# Supplemetary information: Solvent influence on spectroscopic properties: A thorough study of water/methanol mixtures on aromatic systems: The BTP ligand

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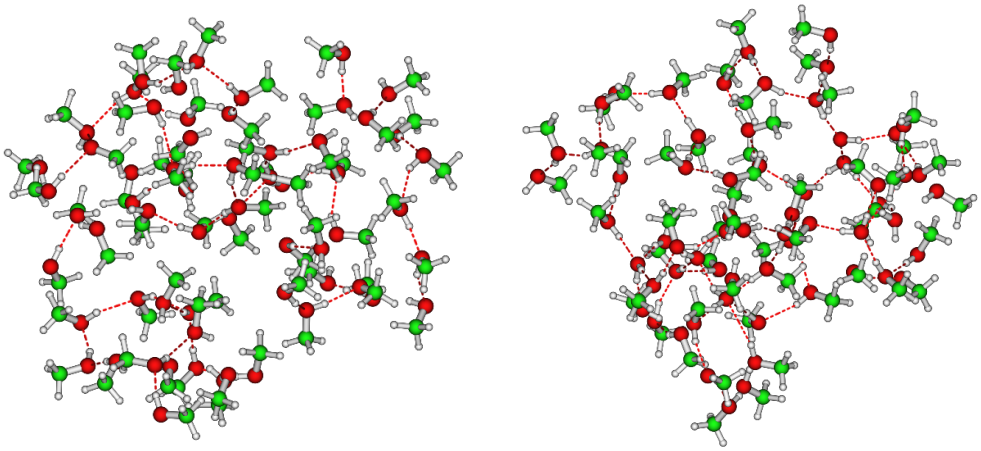

**Figure 1:** Composition of the 62 MeOH (left) and the 54 MeOH + 8 $H_2O$ (right) clusters used in the force-field parameter assessment.

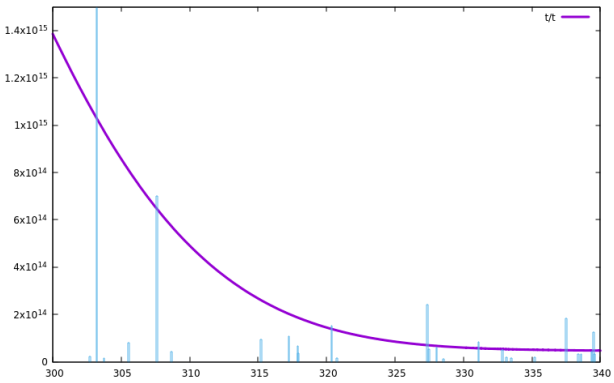


**Figure 2:** Calculated excitations in the 300 to 340 nm region calculated from the 50 MD snapshots MeOH:$H_2O$ 1:1, t/t conformer.

