

Density Functional Method Study on the Cooperativity of Intermolecular H-bonding and π - π^+ Stacking Interactions in Thymine- $[\text{C}_n\text{mim}]\text{Br}$ ($n = 2, 4, 6, 8, 10$) Microhydrates

Yanni Wang¹, Chaowu Dai¹, Wei Huang¹, Tingting Ni², Jianping Cao², Jiangmei Pang², Huining Wei² and Chaojie Wang^{2*}

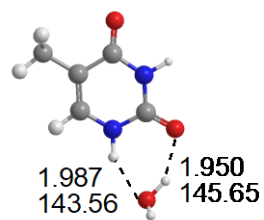
¹The Third Affiliated Hospital of Wenzhou Medical University; the Pharmacy Department of Ruian People's Hospital, Wenzhou 325000, Zhejiang, China.

²School of Pharmaceutical Sciences, Wenzhou Medical University, Wenzhou 325035, Zhejiang, China.

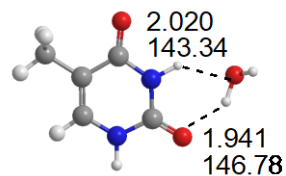
* Correspondence: chjwang@wmu.edu.cn

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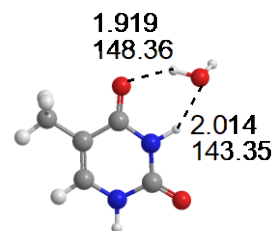
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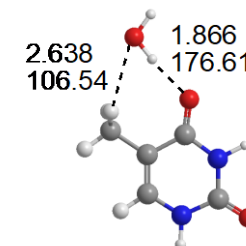
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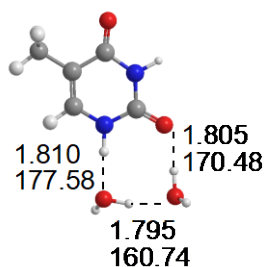
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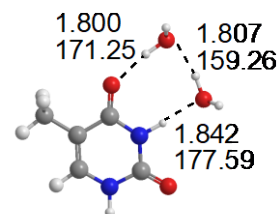
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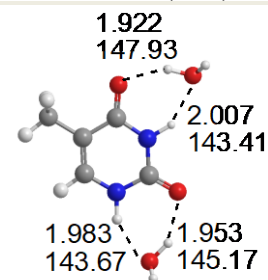
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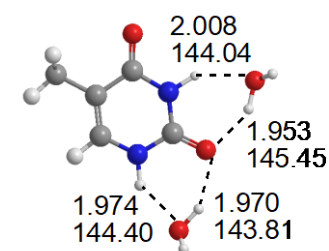
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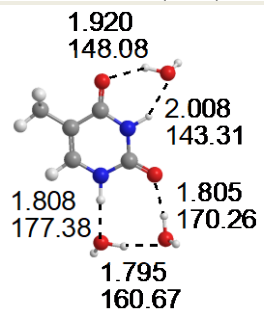
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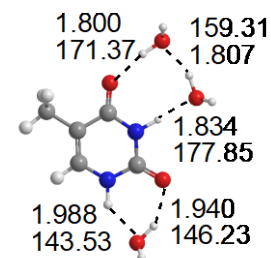
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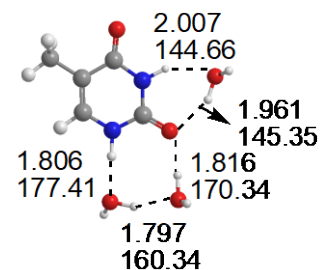
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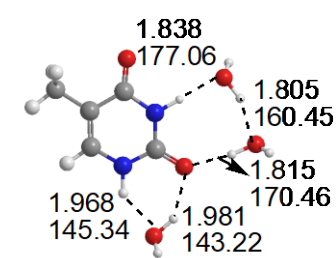
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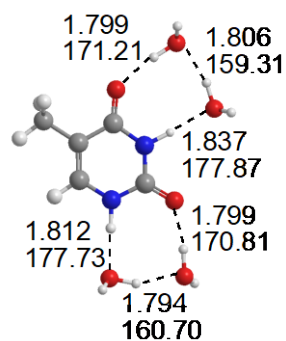
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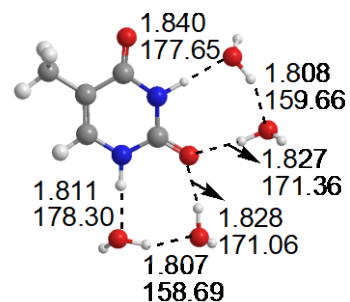
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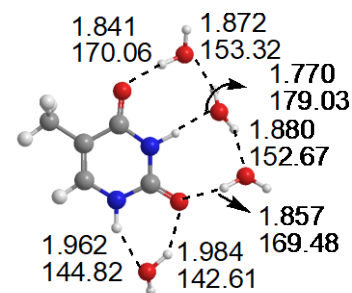
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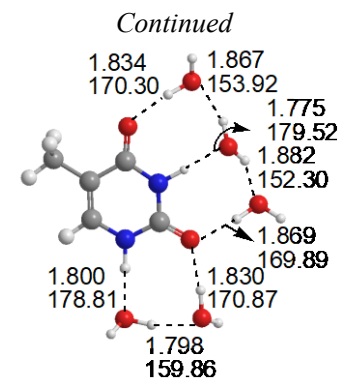
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T-4H₂O-2 (2.21)

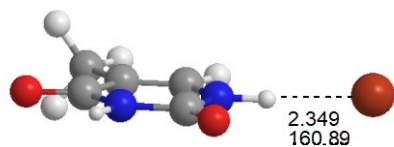


T-4H₂O-3 (4.07)

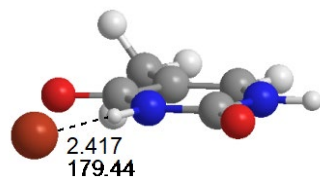


T-5H₂O-1 (-97.39 kJ/mol)

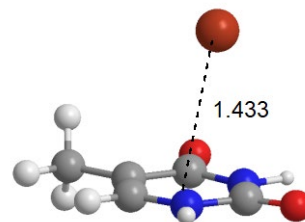
Figure S1. Optimized molecular structures of micro-hydrated T- w H₂O ($w = 1, 2, 3, 4, 5$) at the M06-2X/6-311++G(2*d*, *p*)/PCM/water level. The ZPVE-corrected stability decreases from left to right (in kJ/mol), but T-5H₂O-1 system the binding energy listed.



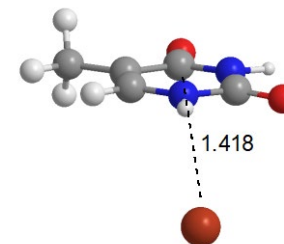
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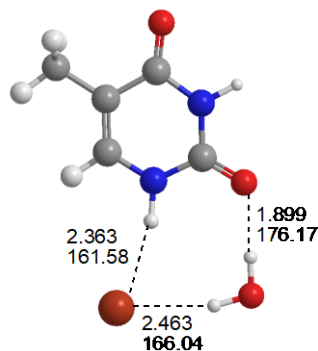
T-Br-2 (5.71)



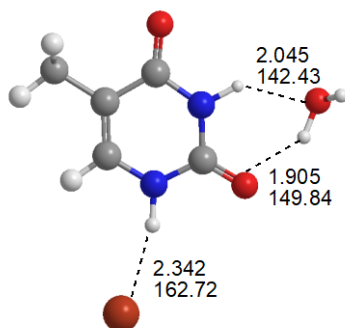
T-Br-3 (15.75)



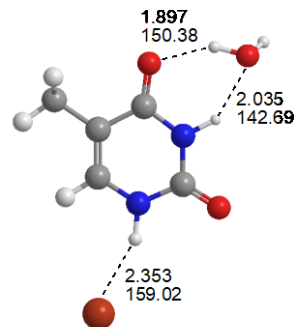
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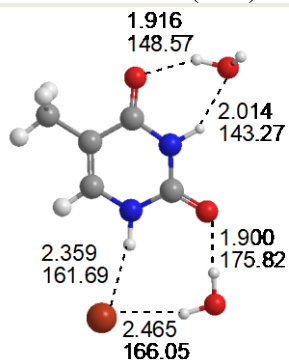
T-1H₂O-Br-1 (0.00)



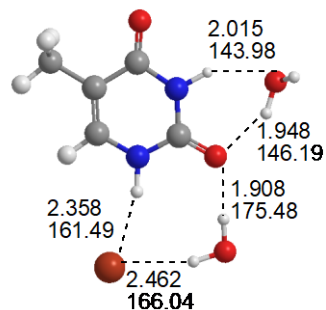
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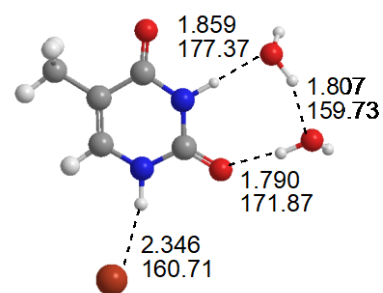
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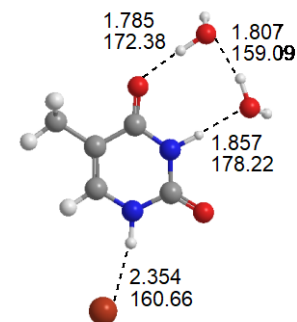
T-2H₂O-Br-1 (0.00)



T-2H₂O-Br-2 (0.66)



T-2H₂O-Br-3 (0.79)



T-2H₂O-Br-4 (1.17)

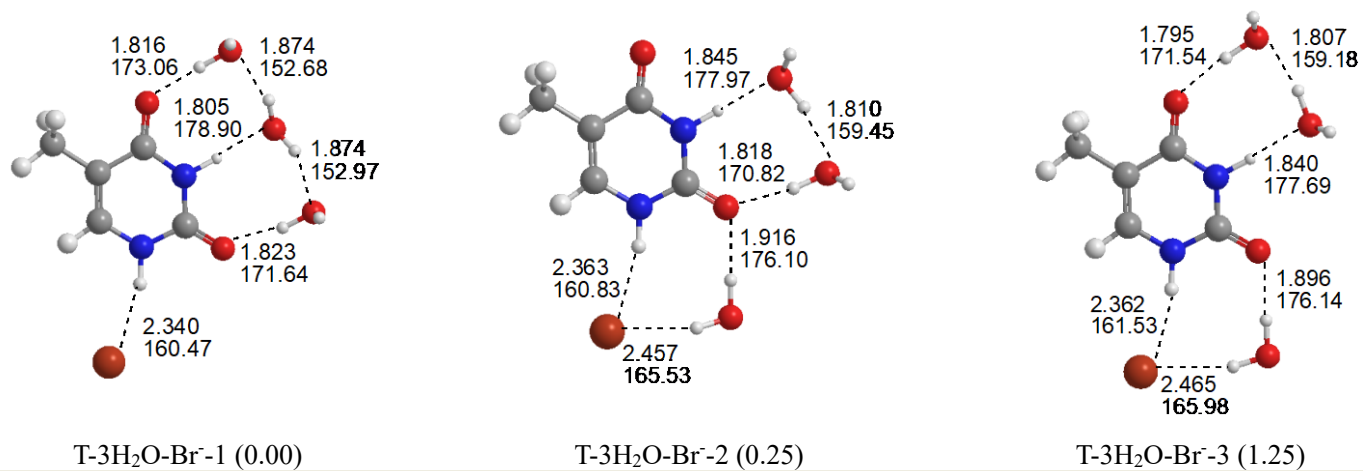
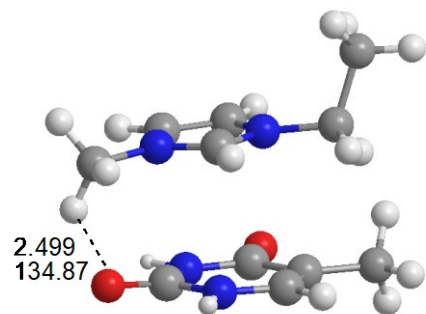
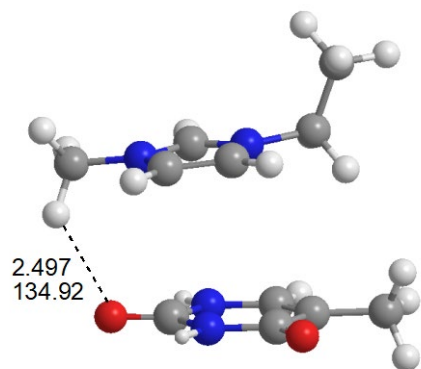


Figure S2. Optimized molecular structures of mono-anionic T- w H₂O-Br⁻ ($w = 1, 2, 3$) at the M06-2X/6-311++G(2d, p)/PCM/water level. The ZPVE-corrected stability decreases from left to right (in kJ/mol).

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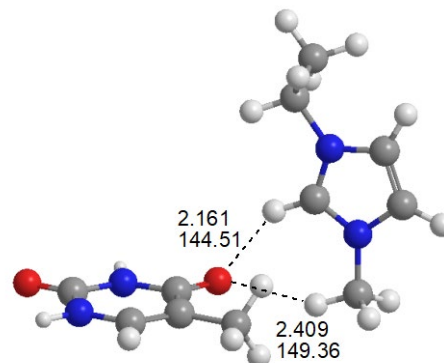


T-[C₂mim]⁺-1 (0.00)

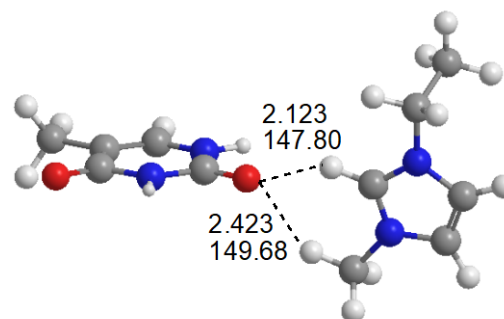


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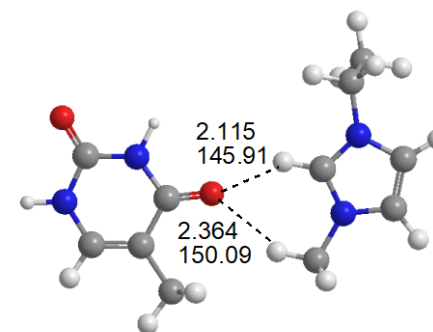


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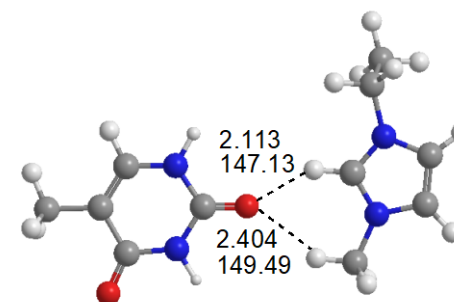


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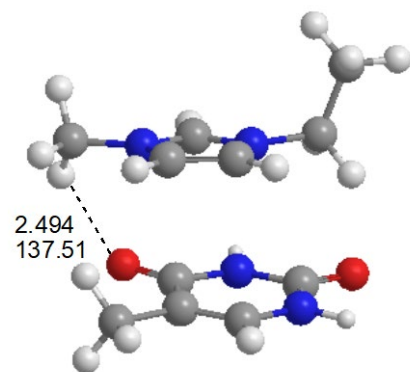
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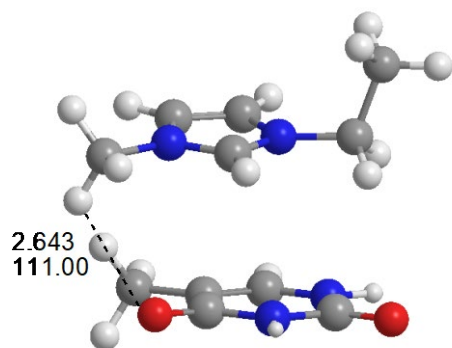
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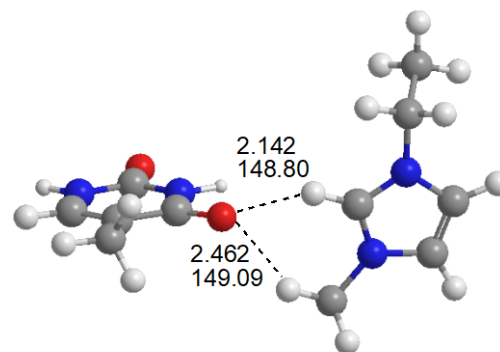
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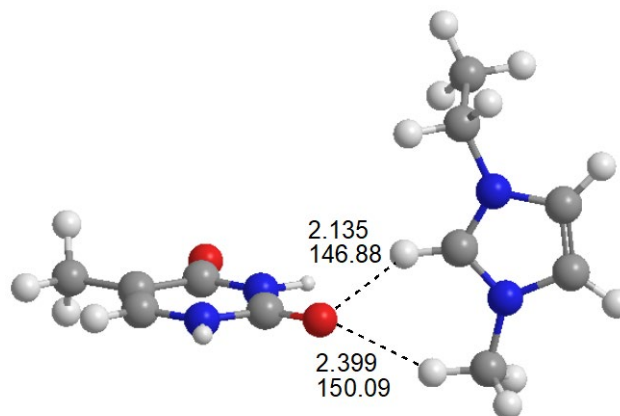
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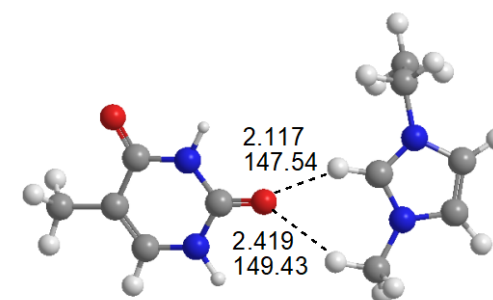
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T-[C₂mim]⁺-7 (3.10)



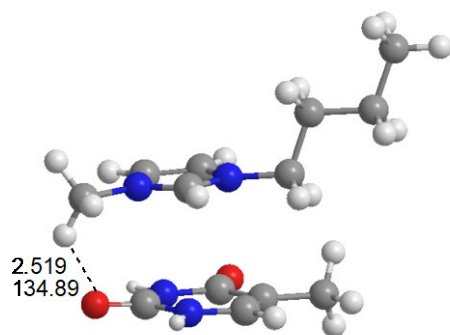
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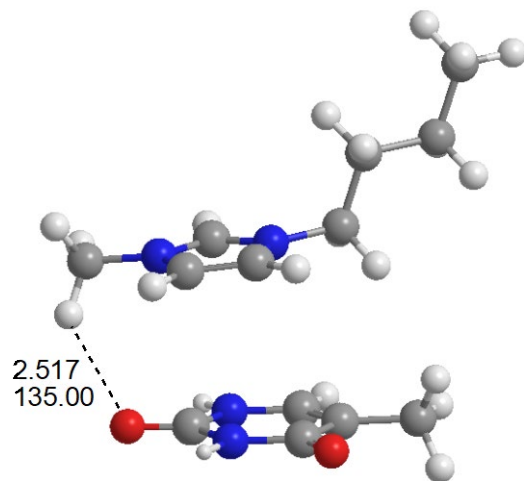
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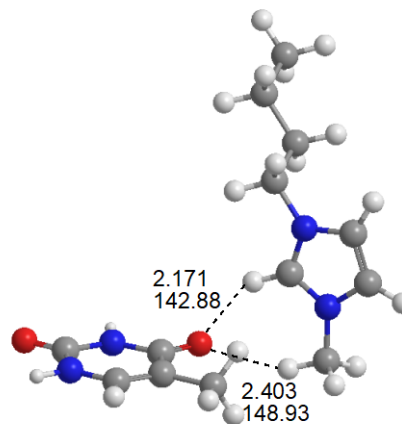


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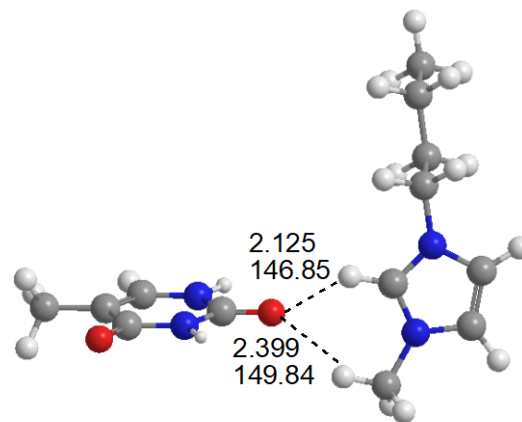


