvent using the pre-set parameters for acetonitrile. The same initial geometries have been reoptimized using DFTB3 within an SMD [4] solvent model with the default parameters for acetonitrile. The association energies of the 6 dimers are reported in Tables S1 and S2 for DFT and DFTB respectively.

Table S1: Association energies in kcal/mol of the various dimeric conformers as computed using B3LYP/6-311+G(d,p) in gas phase and using an acetonitrile PCM model solvent.

CONFORMER	**1**		**2**		**3**		**4**	
	GAS	PCM	GAS	PCM	GAS	PCM	GAS	PCM
$[EMIM]^+ [ATMP]^-$	-94.0	-24.6	-112.0	-21.0	-96.3	0.70	-108.3	-15.2
$[EMIM]^+ [ATMP]^{2-}$	-150.7	-17.9	-163.4	-18.3	-163.1	-22.4	-164.6	-21.0
$[ATMP]^- [ATMP]^-$	24.4	-38.0	-18.9	-9.4	-8.70	-11.7	-18.8	-20.3
$[ATMP]^{2-} [ATMP]^{2-}$	125.2	-15.2	89.3	-25.9	111.5	-10.8	96.6	-19.9
$[ATMP]^-[ATMP]^{2-}$	25.8	-36.3	15.0	-22.3	17.1	-16.9	4.0	-21.1
$[ATMP] [ATMP]^{2-}$	69.8	-34.4	-90.0	-31.6	-64.4	-22.7	-79.7	-29.4

Table S2: Association energies in kcal/mol of the various dimeric conformers as computed using DFTB3 in gas phase and using an acetonitrile SMD model solvent.

CONFORMER	**1**		**2**		**3**		**4**	
	GAS	SMD	GAS	SMD	GAS	SMD	GAS	SMD
$[EMIM]^+ [ATMP]^-$	-115.5	-4.6	-113.6	-24.4	-108.4	-6.3	-110.6	-17.6
$[EMIM]^+ [ATMP]^{2-}$	-158.8	-13.5	-152.5	-17.4	-152.6	-8.6	-153.8	-20.5
$[ATMP]^- [ATMP]^-$	-3.4	-15.9	-26.0	-35.4	-10.8	-16.1	-10.1	-27.8
$[ATMP]^{2-} [ATMP]^{2-}$	121.6	-2.6	130.2	-11.8	119.9	-2.4	130.0	-8.9
$[ATMP]^-[ATMP]^{2-}$	241.6	-26.1	31.5	-12.5	46.2	-19.2	27.2	-13.7
$[ATMP] [ATMP]^{2-}$	163.3	-30.3	-74.8	-31.4	-36.9	-13.8	-64.0	-22.6

A pictorial comparison of the two methods is presented in Figure S1, where we have isolated the most stable dimers of each specie and we compare the DFT results with the DFTB ones. We have presented only the results obtained in a model solvent. Evidently, the DFTB method is able to provide a description of the dimeric association energies which is in line with the more accurate DFT results, except for the [ATMP]$^{2-}$ [ATMP]$^{2-}$ highly charged dimer where it predicts an association energy which is less than half the DFT value. In particular, DFTB is able to consistently reproduce the large stabilization energies of the like-charged dimers with respect to the oppositely charged ones that is the leitmotif of the present computations.