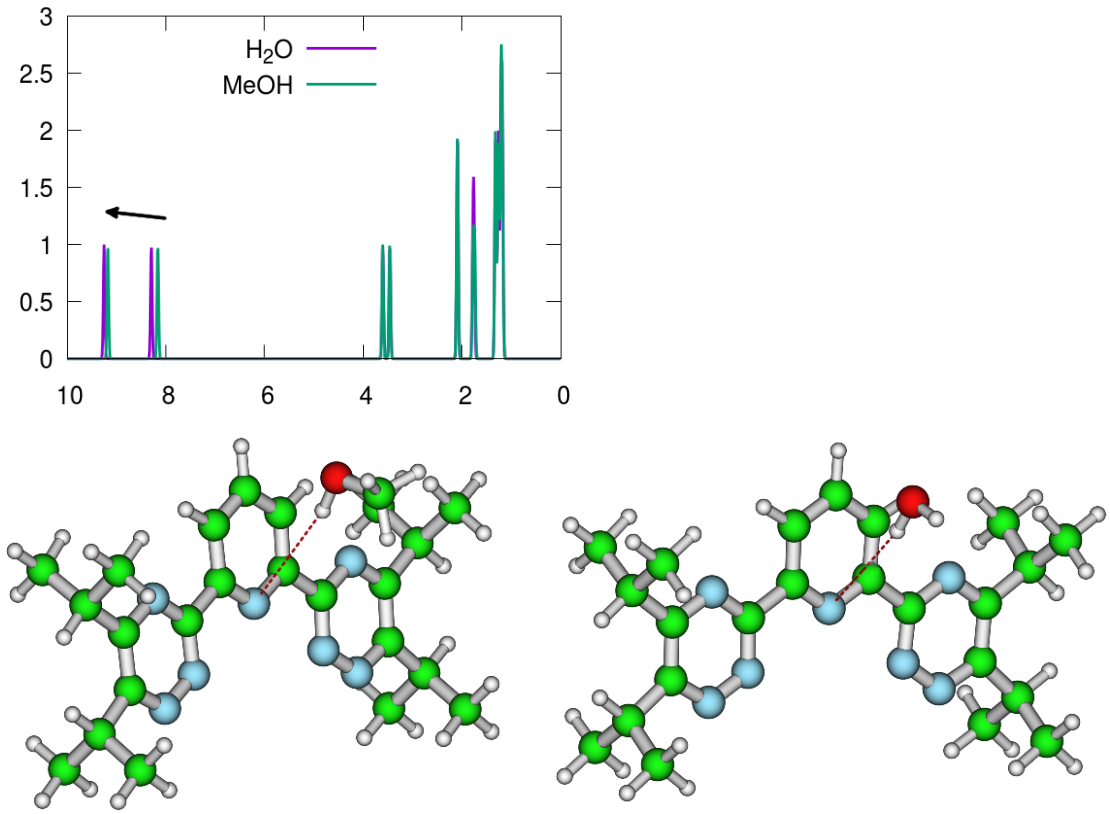


**Figure 3:** Hydrogen bonded structure of MeOH (left) and $H_2O$ (right) with corresponding computed NMR spectra (top).

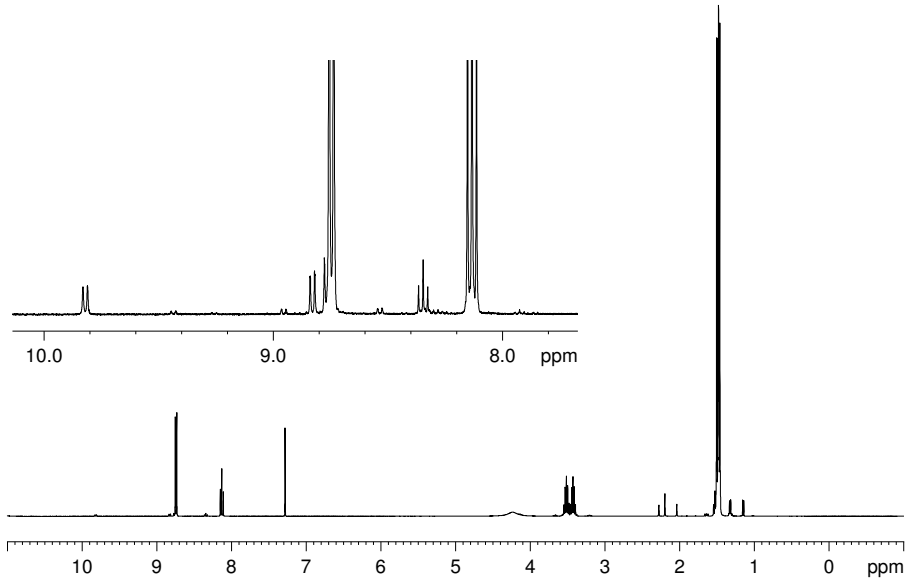


**Figure 4:** NMR spectrum of *i*Pr-BTP in pure $CDCl_3$ at a concentration of 30 mM. The expansion shows the Signals of minor species in the aromatic region.