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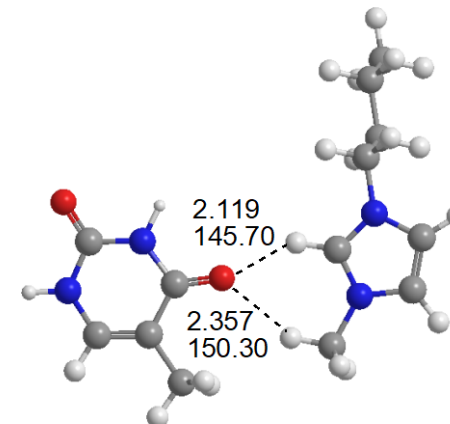


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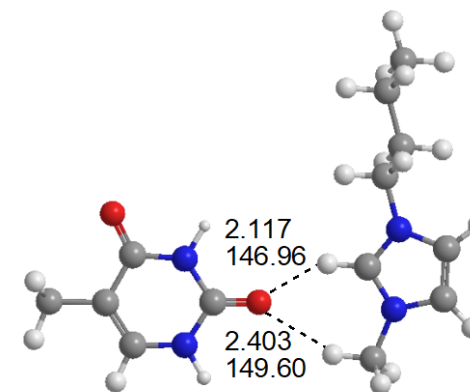


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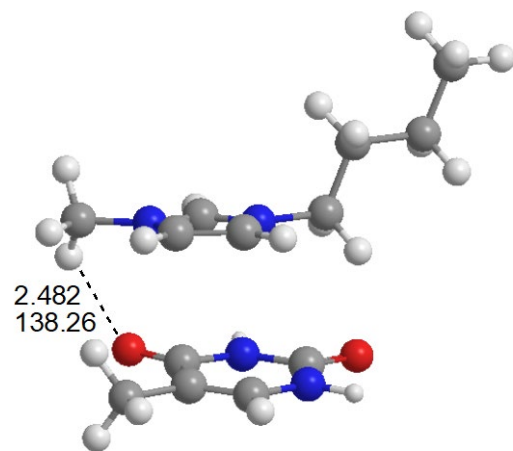
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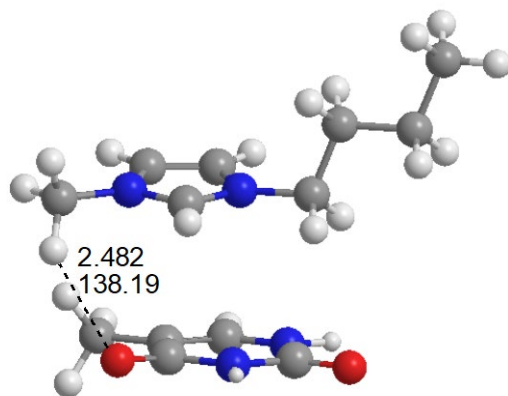
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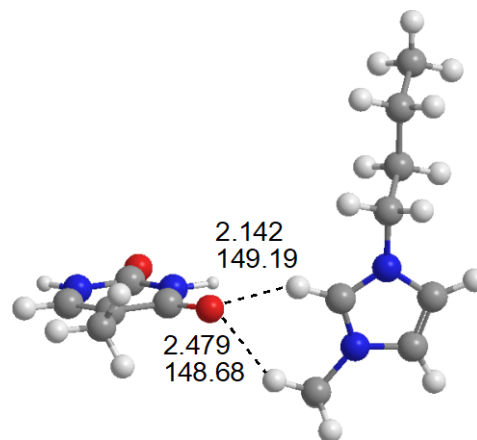
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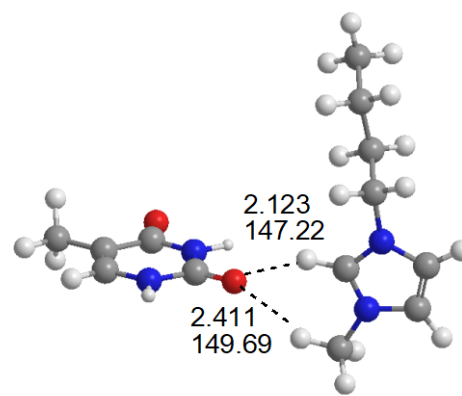
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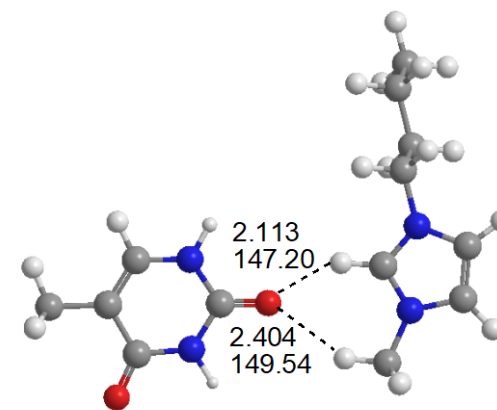


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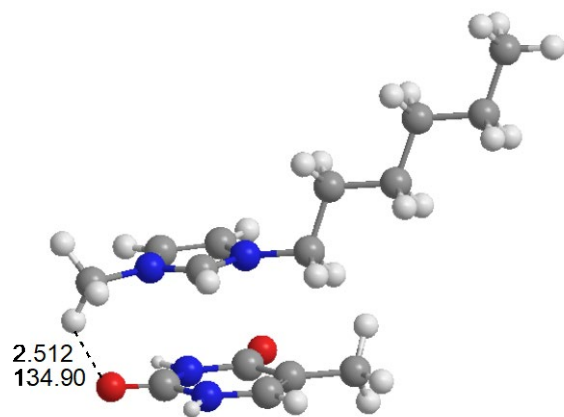
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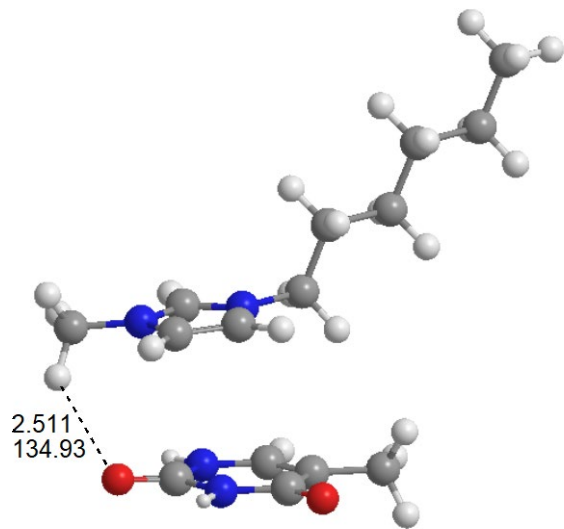


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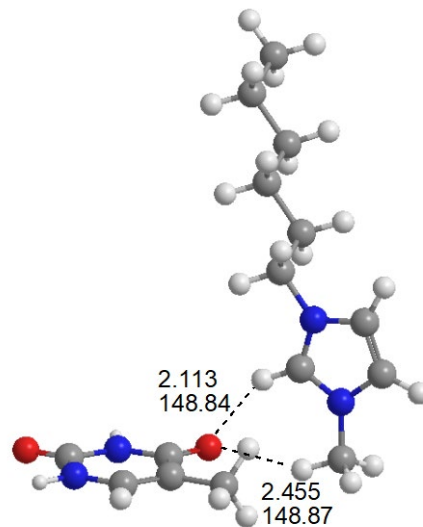


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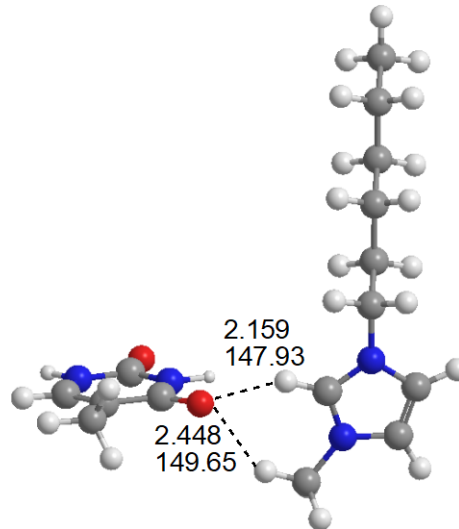


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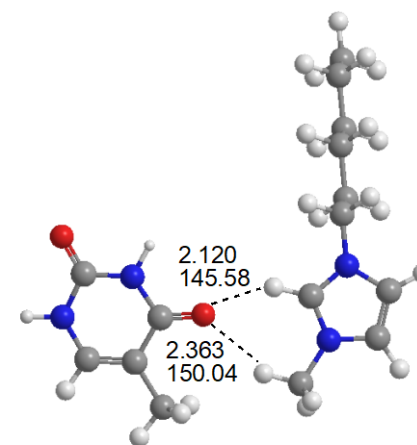


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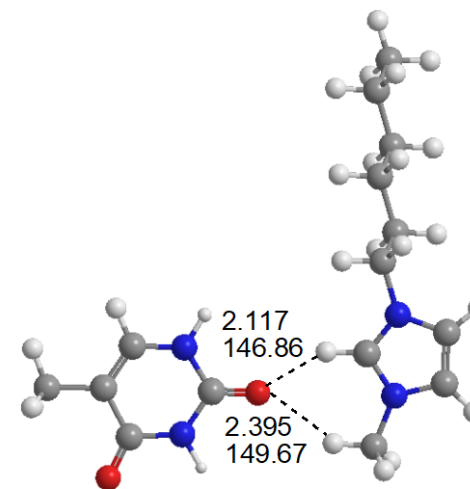


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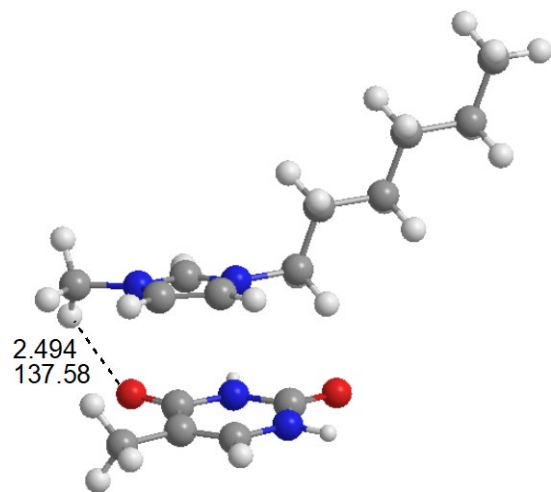
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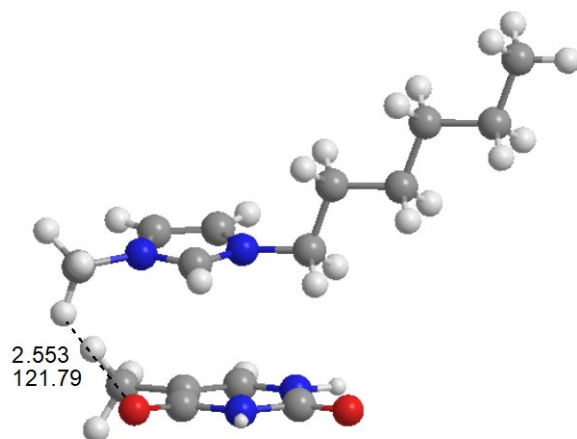
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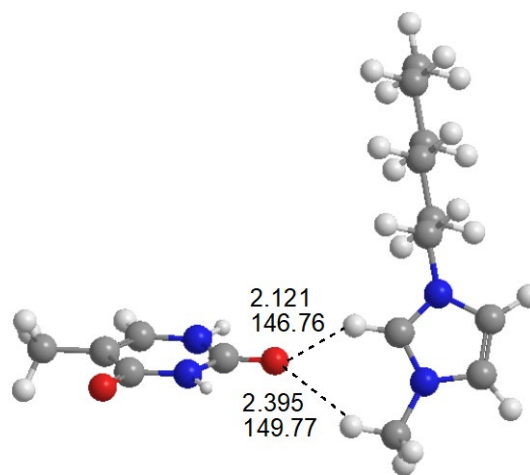
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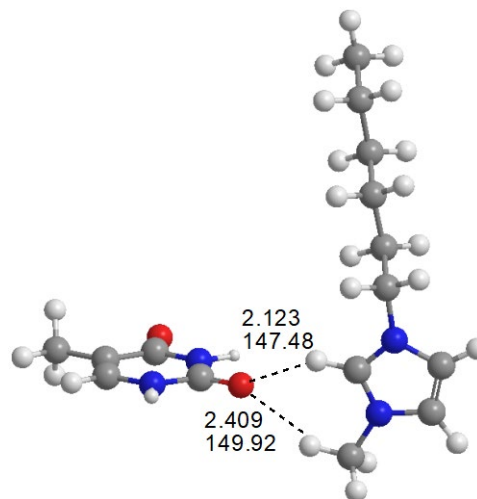
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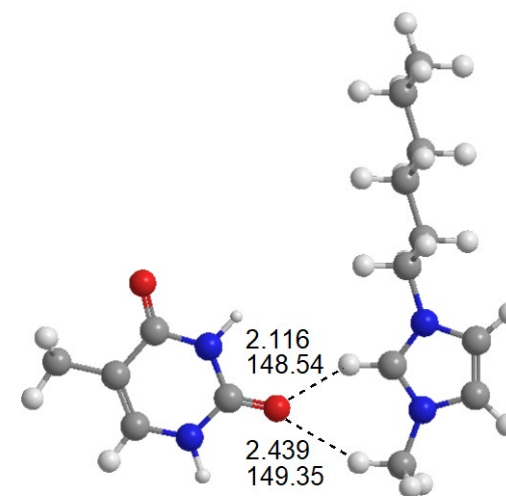
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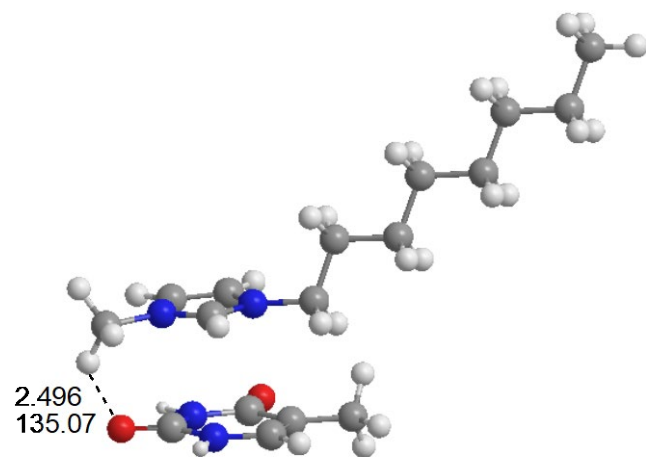
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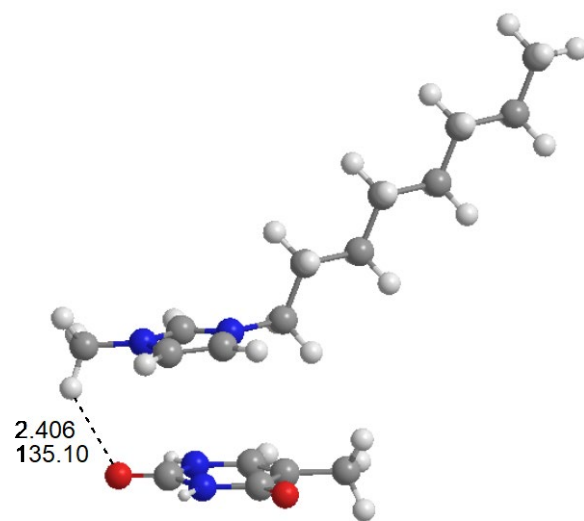
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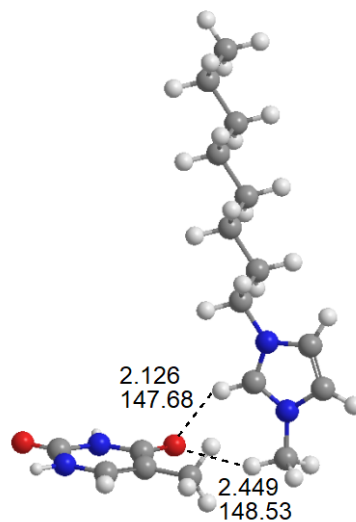


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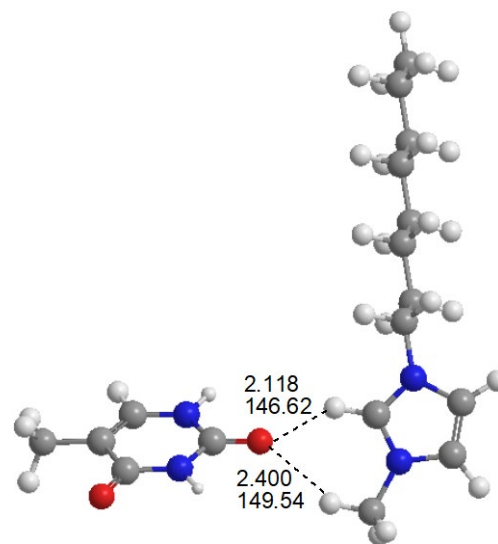


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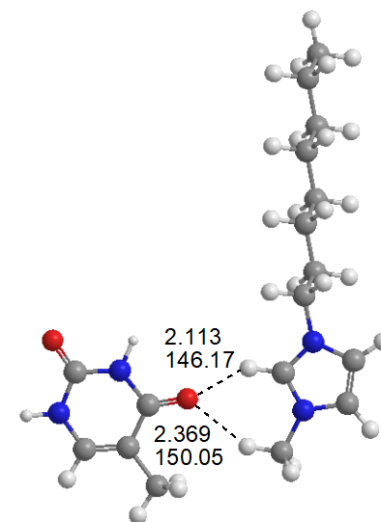


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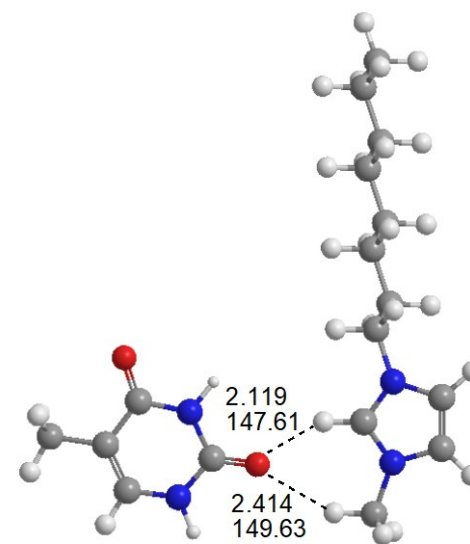


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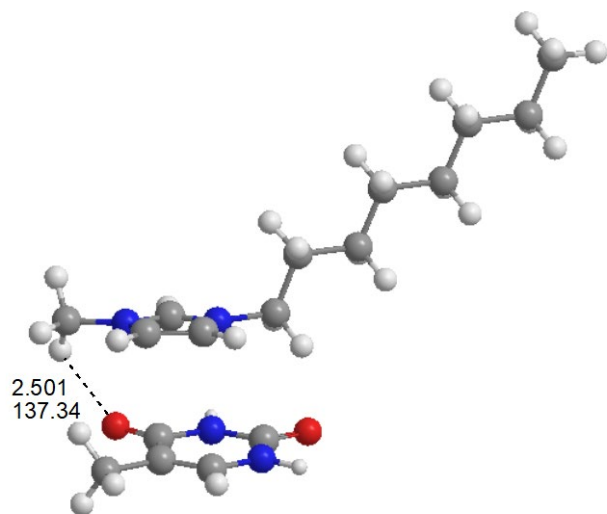
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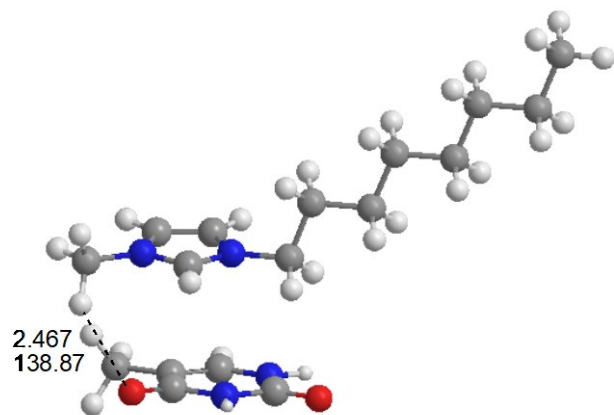
T-[C₈mim]⁺-9 (0.00)