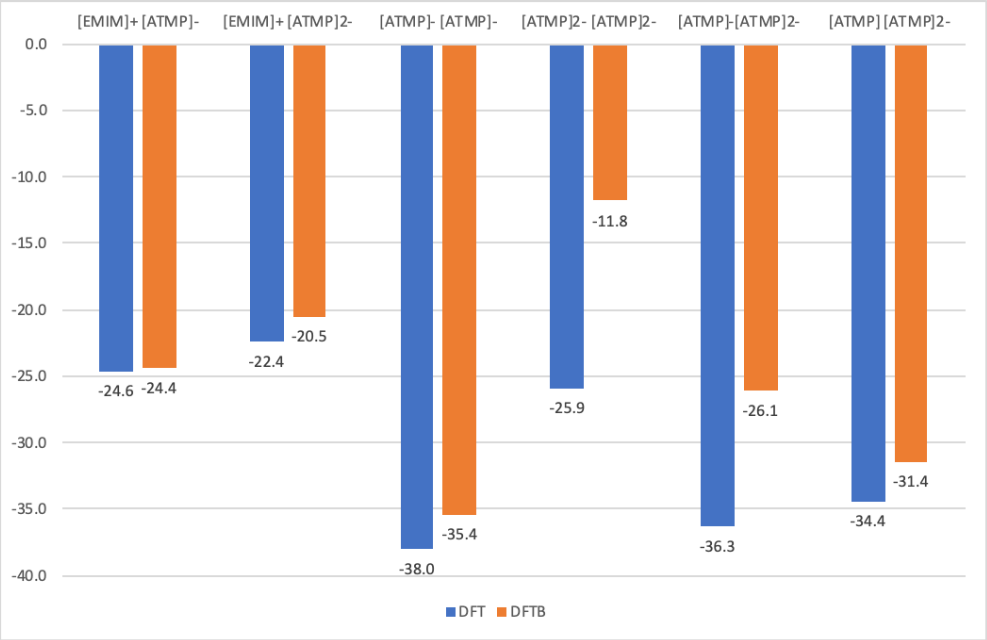

Figure S1: Comparison of the minimum association energies between the two methods: DFT and DFTB.

S2 Additional data and figures relevant for discussion

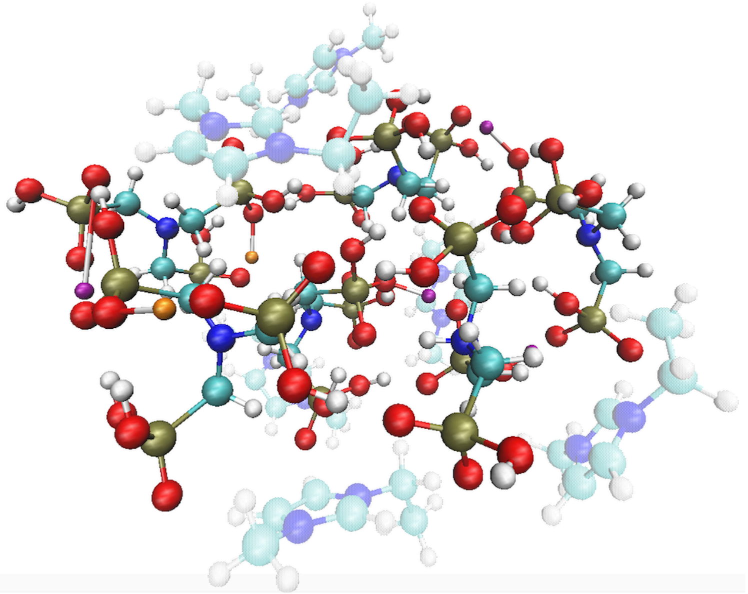

Figure S2: Snapshot of the 6 ionic couple cluster at around 60 ps. Migrating protons in orange (intramolecular) and in purple (intermolecular). Cations have been faded for clarity.