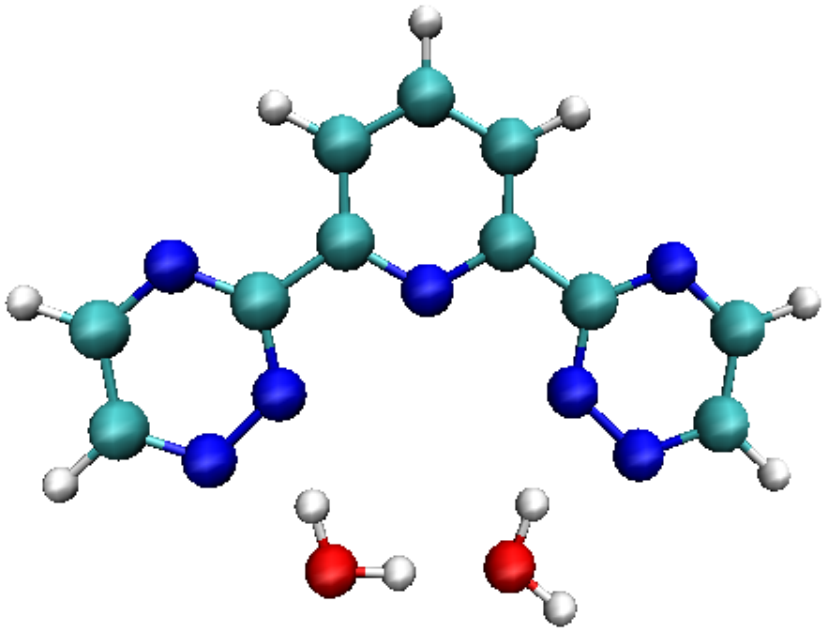

**Figure 5:** Hydrogen bond network within the $N_2N_1N_2'$ cavity of the c/c configuration.

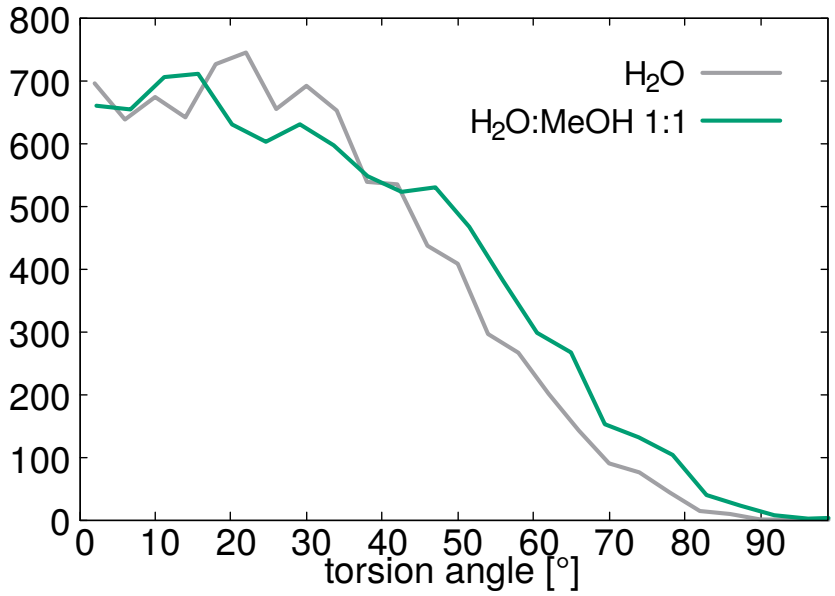


**Figure 6:** Change in NCCN torsional angle with increasing molar MeOH fraction.

$$U^{hb} = \sum f(r)g(\psi) = d_e \left[1 - \xi \sum \exp\left(\frac{-(r-r_e)^2}{\gamma_{rt}}\right)\right] \exp\left(\frac{-(r-r_e)^2}{\gamma_r}\right) \exp\left(\frac{-(\psi-\psi_e)^2}{\gamma_\psi}\right) \tag{1}$$

$$U^{pol} = \frac{1}{2}\sum_i \frac{\mu_i^2}{\alpha_i} - \sum_i \mu_i E_i^q - \frac{1}{2}\sum_i \sum_{k\neq i} \mu_i T_{ik} \mu_k. \tag{2}$$

$$T_{ik} = 3\lambda_5 \frac{\mathbf{r}_i \cdot \mathbf{r}_k}{|\mathbf{r}_i - \mathbf{r}_k|^5} - \lambda_3 \frac{\mathbf{1}}{|\mathbf{r}_i - \mathbf{r}_k|^3} \tag{3}$$

$$\lambda_5 = 1 - \exp(-\kappa r_{ik}^3) \tag{4}$$

$$\lambda_3 = 1 - (1 + \kappa r_{ik}^3)\exp(-\kappa r_{ik}) \tag{5}$$

$$U^{rep} = \sum_{i<k} A_{ik} \exp\left(-B_{ik} r_{ik}\right) \tag{6}$$

# References

[1] S. Höfener, M. Trumm, C. Koke, J. Heuser, U. Ekström, A. Skerenchak-Frech, B. Schimmelpfennig and P. J. Panak, *Phys. Chem. Chem. Phys.*, 2016, **18**, 7728.

[2] M. Masella and P. Cuniasse, *J. Chem. Phys.*, 2003, **119**, 1866.