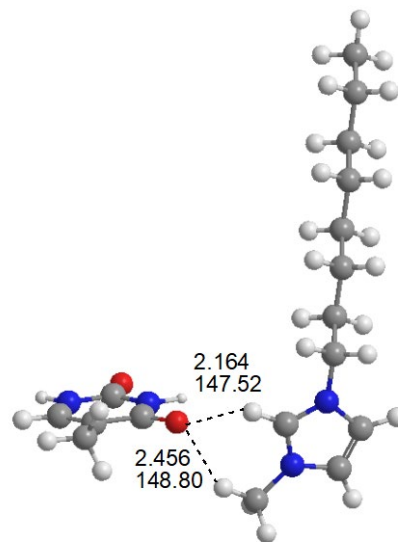
T-[C₈mim]⁺-10 (2.17)



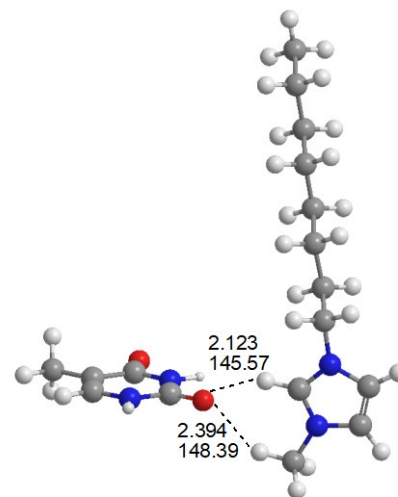
T-[C₈mim]⁺-3 (0.77)



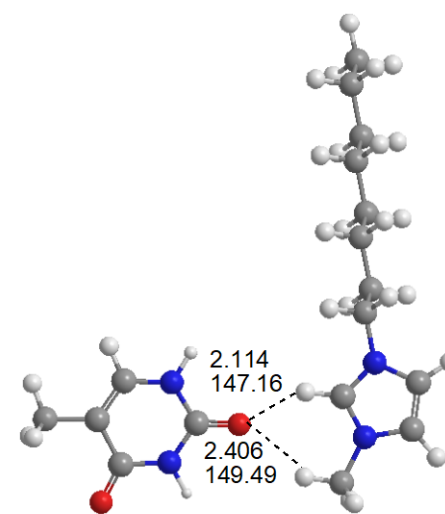
T-[C₈mim]⁺-4 (0.85)



T-[C₈mim]⁺-7 (3.80)



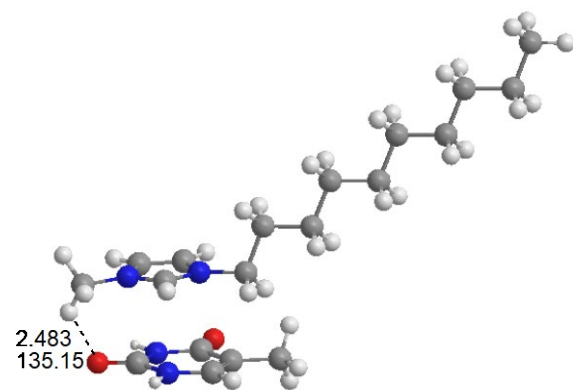
T-[C₈mim]⁺-8 (4.07)



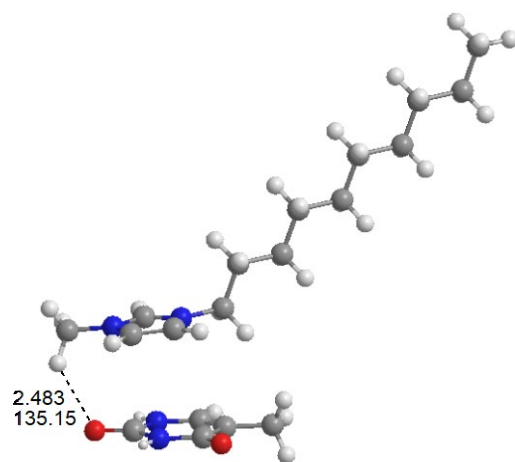
T-[C₈mim]⁺-11 (2.26)

Continued

Stacking (S)

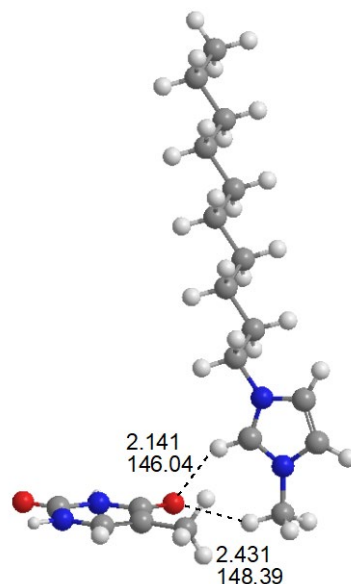


T-[C₁₀mim]⁺-1 (0.00)

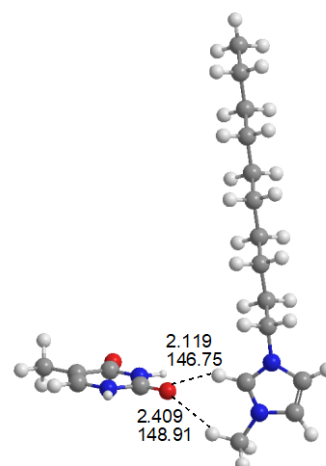


T-[C₁₀mim]⁺-2 (0.34)

Perpendicular (P)

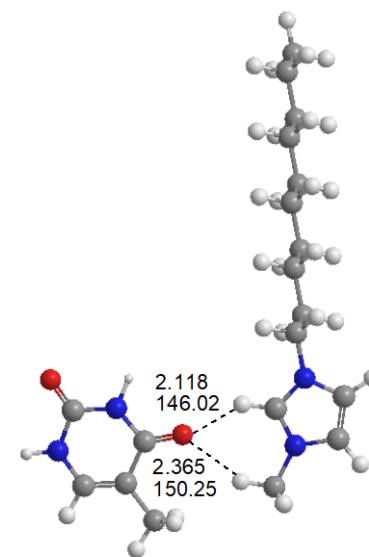


T-[C₁₀mim]⁺-5 (0.00)

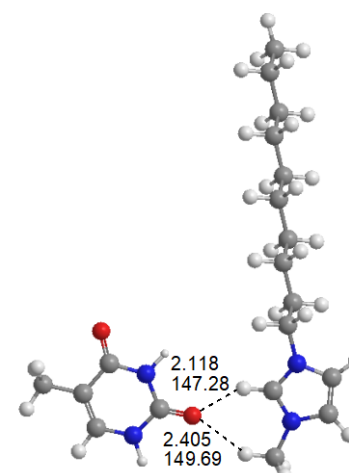


T-[C₁₀mim]⁺-6 (1.45)

Coplanar (H)



T-[C₁₀mim]⁺-9 (0.00)



T-[C₁₀mim]⁺-10 (1.18)

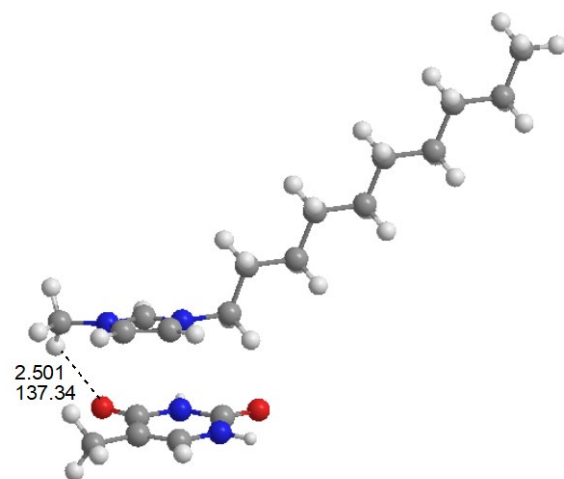
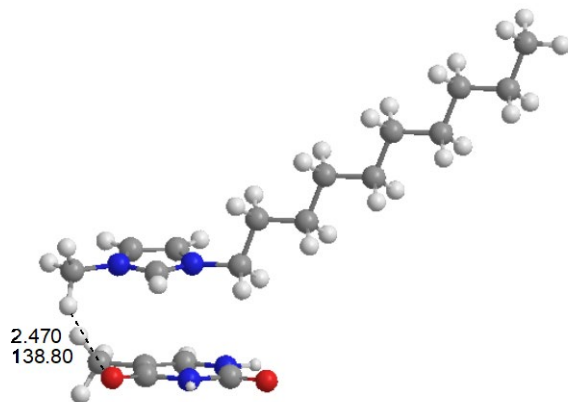
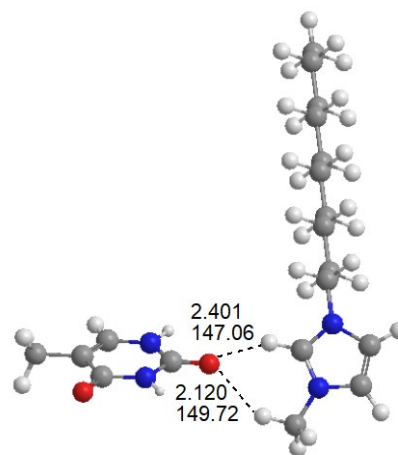
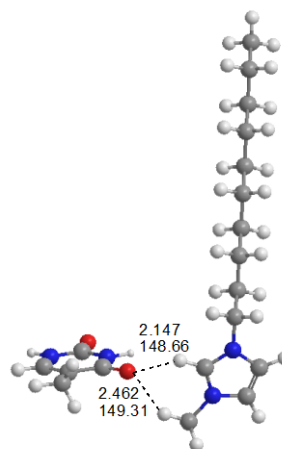
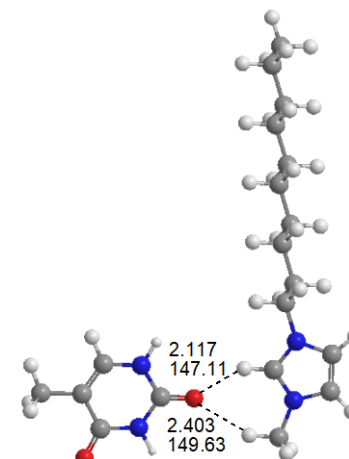
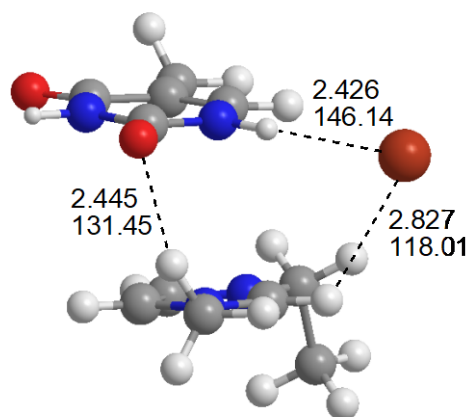
T-[C₁₀mim]⁺-3 (1.15)T-[C₁₀mim]⁺-4 (1.42)T-[C₁₀mim]⁺-7 (2.91)T-[C₁₀mim]⁺-9 (3.45)T-[C₁₀mim]⁺-11 (1.49)

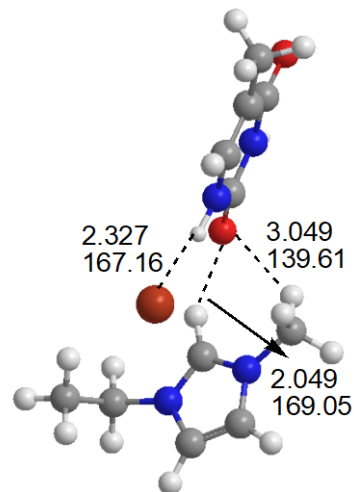
Figure S3. 11 of the mono-cationic structures of thymine with five imidazolium cations (T-[C_nmim]⁺, n = 2, 4, 6, 8, 10) calculated at the M06-2X/6-311++G(2d, p)/PCM/water level of theory. The ZPVE-corrected stability decreases from top to bottom for each configuration (in kJ/mol).

Stacking (S)



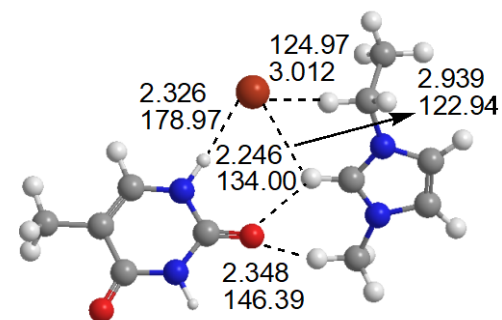
T-[C₂mim]⁺-Br⁻-1 (0.00)

Perpendicular (P)

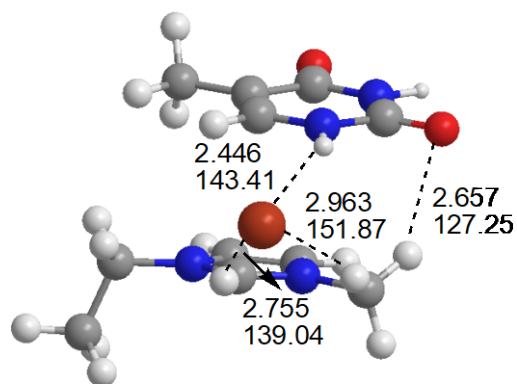


T-[C₂mim]⁺-Br⁻-5 (0.00)

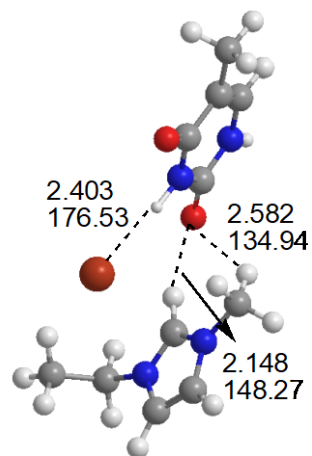
Coplanar (H)



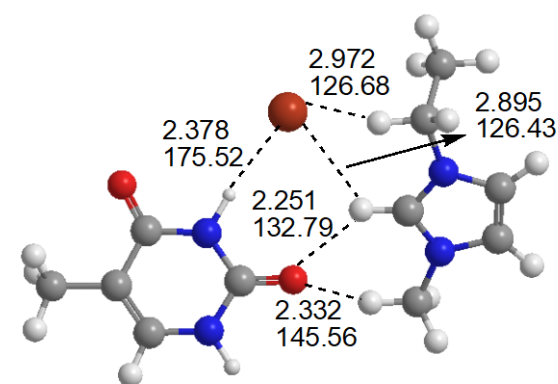
T-[C₂mim]⁺-Br⁻-9 (0.00)



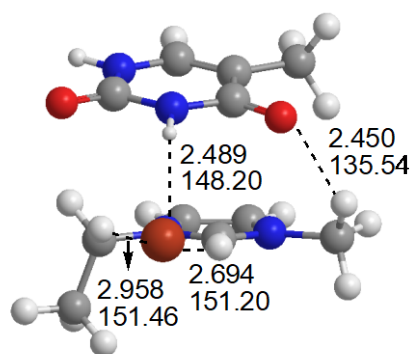
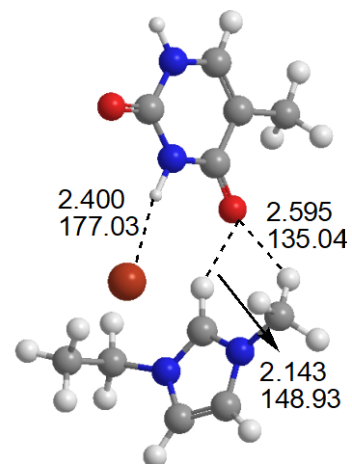
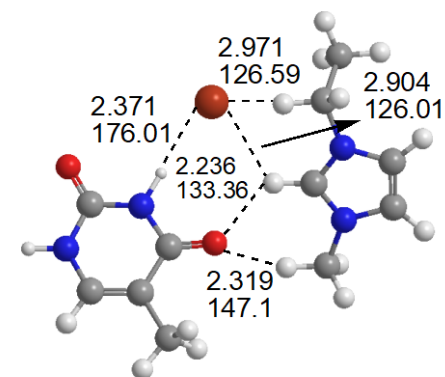
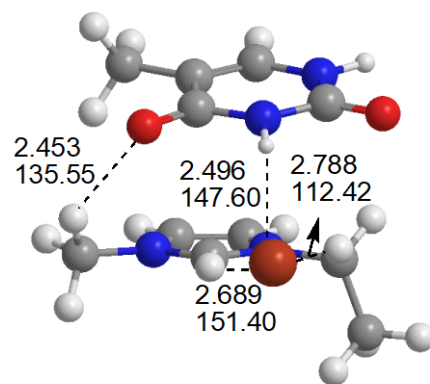
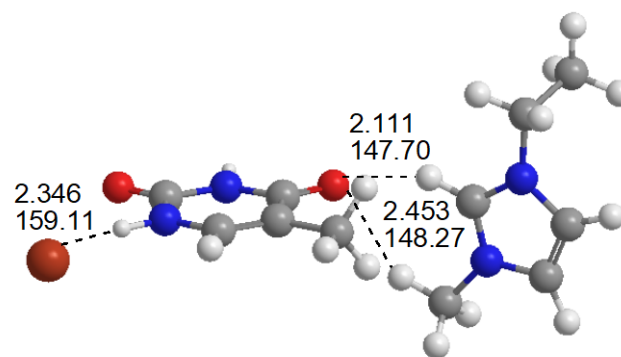
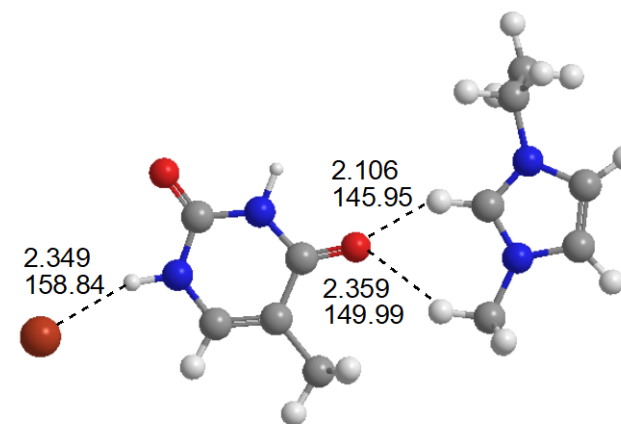
T-[C₂mim]⁺-Br⁻-2 (2.57)



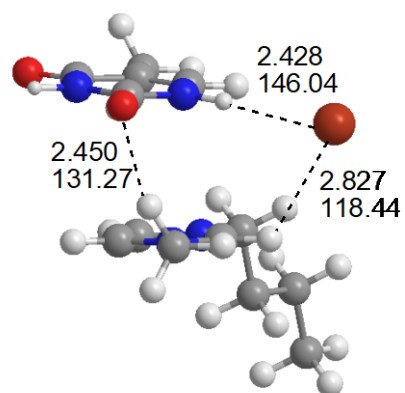
T-[C₂mim]⁺-Br⁻-6 (4.83)



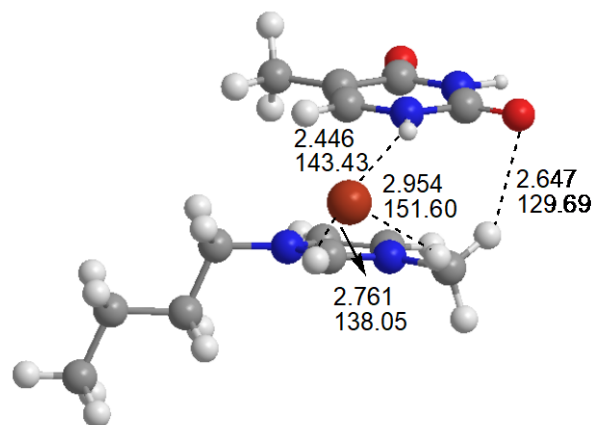
T-[C₂mim]⁺-Br⁻-10 (2.95)