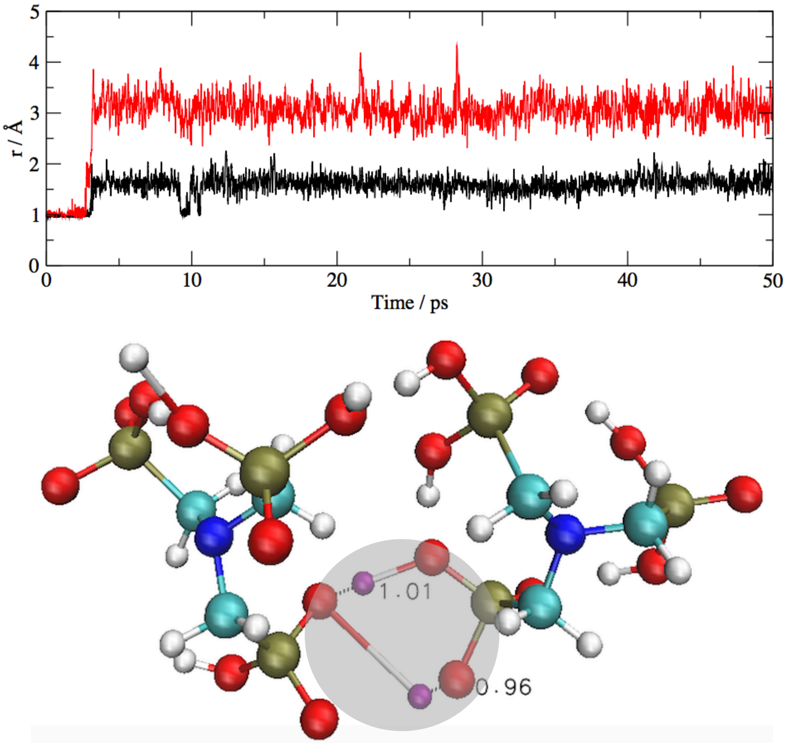

Figure S3. Bulk simulation. Simultaneous double proton transfer. Top: time dependence of the distances of two initially bound O—H. Bottom: snapshot of the relevant anionic dimer at around 10 ps where the proton transfer is proceeding simultaneously.

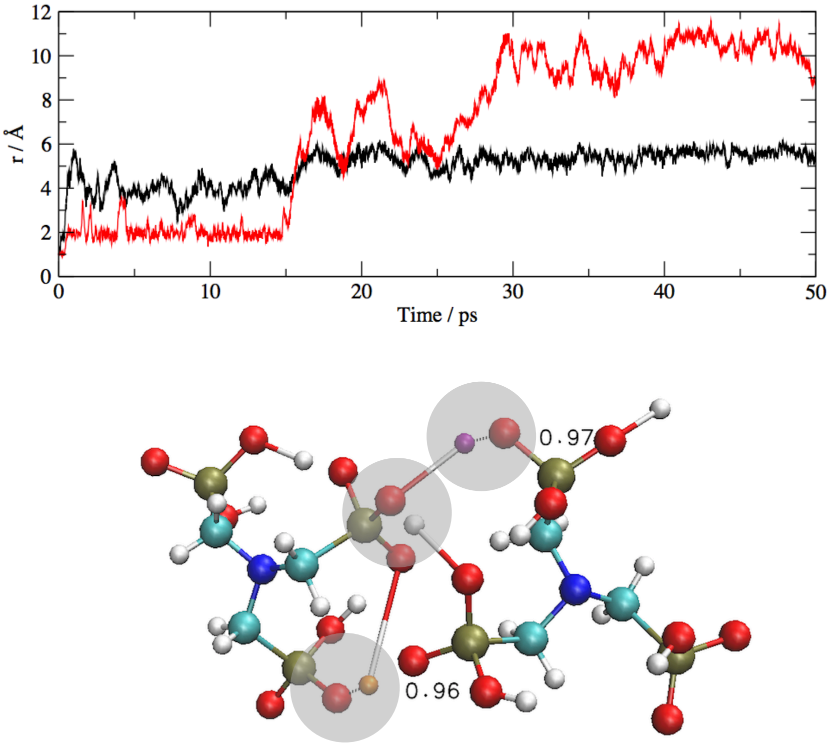

Figure S4. Bulk simulation: Triple proton transfer. Top: time dependence of the distances of two initially bound O—H. Bottom: corresponding snapshot of the relevant dimer with the three migrating protons highlighted by shaded areas.