**Table 1:** Force-fields parameters $A^{ij}$ [kcal/mol] and $B^{ij}$ [$Å^{-1}$] of the repulsive term $U^{rep}$.

| | $N_{BTP}$ | $H_{BTP}$ | $C^{chain}_{BTP}$ | $C^{ring}_{BTP}$ | $O_{MeOH}$ | $C_{MeOH}$ | $H^{CH_3}_{MeOH}$ | $H^{OH}_{MeOH}$ | $O_{H_2O}$ | $H_{H_2O}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $N_{BTP}$ | 30000/3.700 | | | | | | | | | |
| $H_{BTP}$ | 481209/6.497 | 83896/6.831 | | | | | | | | |
| $C^{chain}_{BTP}$ | 1000000/4.100 | 89407/4.320 | 1000000/4.200 | | | | | | | |
| $C^{ring}_{BTP}$ | 30000/5.500 | 30000/6.500 | 1000000/3.900 | 59217/3.282 | | | | | | |
| $O_{MeOH}$ | 1011314/4.828 | 475554/6.096 | 50000/6.500 | 104792/5.238 | 50961/3.906 | | | | | |
| $C_{MeOH}$ | 50000/3.813 | 151609/5.013 | 84013/4.638 | 1200000/3.936 | 222326/5.122 | 259743/4.637 | | | | |
| $H^{CH_3}_{MeOH}$ | 481209/6.497 | 83896/6.831 | 53972/4.294 | 88155/5.283 | 475554/6.096 | 151609/5.013 | 83896/6.891 | | | |
| $H^{OH}_{MeOH}$ | 50000/6.026 | 50000/7.500 | 53972/4.294 | 88155/5.283 | 50000/6.254 | 50000/4.550 | 7500/6.500 | 5000/7.5 | | |
| $O_{H_2O}$ | ref. 1 | | | | 88416/4.016 | 32805/6.188 | 78159/6.411 | 78159/6.411 | ref. 2 | |
| $H_{H_2O}$ | ref. 1 | | | | 75000/6.700 | 2525939/7.500 | 4000000/7.500 | 641506/7.500 | ref. 2 | |

**Table 2:** Force-fields damping parameters $\kappa_{ij}$ of the polarization term term $U^{pol}$.

| | $N_{BTP}$ | $H_{BTP}$ | $C^{chain}_{BTP}$ | $C^{ring}_{BTP}$ | $O_{MeOH}$ | $C_{MeOH}$ | $H^{CH_3}_{MeOH}$ | $H^{OH}_{MeOH}$ | $O_{H_2O}$ | $H_{H_2O}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $N_{BTP}$ | 0.500 | | | | | | | | | |
| $H_{BTP}$ | 0.300 | 0.500 | | | | | | | | |
| $C^{chain}_{BTP}$ | 0.300 | 0.300 | 0.300 | | | | | | | |
| $C^{ring}_{BTP}$ | 0.110 | 0.300 | 0.300 | 0.110 | | | | | | |
| $O_{MeOH}$ | 0.500 | 0.050 | 0.110 | 0.467 | 0.500 | | | | | |
| $C_{MeOH}$ | 0.260 | 0.050 | 0.187 | 0.110 | 0.064 | 0.204 | | | | |
| $H^{CH_3}_{MeOH}$ | 0.300 | 0.500 | 0.300 | 0.300 | 0.050 | 0.050 | 0.500 | | | |
| $H^{OH}_{MeOH}$ | 0.110 | 0.500 | 0.300 | 0.300 | 0.362 | 0.189 | 0.500 | 0.489 | | |
| $O_{H_2O}$ | ref. 1 | | | | 0.191 | 0.099 | 0.060 | 0.060 | ref. 2 | |
| $H_{H_2O}$ | ref. 1 | | | | 0.300 | 0.151 | 0.500 | 0.360 | ref. 2 | |

**Table 3:** Force-fields parameters $d_e^{ij}$ [kcal/mol], $r_e^{ij}$ [Å], $\xi^{ij}$, $\gamma_r^{ij}$ [Å$^2$], $\gamma_\psi^{ij}$ [rad$^2$] and $\gamma_{rt}$ of the hydrogen bond term $U^{hb}$.

| | $N_{BTP}$ | $O_{MeOH}$ | $O_{H_2O}$ |
|---|---|---|---|
| $N_{BTP}$ | - | | |
| $O_{MeOH}$ | 12.40/1.472/0.268/0.533/15.20/0.10 | 3.29/2.656/-0.20/0.08/3.00/0.25 | |
| $O_{H_2O}$ | ref. 1 | 6.11/1.152/0.10/0.03/5.20/0.25 | ref. 2 |

**Table 4:** Force-fields parameters $d^{ij}$ of the dispersion term $U^{disp}$.

| | $N_{BTP}$ | $C_{BTP}^{chain}$ | $C_{BTP}^{ring}$ | $C_{MeOH}$ |
|---|---|---|---|---|
| $N_{BTP}$ | 0 | | | |
| $C_{BTP}^{chain}$ | 850 | 1200 | | |
| $C_{BTP}^{ring}$ | 250 | 2350 | 2300 | |
| $O_{MeOH}$ | 0 | 1200 | 0 | 1200 |