T-[C₂mim]⁺-Br⁻-3 (4.28)T-[C₂mim]⁺-Br⁻-7 (4.95)T-[C₂mim]⁺-Br⁻-11 (3.08)T-[C₂mim]⁺-Br⁻-4 (4.33)T-[C₂mim]⁺-Br⁻-8 (13.43)T-[C₂mim]⁺-Br⁻-12 (10.76)

Stacking (S)

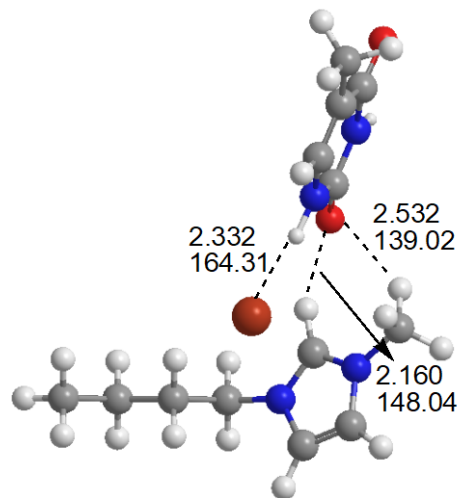


T-[C4mim]⁺-Br⁻-1 (0.00)

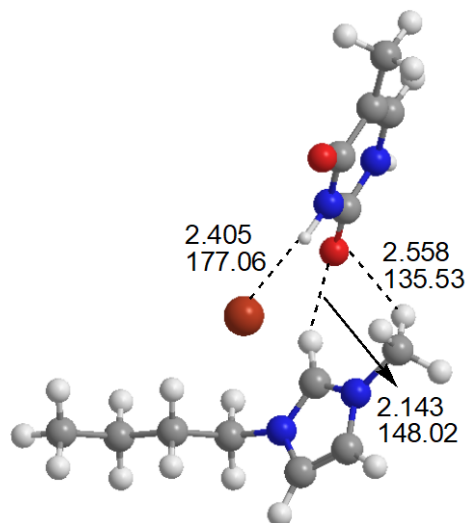


T-[C4mim]⁺-Br⁻-2 (2.27)

Perpendicular (P)

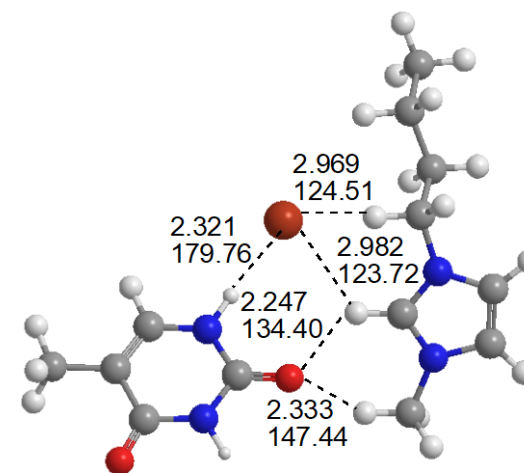


T-[C4mim]⁺-Br⁻-5 (0.00)

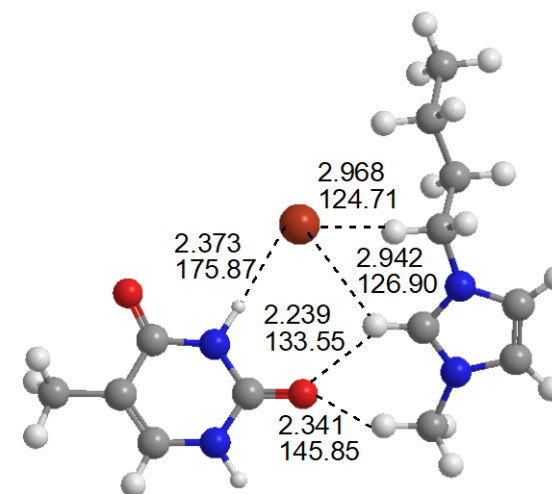


T-[C4mim]⁺-Br⁻-6 (4.21)

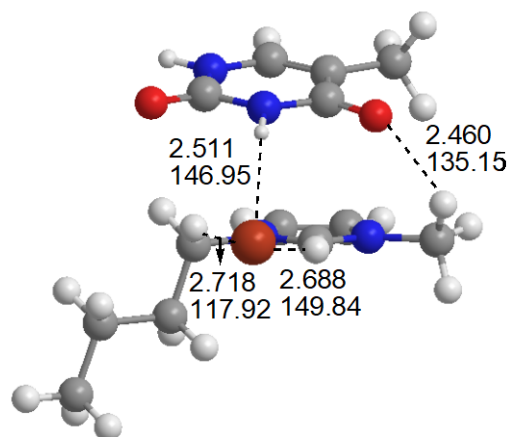
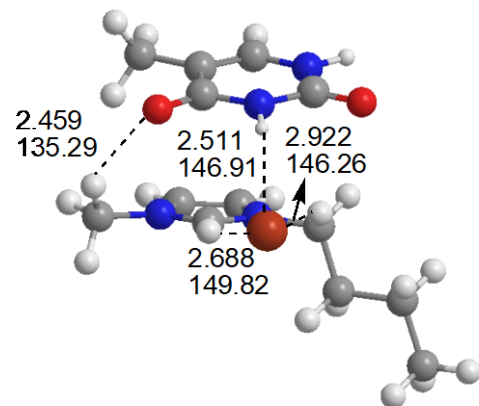
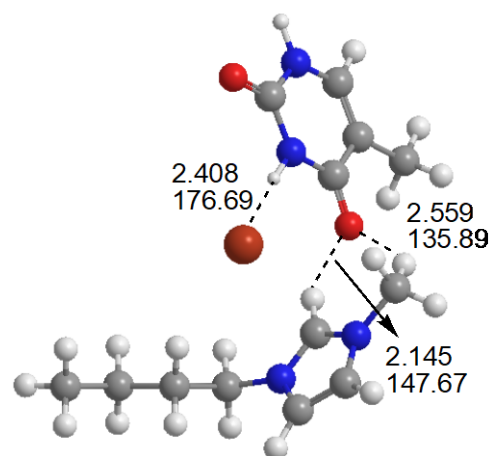
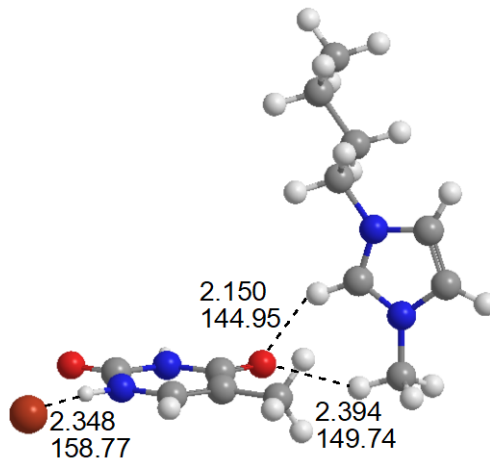
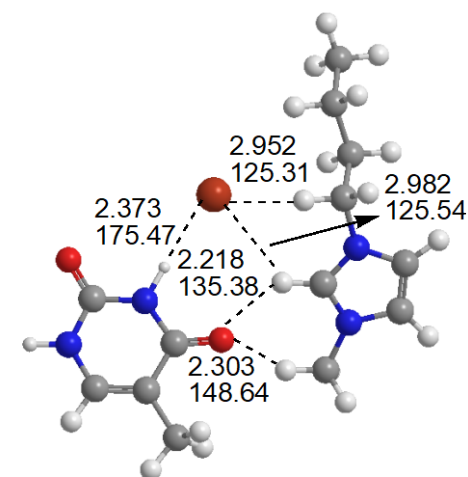
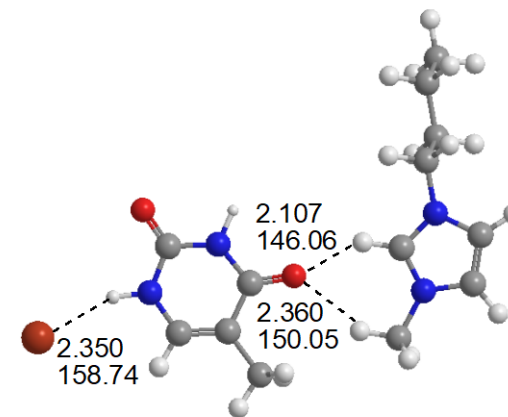
Coplanar (H)



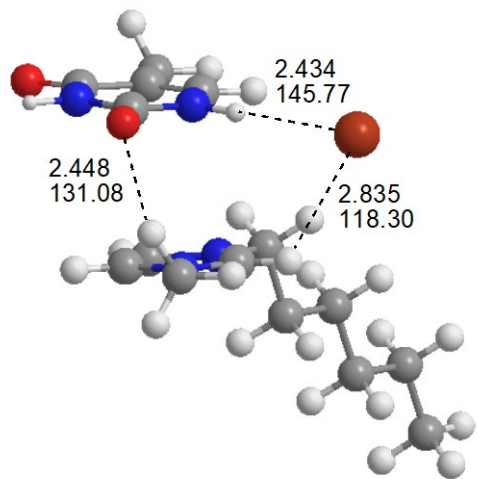
T-[C4mim]⁺-Br⁻-9 (0.00)



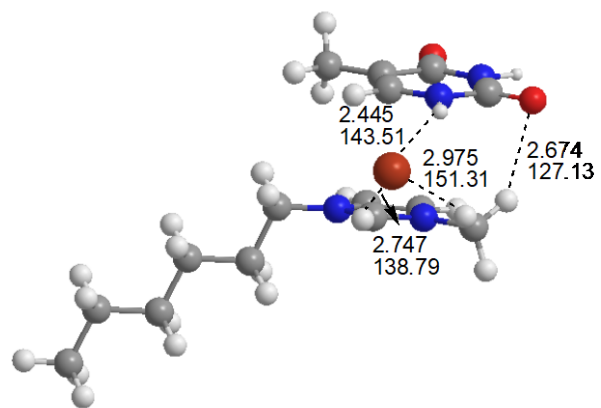
T-[C4mim]⁺-Br⁻-10 (3.23)

T-[C₄mim]⁺-Br⁻-3 (3.92)T-[C₄mim]⁺-Br⁻-4 (3.92)T-[C₄mim]⁺-Br⁻-7 (5.00)T-[C₄mim]⁺-Br⁻-8 (14.25)T-[C₄mim]⁺-Br⁻-11 (3.66)T-[C₄mim]⁺-Br⁻-12 (12.77)

Stacking (S)

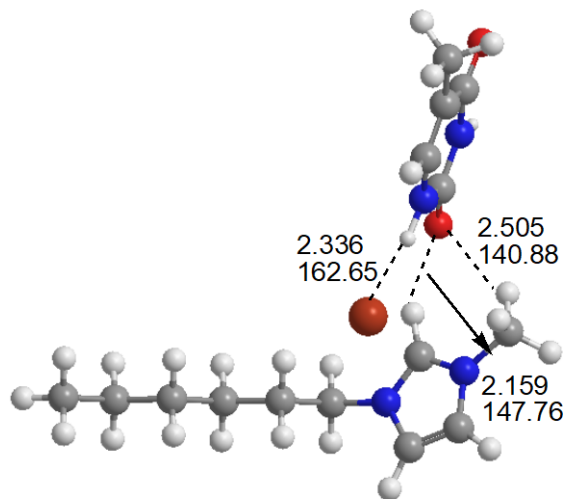


T-[C₆mim]⁺-Br⁻-1 (0.00)

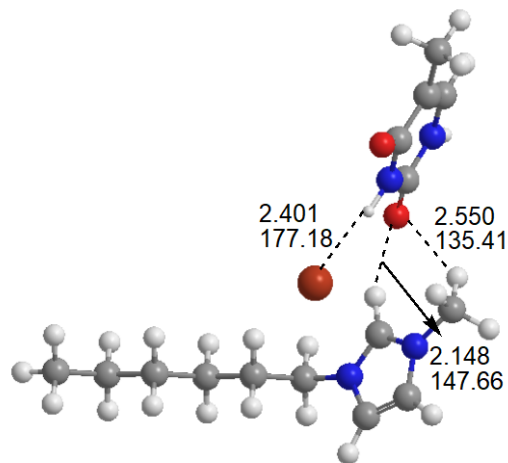


T-[C₆mim]⁺-Br⁻-2 (2.42)

Perpendicular (P)

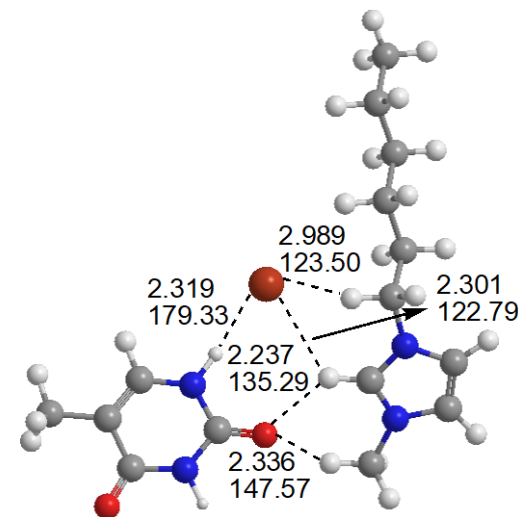


T-[C₆mim]⁺-Br⁻-5 (0.00)

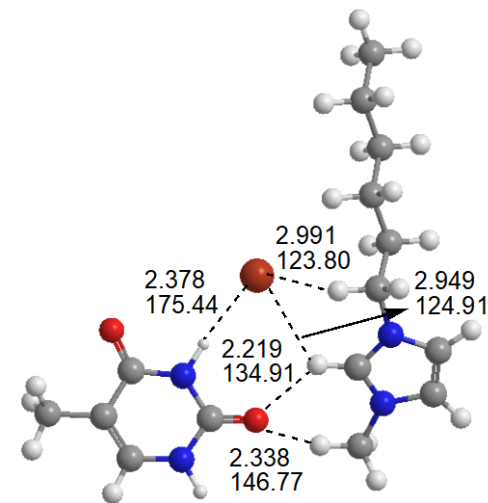


T-[C₆mim]⁺-Br⁻-6 (4.36)

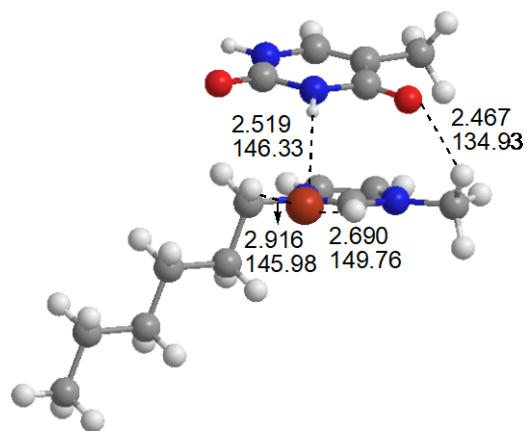
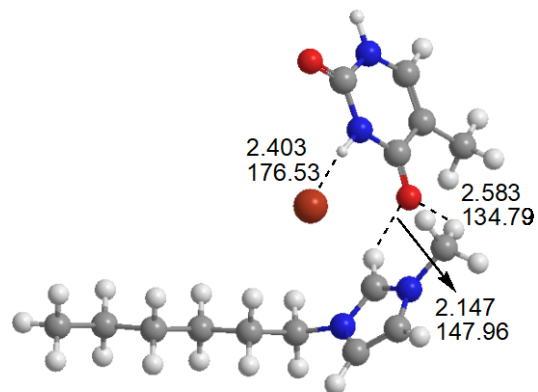
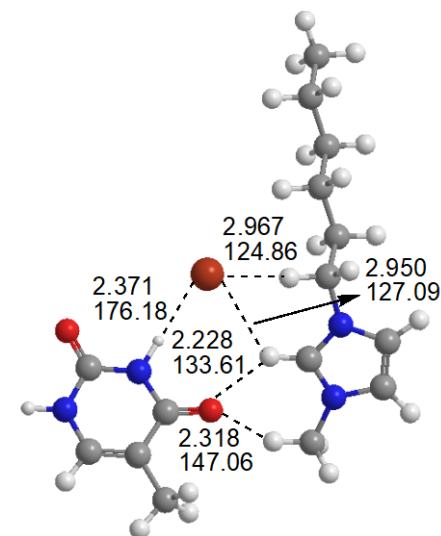
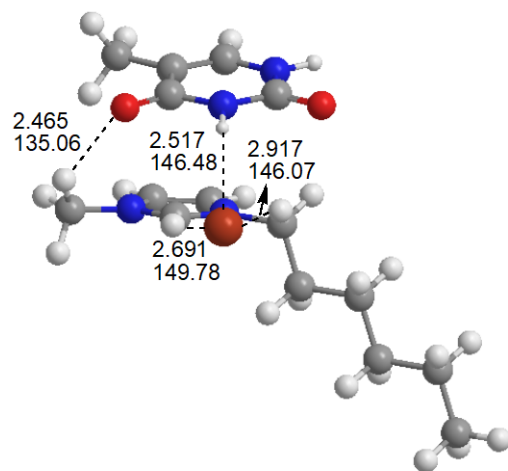
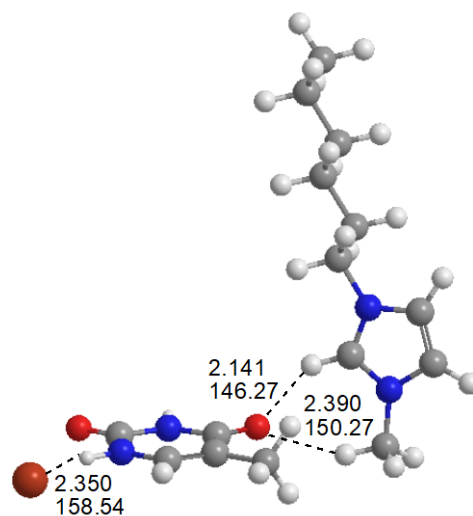
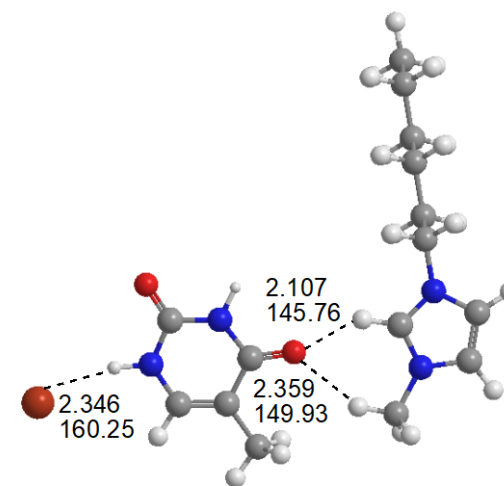
Coplanar (H)



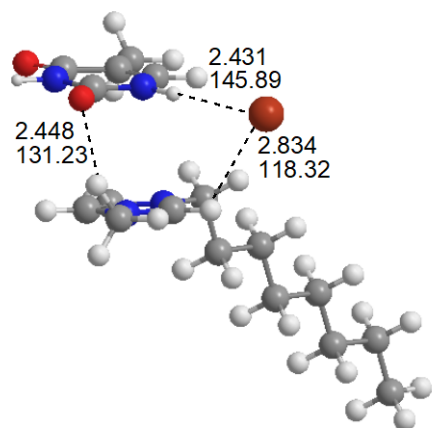
T-[C₆mim]⁺-Br⁻-9 (0.00)



T-[C₆mim]⁺-Br⁻-10 (2.81)