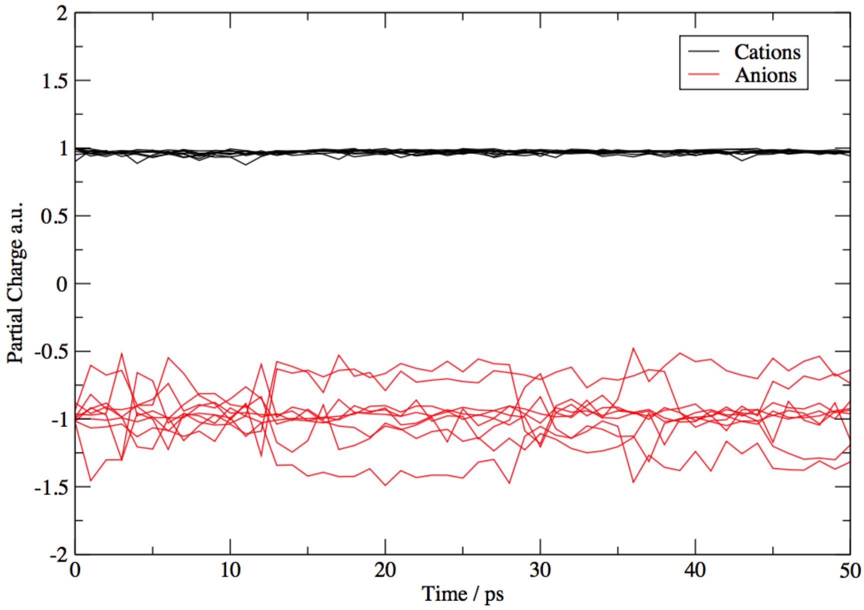

Figure S5: Bulk simulation. Partial charge vs simulation time of 9 cations and anions. Cation localized at +1 a.u. and anion charge fluctuating between -0.5 to -1.5 a.u.

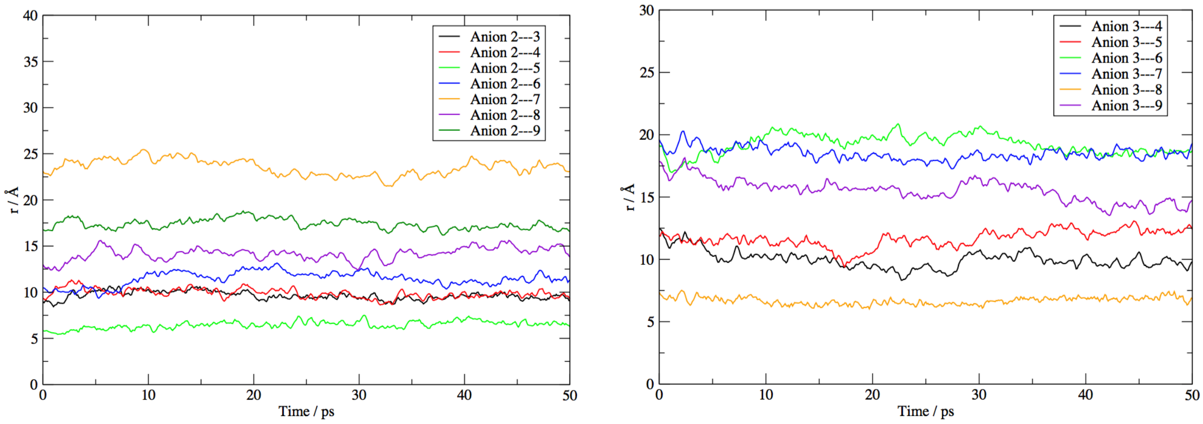

Figure S6: Bulk simulation. Inter-anionic center of mass distance vs simulation time for anion 2 (left) and 3 (right).

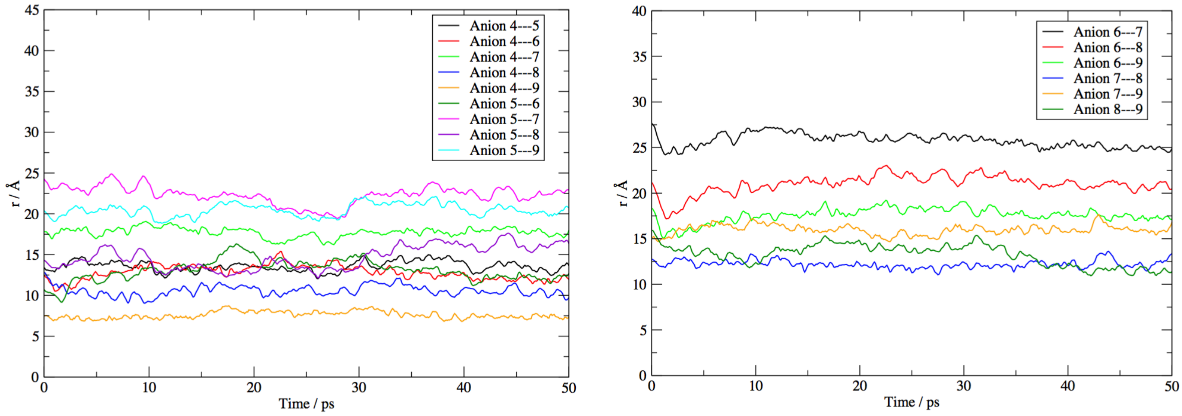

Figure S7: Bulk simulation. Inter-anionic centre of mass distance vs simulation time for anion 4,5 (left) and 6,7 (right).

References

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