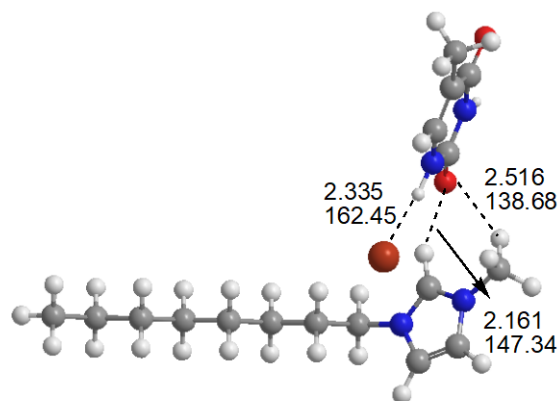
T-[C₆mim]⁺-Br⁻-3 (4.07)T-[C₆mim]⁺-Br⁻-7 (4.86)T-[C₆mim]⁺-Br⁻-11 (3.52)T-[C₆mim]⁺-Br⁻-4 (4.08)T-[C₆mim]⁺-Br⁻-8 (14.20)T-[C₆mim]⁺-Br⁻-12 (12.58)

Stacking (S)



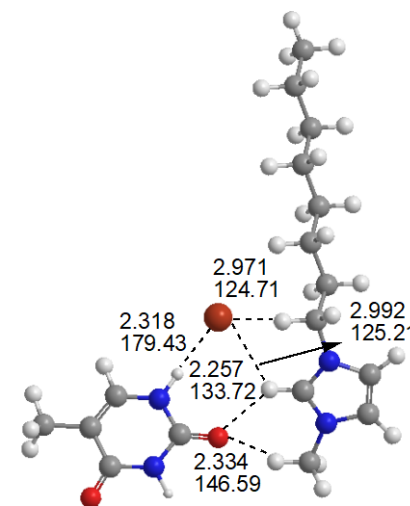
T-[C₈mim]⁺-Br⁻-1 (0.00)

Perpendicular (P)

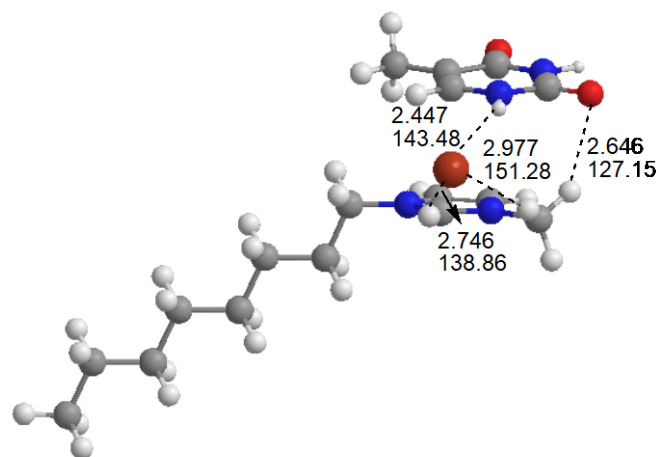


T-[C₈mim]⁺-Br⁻-5 (0.00)

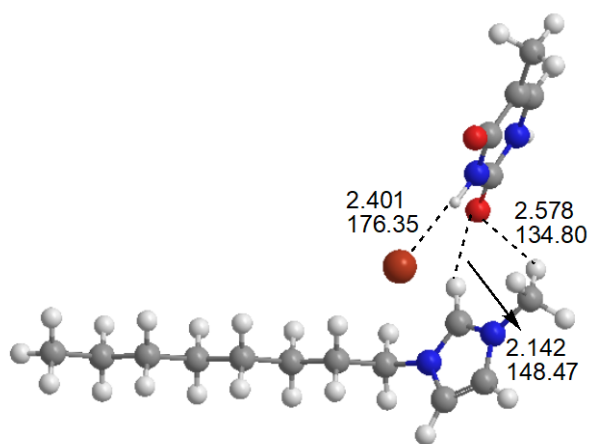
Coplanar (H)



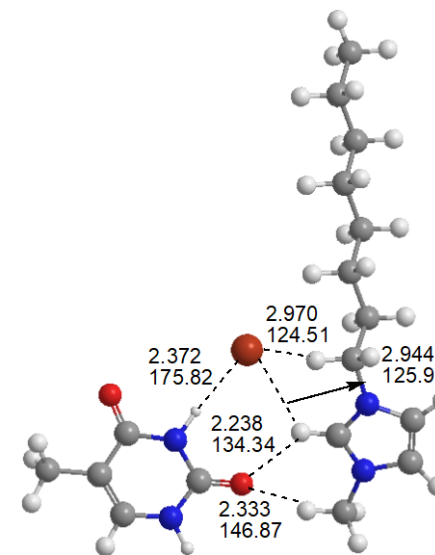
T-[C₈mim]⁺-Br⁻-9 (0.00)



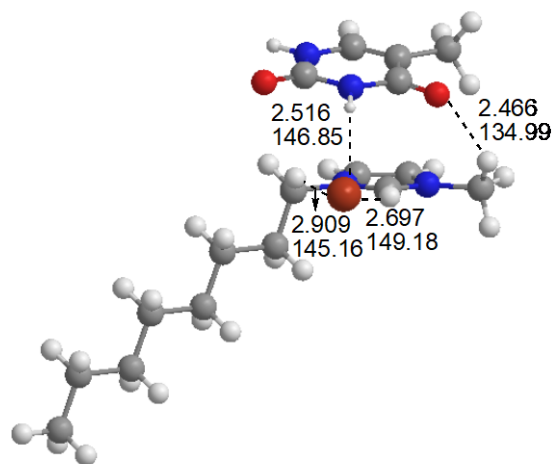
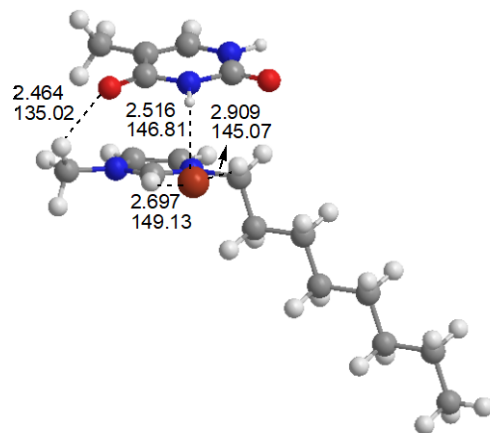
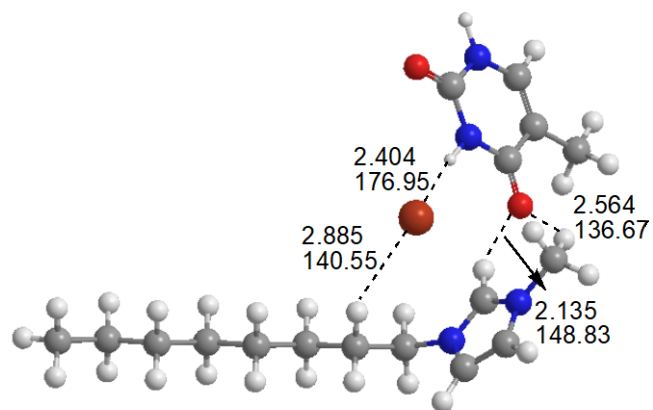
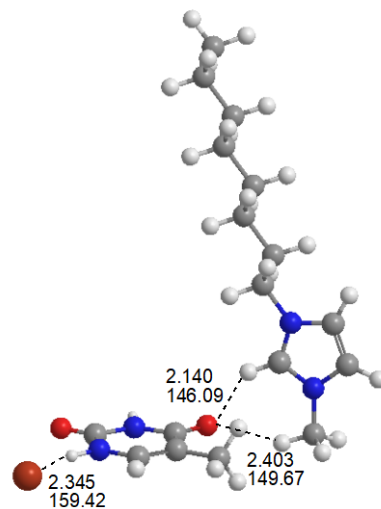
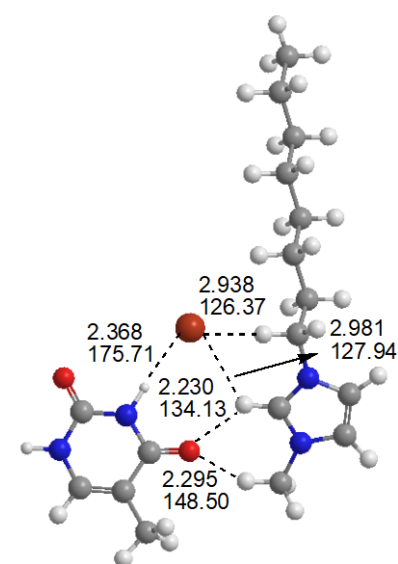
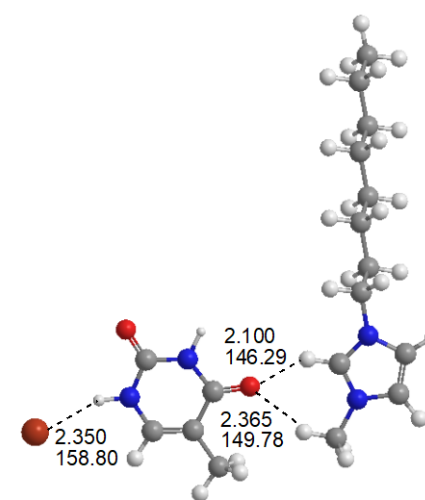
T-[C₈mim]⁺-Br⁻-2 (2.33)



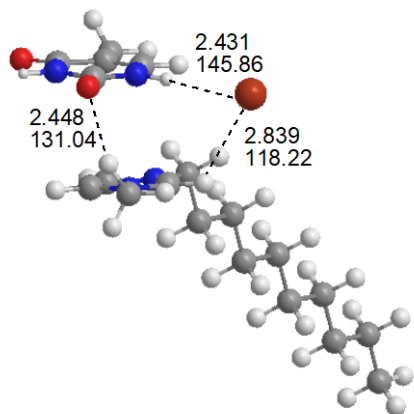
T-[C₈mim]⁺-Br⁻-6 (4.20)



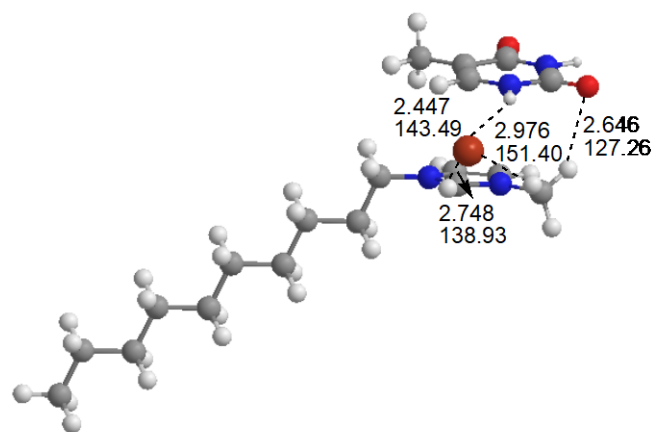
T-[C₈mim]⁺-Br⁻-10 (3.81)

T-[C₈mim]⁺-Br⁻-3 (4.20)T-[C₈mim]⁺-Br⁻-4 (4.26)T-[C₈mim]⁺-Br⁻-7 (5.04)T-[C₈mim]⁺-Br⁻-8 (14.02)T-[C₈mim]⁺-Br⁻-11 (4.10)T-[C₈mim]⁺-Br⁻-12 (13.76)

Stacking (S)

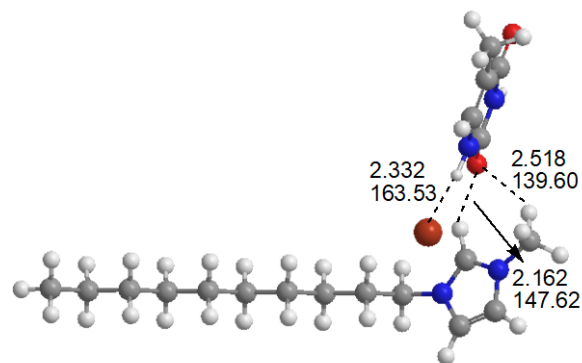


T-[C₁₀mim]⁺-Br⁻-1 (0.00)

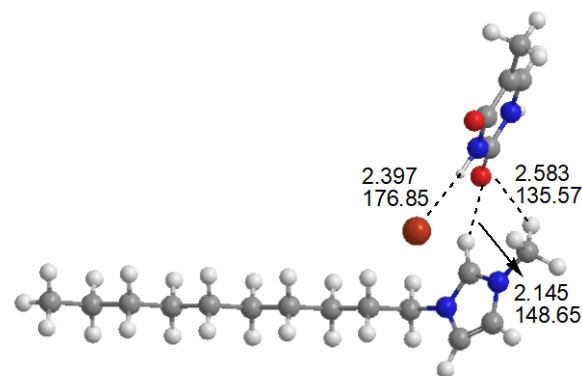


T-[C₁₀mim]⁺-Br⁻-2 (3.07)

Perpendicular (P)

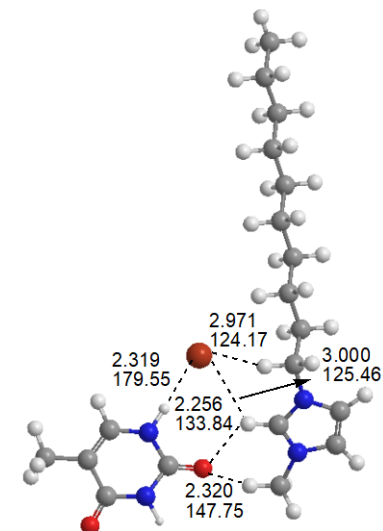


T-[C₁₀mim]⁺-Br⁻-5 (0.00)

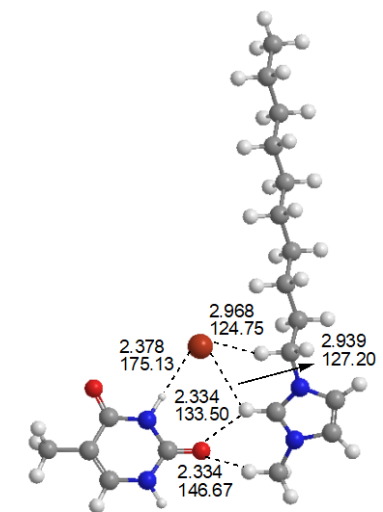


T-[C₁₀mim]⁺-Br⁻-6 (4.31)

Coplanar (H)



T-[C₁₀mim]⁺-Br⁻-9 (0.00)



T-[C₁₀mim]⁺-Br⁻-10 (3.15)

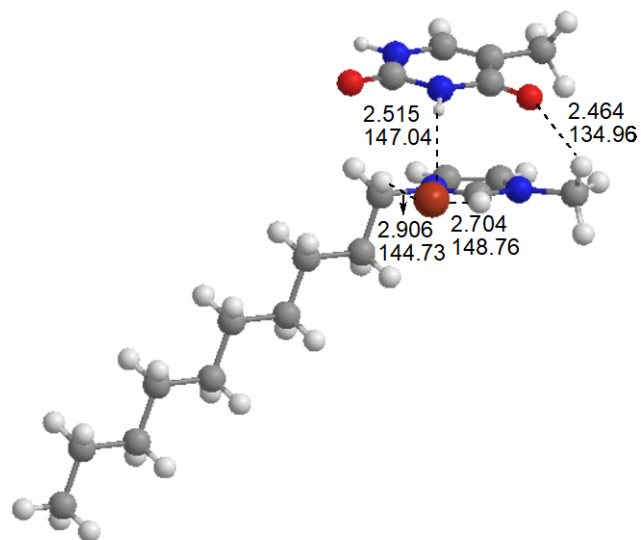
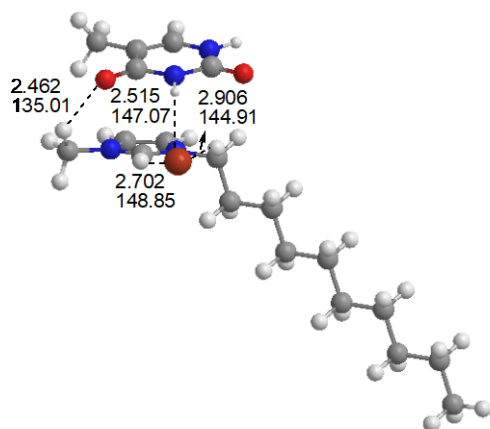
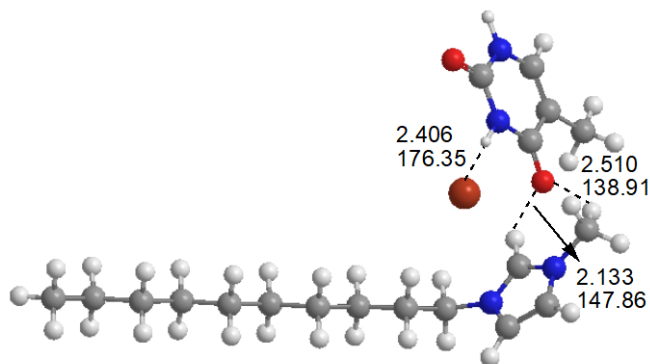
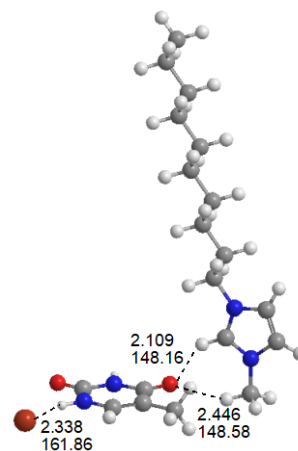
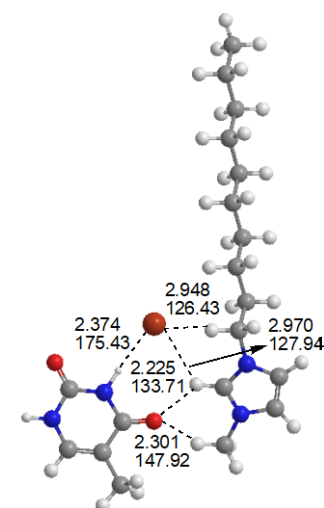
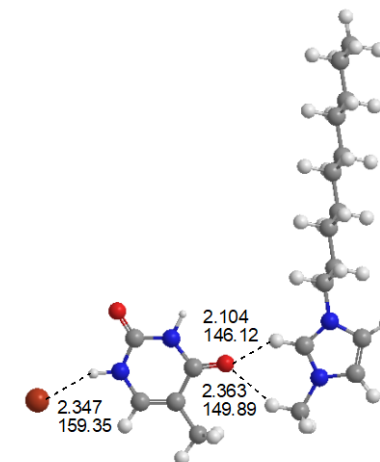
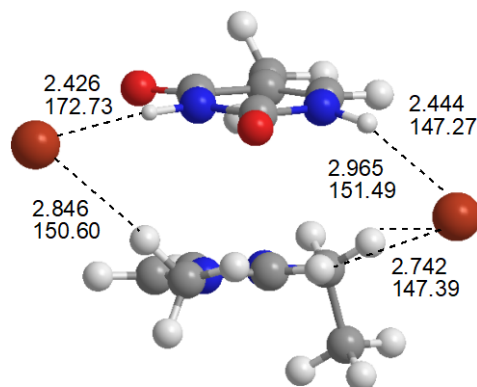
T-[C₁₀mim]⁺-Br⁻-3 (4.09)T-[C₁₀mim]⁺-Br⁻-4 (4.27)T-[C₁₀mim]⁺-Br⁻-7 (4.91)T-[C₁₀mim]⁺-Br⁻-8 (12.80)T-[C₁₀mim]⁺-Br⁻-11 (3.67)T-[C₁₀mim]⁺-Br⁻-12 (13.12)

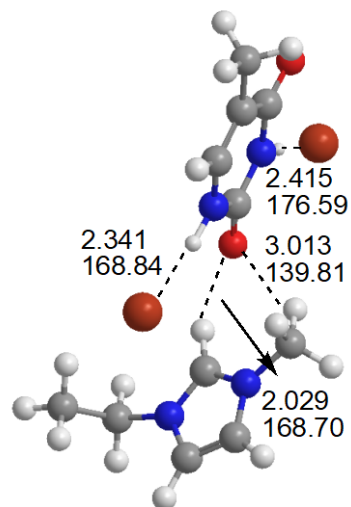
Figure S4. 12 of the di-ionic structures of thymine with five imidazolium ILs (T-[C_nmim]⁺-Br⁻, n = 2, 4, 6, 8, 10) calculated at the M06-2X/6-311++G(2d, p)/PCM/water level of theory. The ZPVE-corrected stability decreases from top to bottom for each configuration (in kJ/mol).

Stacking (S)



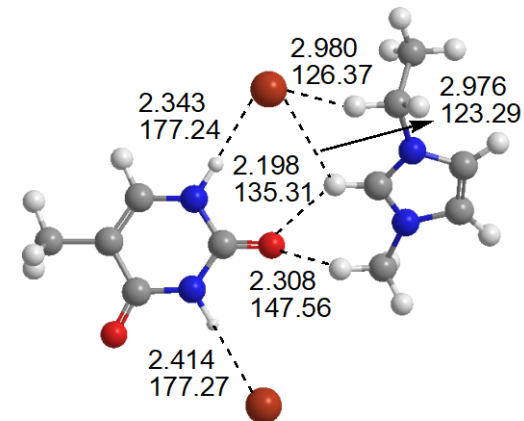
T-[C₂mim]⁺-2Br⁻-1 (0.00)

Perpendicular (P)

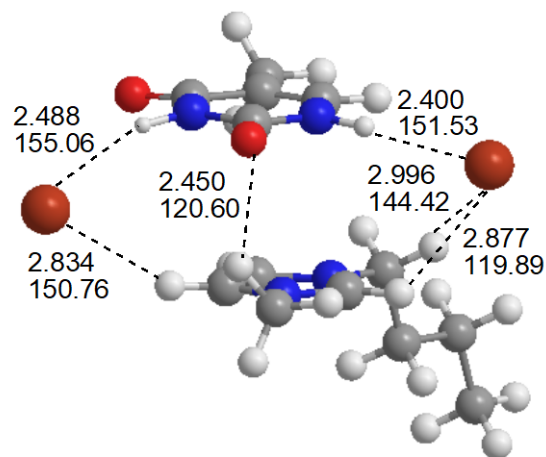


T-[C₂mim]⁺-2Br⁻-2 (15.75)

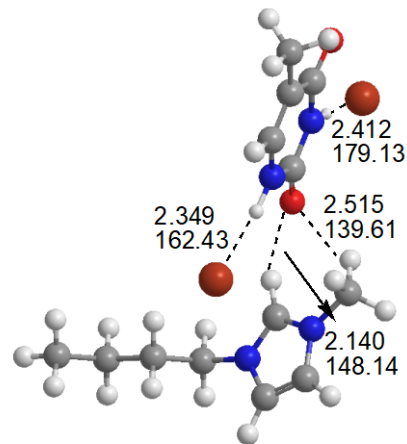
Coplanar (H)



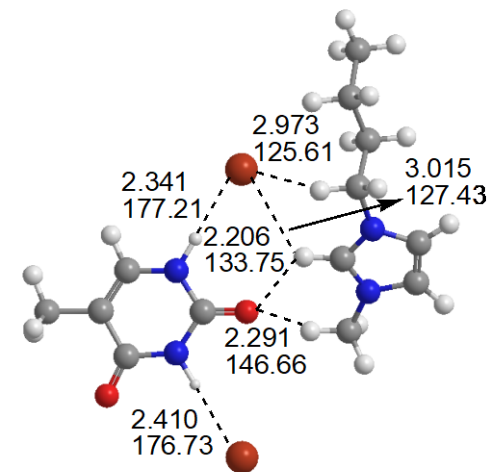
T-[C₂mim]⁺-2Br⁻-3 (18.95)



T-[C₄mim]⁺-2Br⁻-1 (0.00)

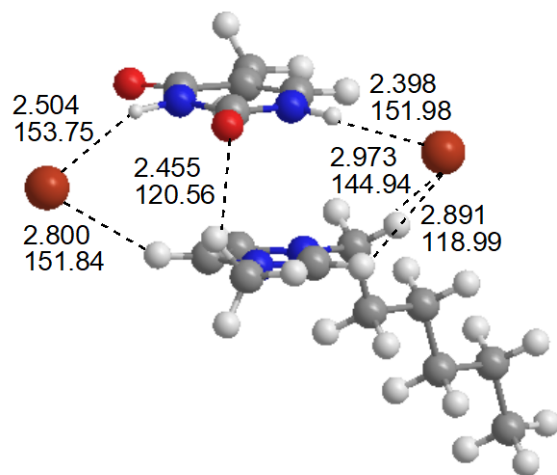


T-[C₄mim]⁺-2Br⁻-2 (11.77)

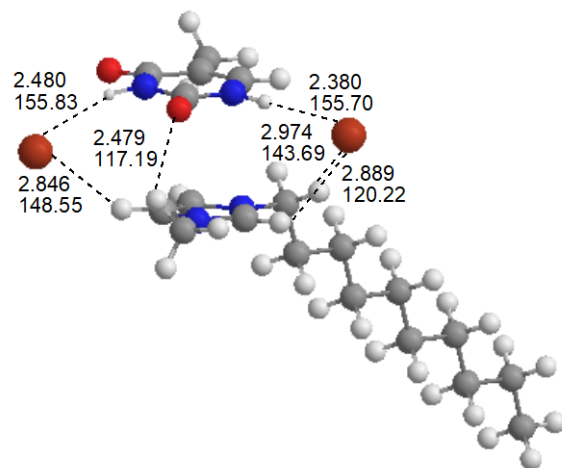


T-[C₄mim]⁺-2Br⁻-3 (13.14)

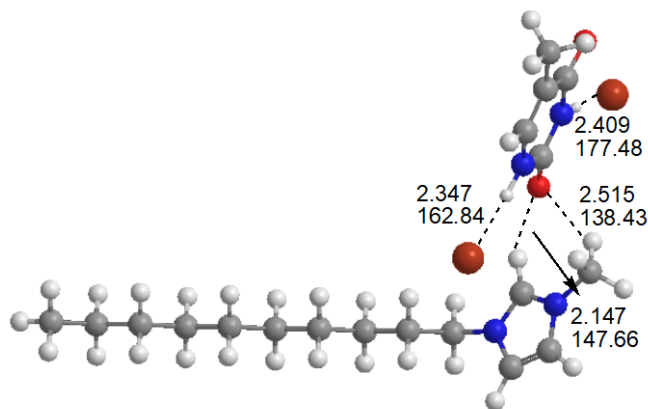
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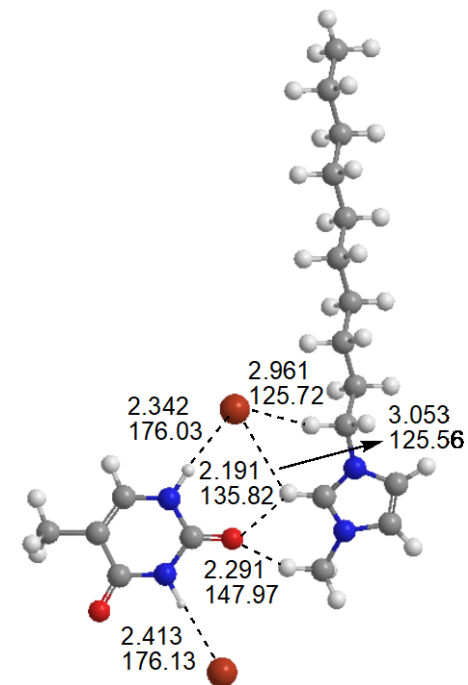
Continued



T-[C₁₀mim]⁺-2Br⁻-1 (0.00)



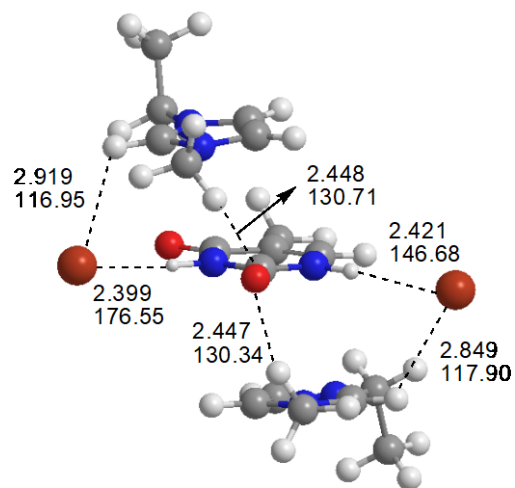
T-[C₁₀mim]⁺-2Br⁻-2 (12.53)



T-[C₁₀mim]⁺-2Br⁻-3 (12.62)

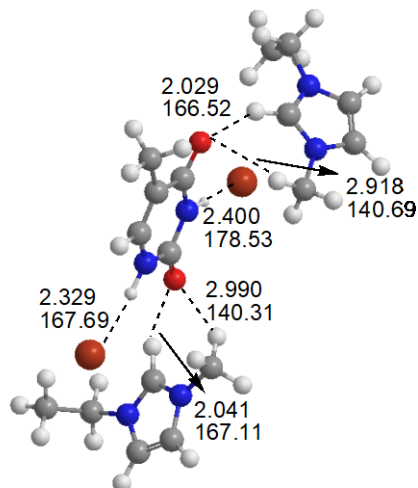
Figure S5. 3 of the tri-ionic structures of thymine with five imidazolium ILs (T-[C_nmim]⁺-2Br⁻, n = 2, 4, 6, 8, 10) based on the stacking, perpendicular, and coplanar configurations and calculated at the M06-2X/6-311++G(2d, p)/PCM/water level of theory. The ZPVE-corrected stability decreases from left to right (in kJ/mol).

Stacking (S)



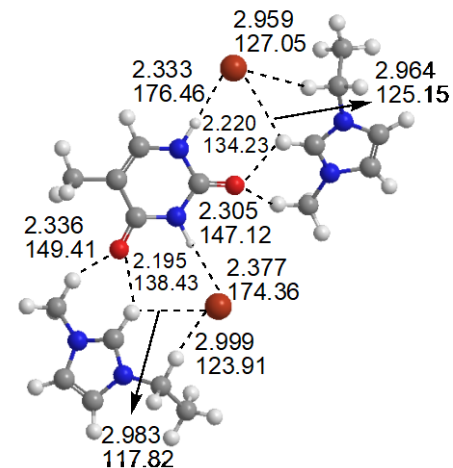
T-2[C₂mim]⁺-2Br⁻-1 (0.00)

Perpendicular (P)

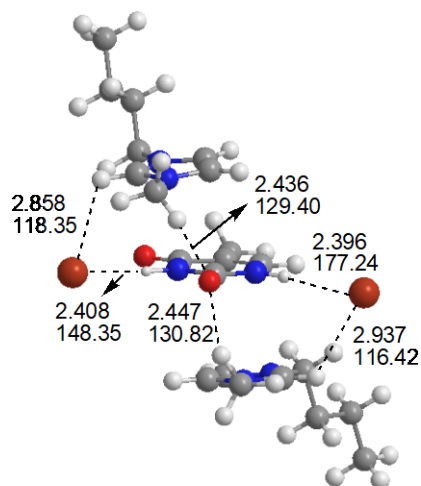


T-2[C₂mim]⁺-2Br⁻-2 (18.69)

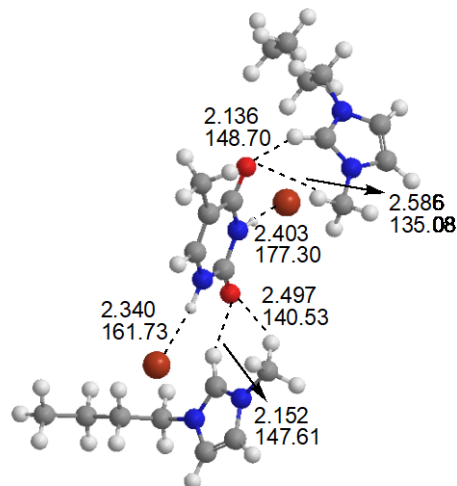
Coplanar (H)



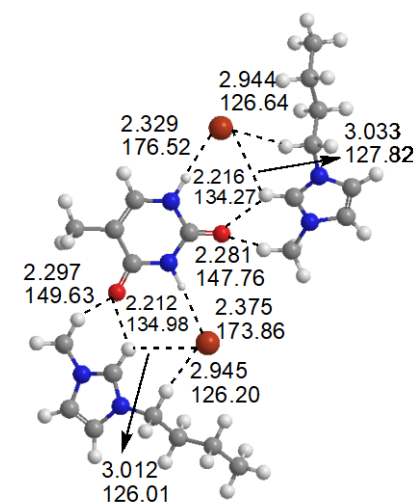
T-2[C₂mim]⁺-2Br⁻-3 (25.38)



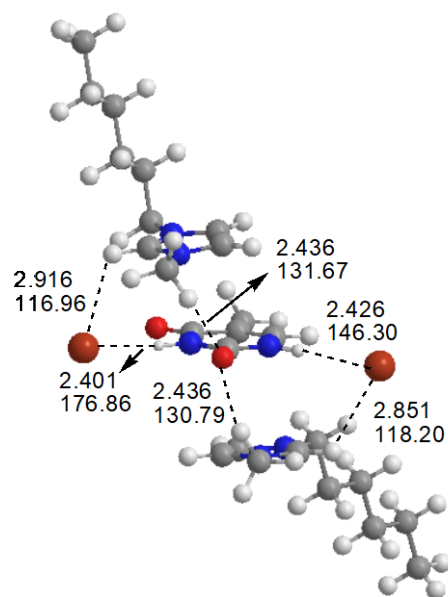
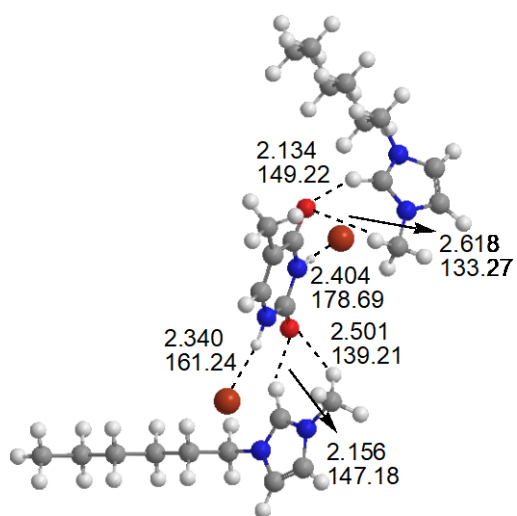
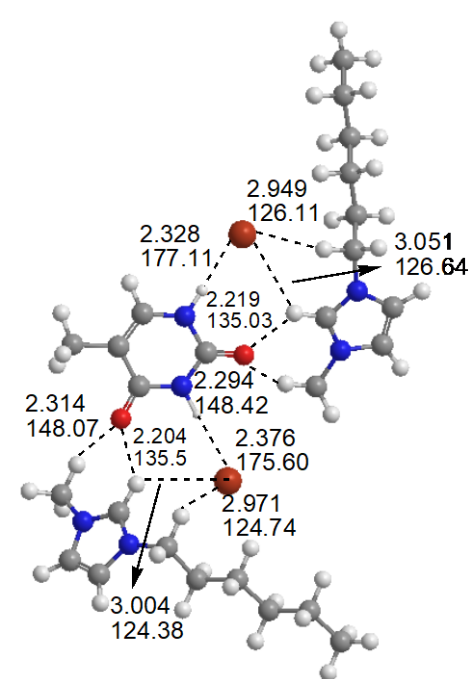
T-2[C₄mim]⁺-2Br⁻-1 (0.00)

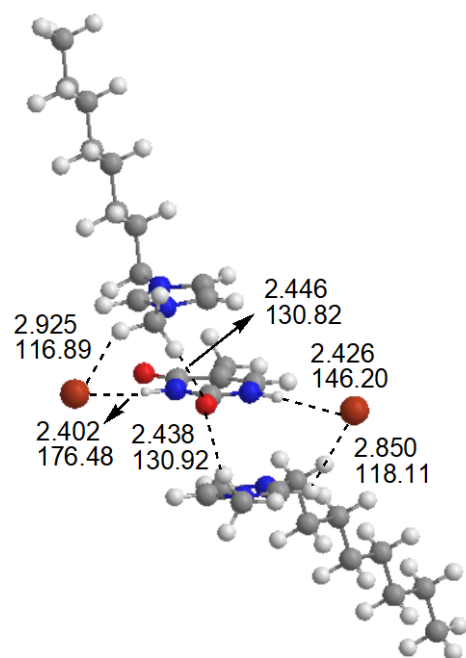
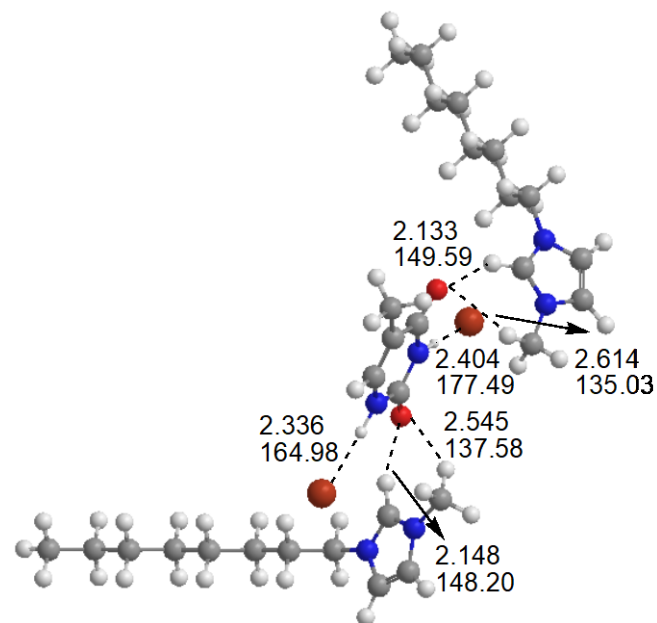
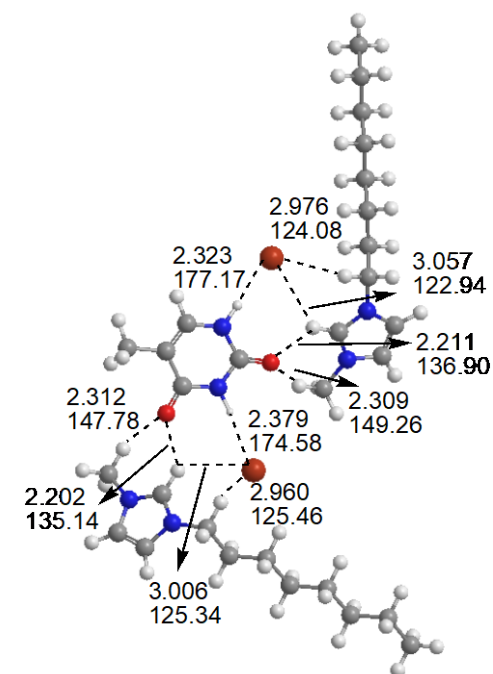


T-2[C₄mim]⁺-2Br⁻-2 (19.17)

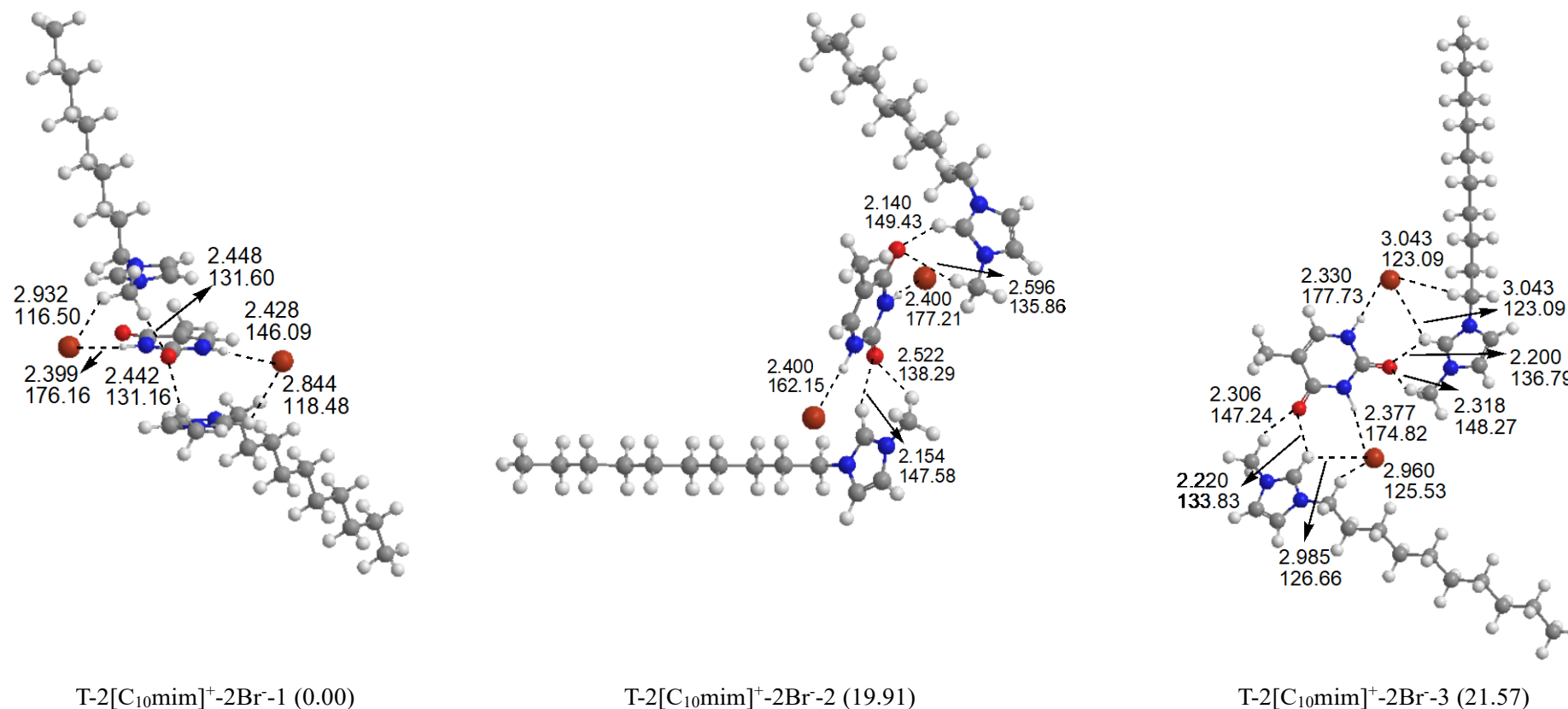


T-2[C₄mim]⁺-2Br⁻-3 (21.95)

T-2[C₆mim]⁺-2Br⁻-1 (0.00)T-2[C₆mim]⁺-2Br⁻-2 (19.13)T-2[C₆mim]⁺-2Br⁻-3 (21.04)

T-2[C₈mim]⁺-2Br⁻-1 (0.00)T-2[C₈mim]⁺-2Br⁻-2 (20.20)T-2[C₈mim]⁺-2Br⁻-3 (21.60)

Continued

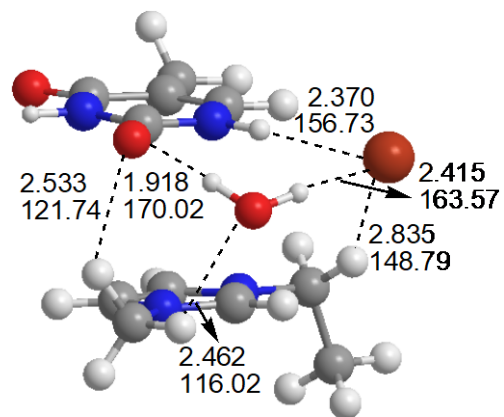


T-2[C₁₀mim]⁺-2Br⁻-1 (0.00)

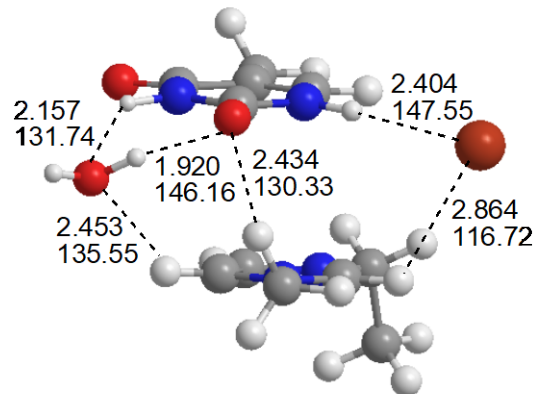
T-2[C₁₀mim]⁺-2Br⁻-2 (19.91)

T-2[C₁₀mim]⁺-2Br⁻-3 (21.57)

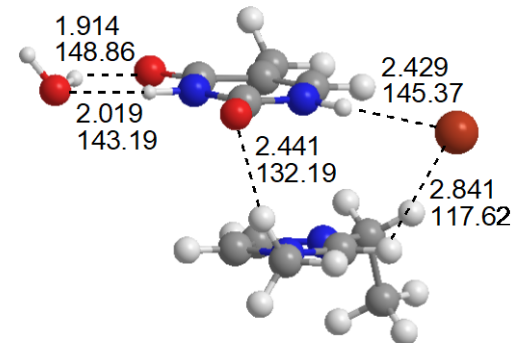
Figure S6. 3 of the tetra-ionic structures of thymine with five imidazolium ILs (T-2[C_nmim]⁺-2Br⁻, n = 2, 4, 6, 8, 10) based on the stacking, perpendicular, and coplanar configurations and calculated at the M06-2X/6-311++G(2d, p)/PCM/water level of theory. The ZPVE-corrected stability decreases from left to right (in kJ/mol).



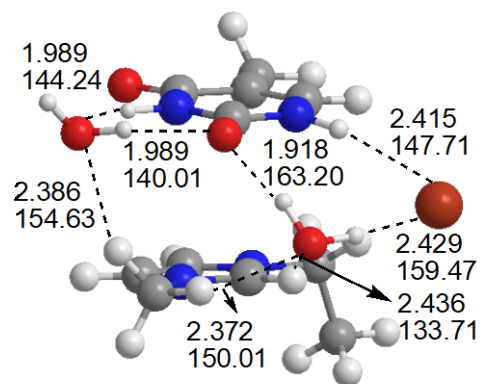
T-1H₂O-[C₂mim]⁺-Br⁻-1 (0.00)



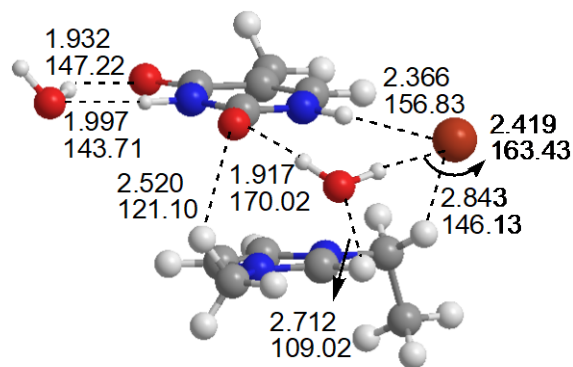
T-1H₂O-[C₂mim]⁺-Br⁻-2 (5.59)



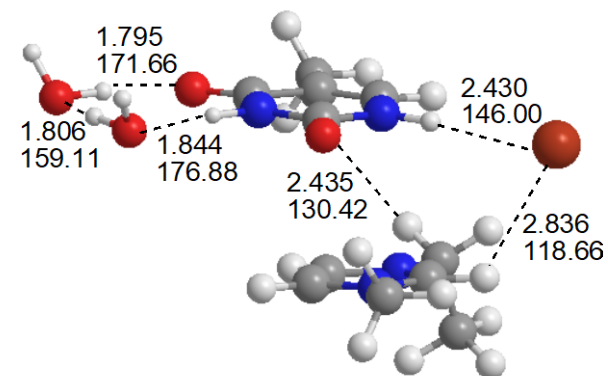
T-1H₂O-[C₂mim]⁺-Br⁻-3 (7.05)



T-2H₂O-[C₂mim]⁺-Br⁻-1 (0.00)

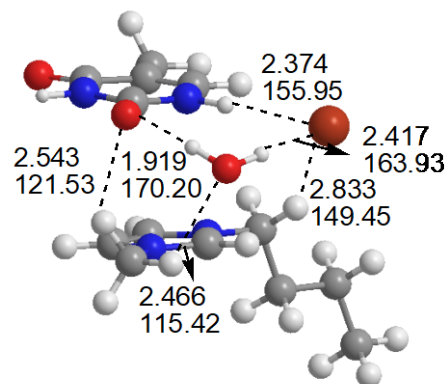


T-2H₂O-[C₂mim]⁺-Br⁻-2 (1.67)

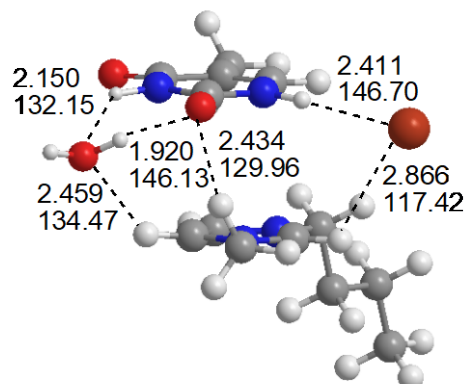


T-2H₂O-[C₂mim]⁺-Br⁻-3 (3.85)

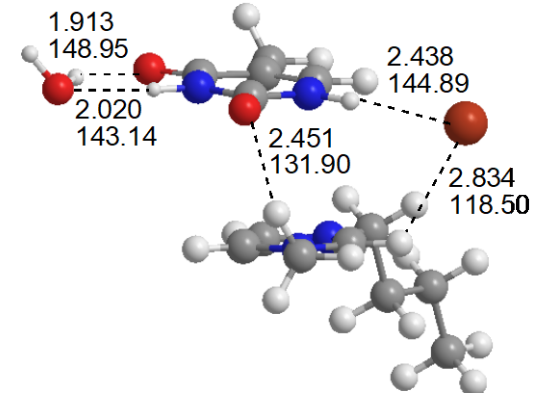
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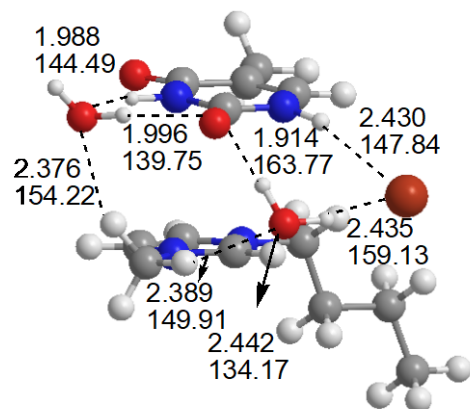
T-1H₂O-[C₄mim]⁺-Br-1 (0.00)



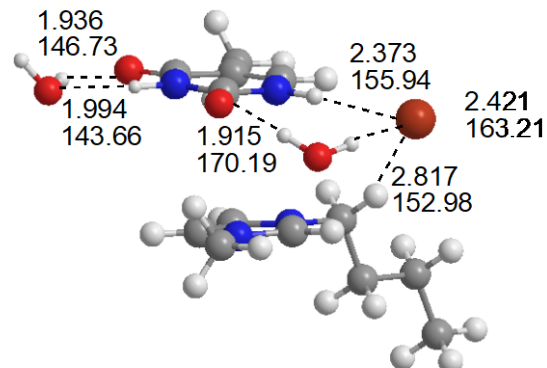
T-1H₂O-[C₄mim]⁺-Br-2 (6.87)



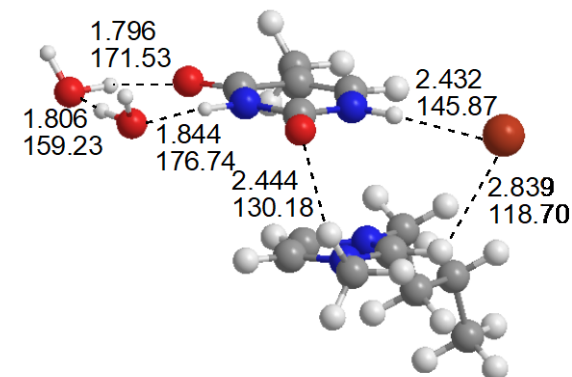
T-1H₂O-[C₄mim]⁺-Br-3 (7.91)



T-2H₂O-[C₄mim]⁺-Br-1 (0.00)

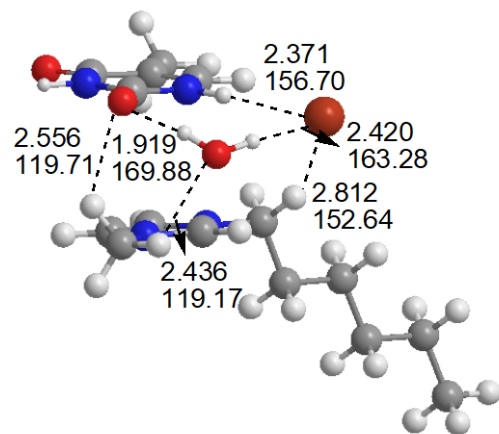


T-2H₂O-[C₄mim]⁺-Br-2 (2.21)

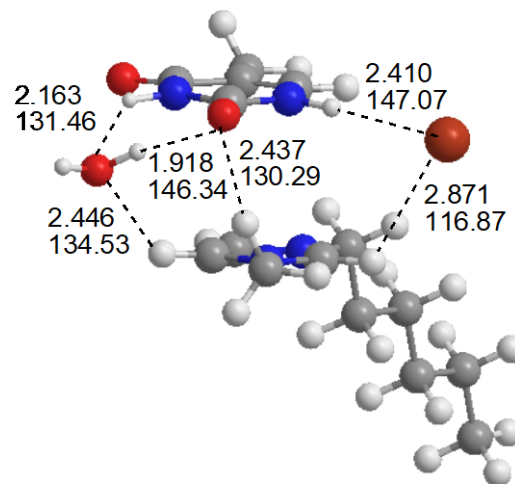


T-2H₂O-[C₄mim]⁺-Br-3 (4.88)

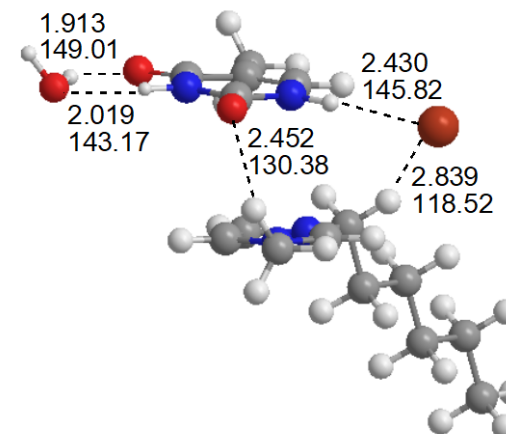
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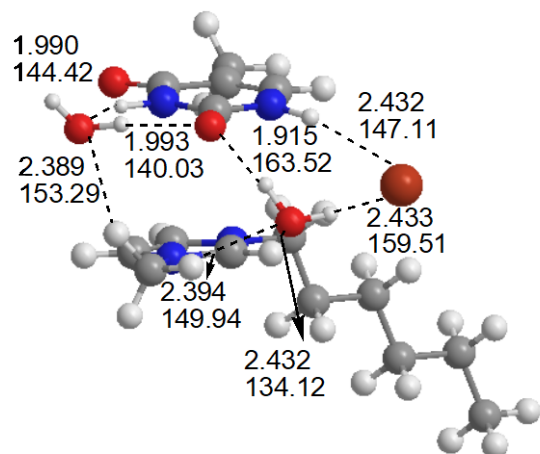
T-1H₂O-[C₆mim]⁺-Br⁻-1 (0.00)



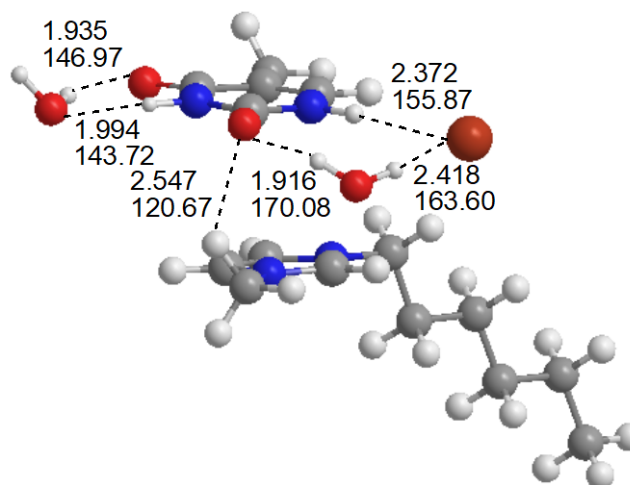
T-1H₂O-[C₆mim]⁺-Br⁻-2 (7.16)



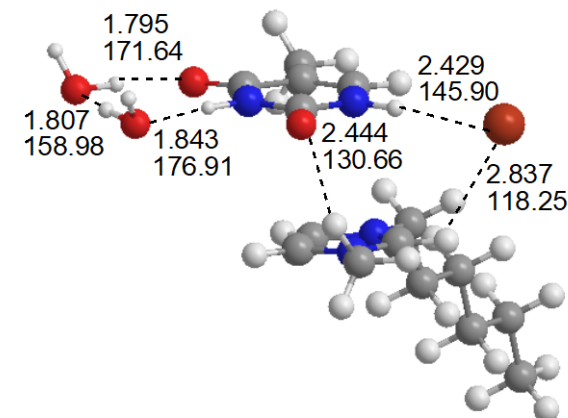
T-1H₂O-[C₆mim]⁺-Br⁻-3 (8.66)



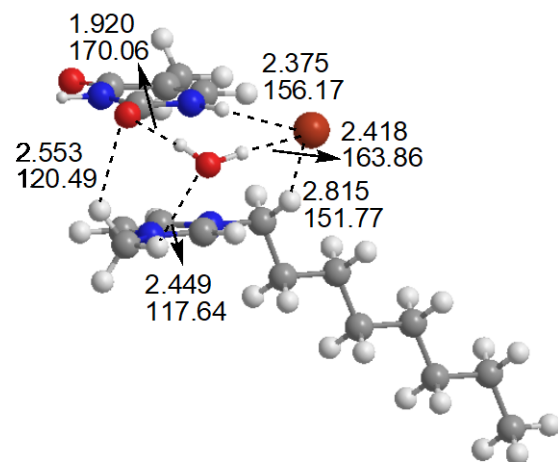
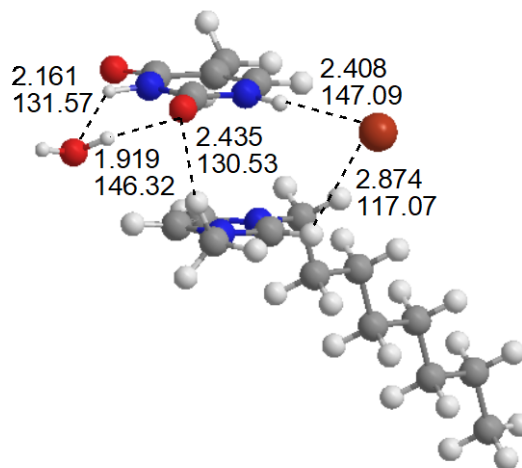
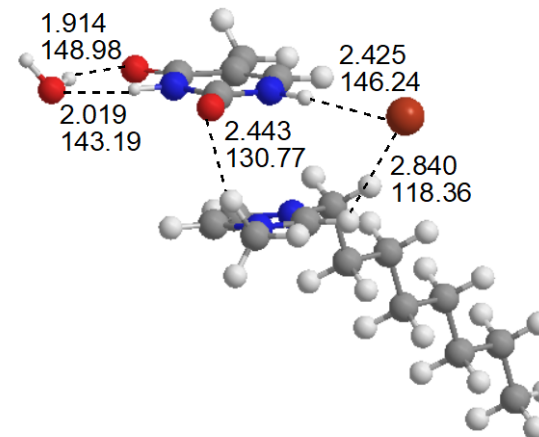
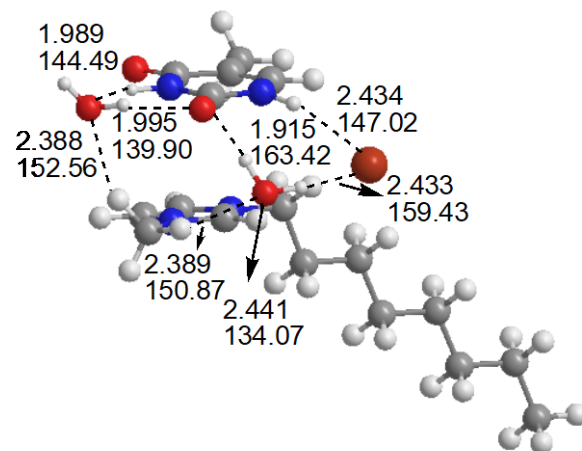
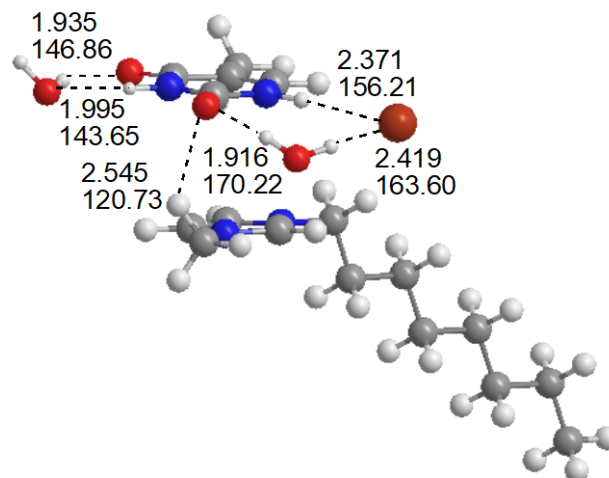
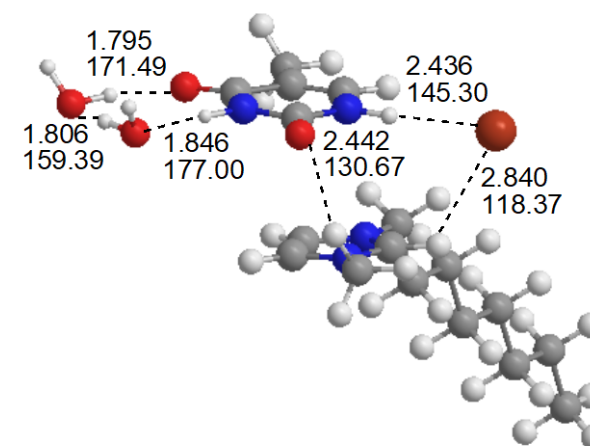
T-2H₂O-[C₆mim]⁺-Br⁻-1 (0.00)



T-2H₂O-[C₆mim]⁺-Br⁻-2 (2.25)



T-2H₂O-[C₆mim]⁺-Br⁻-3 (5.77)

T-1H₂O-[C₈mim]⁺-Br⁻-1 (0.00)T-1H₂O-[C₈mim]⁺-Br⁻-2 (6.89)T-1H₂O-[C₈mim]⁺-Br⁻-3 (8.29)T-2H₂O-[C₈mim]⁺-Br⁻-1 (0.00)T-2H₂O-[C₈mim]⁺-Br⁻-2 (3.30)T-2H₂O-[C₈mim]⁺-Br⁻-3 (5.77)

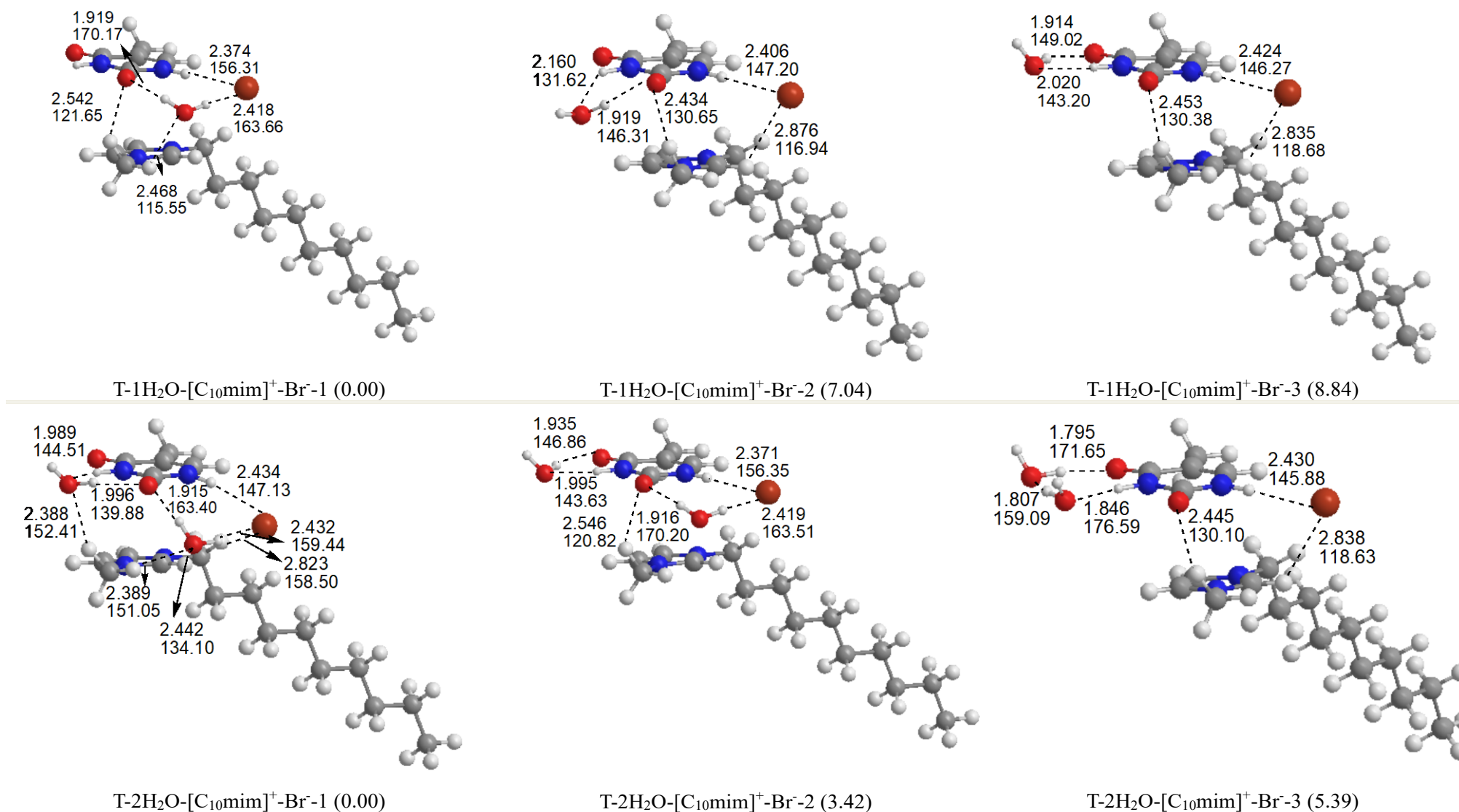
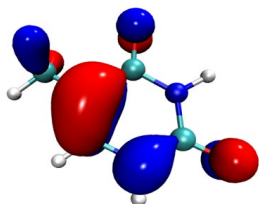


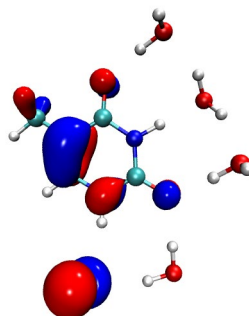
Figure S1. Optimized molecular structures of micro-hydrated T-*w*H₂O-[C_{*n*}mim]⁺-Br⁻ (*w* = 1, 2 and *n* = 2, 4, 6, 8, 10) at the M06-2X/6-311++G(2*d*, *p*)/PCM/water level. The ZPVE-corrected stability decreases from left to right (in kJ/mol).

Occupied orbitals

T

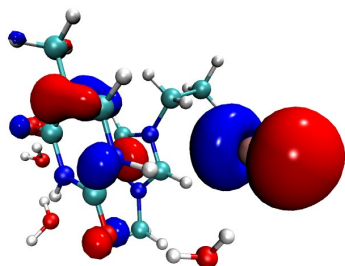


T-4H₂O-Br-1



HOMO

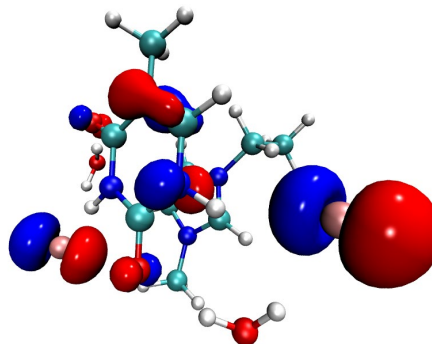
T-3H₂O-[C₂mim]⁺-Br-1



HOMO

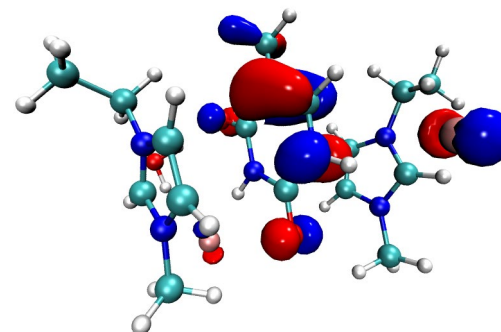
HOMO-2

T-2H₂O-[C₂mim]⁺-2Br-1

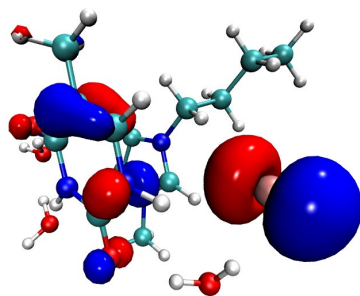


HOMO-1

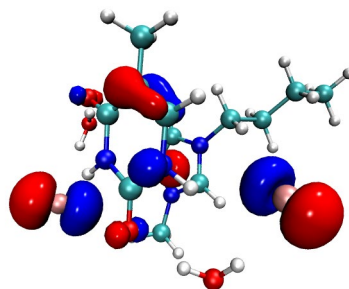
T-1H₂O-2[C₂mim]⁺-2Br-1



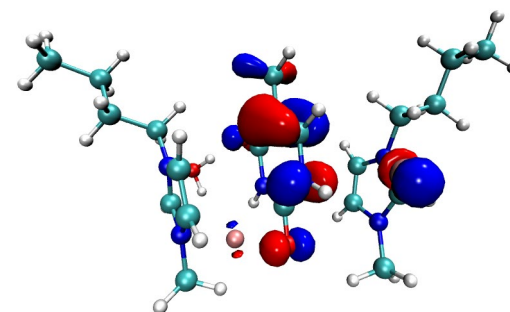
HOMO-3

T-3H₂O-[C₄mim]⁺-Br⁻-1

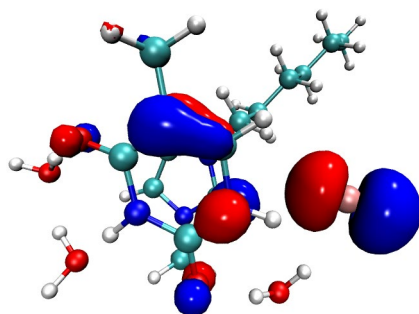
HOMO

T-2H₂O-[C₄mim]⁺-2Br⁻-1

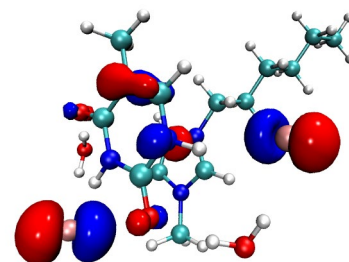
HOMO

T-1H₂O-2[C₄mim]⁺-2Br⁻-1

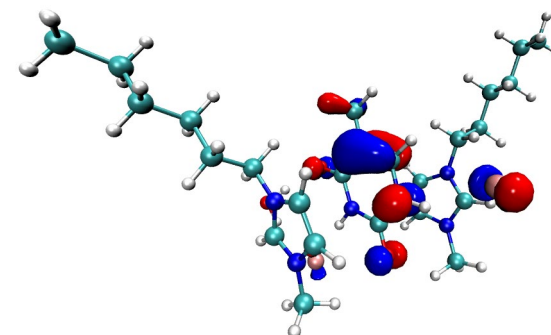
HOMO-3

T-3H₂O-[C₆mim]⁺-Br⁻-1

HOMO

T-2H₂O-[C₆mim]⁺-2Br⁻-1

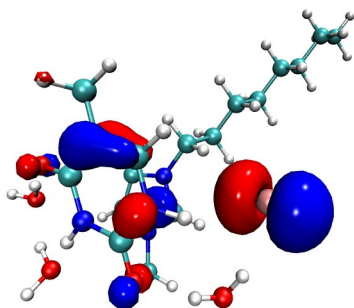
HOMO

T-1H₂O-2[C₆mim]⁺-2Br⁻-1

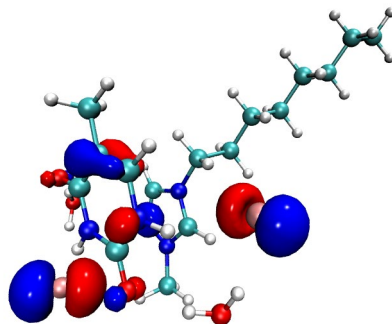
HOMO-3

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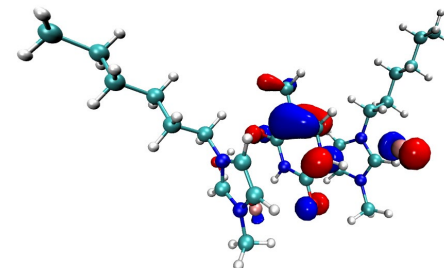
T-3H₂O-[C₈mim]⁺-Br⁻-1



T-2H₂O-[C₈mim]⁺-2Br⁻-1

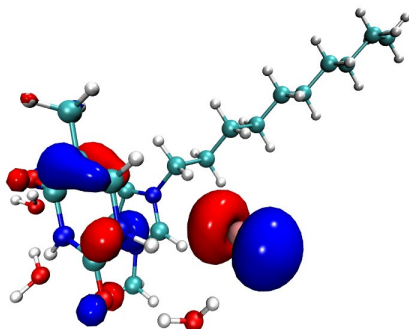


T-1H₂O-2[C₈mim]⁺-2Br⁻-1



HOMO

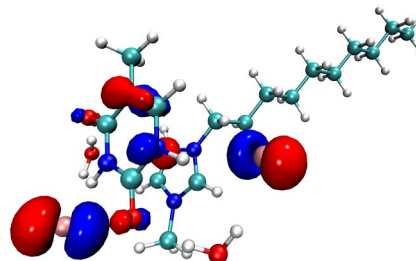
T-3H₂O-[C₁₀mim]⁺-Br⁻-1



HOMO

HOMO

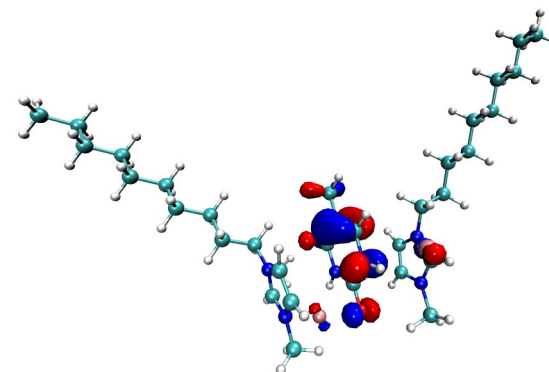
T-2H₂O-[C₁₀mim]⁺-2Br⁻-1



HOMO

HOMO-3

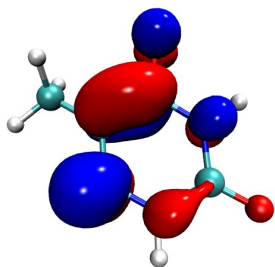
T-1H₂O-2[C₁₀mim]⁺-2Br⁻-1



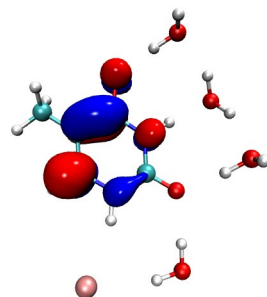
HOMO-3

Unoccupied orbitals

T

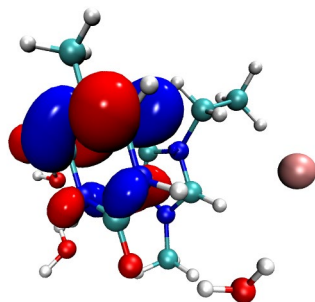


T-4H₂O-Br⁻-1



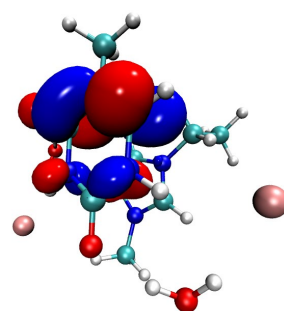
LUMO

T-3H₂O-[C₂mim]⁺-Br⁻-1

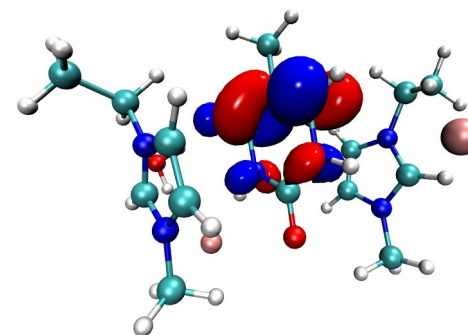


LUMO

T-2H₂O-[C₂mim]⁺-2Br⁻-1



T-1H₂O-2[C₂mim]⁺-2Br⁻-1



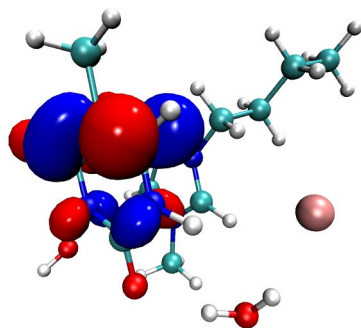
LUMO

LUMO

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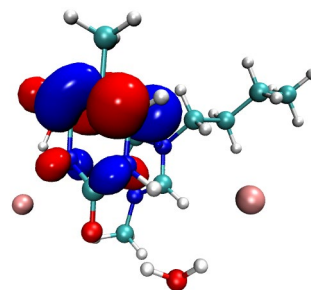
continued

T-3H₂O-[C₄mim]⁺-Br⁻1



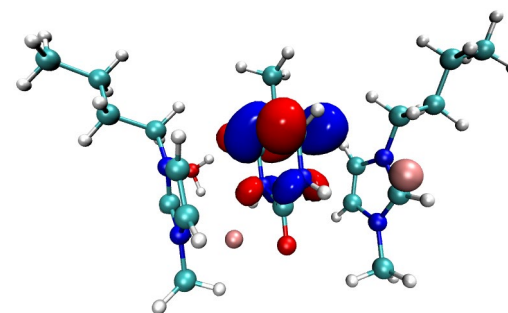
LUMO

T-2H₂O-[C₄mim]⁺-2Br⁻1



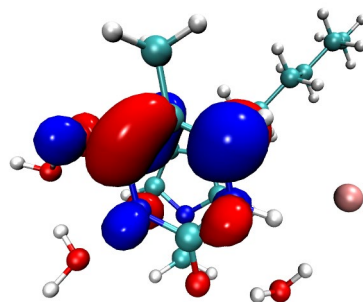
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T-1H₂O-2[C₄mim]⁺-2Br⁻1



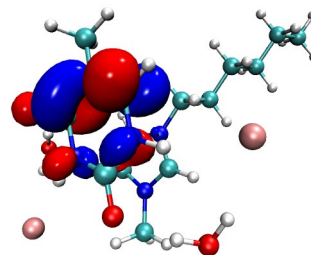
LUMO

T-3H₂O-[C₆mim]⁺-Br⁻1



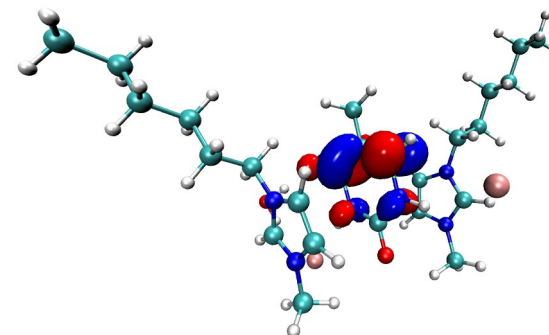
LUMO

T-2H₂O-[C₆mim]⁺-2Br⁻1

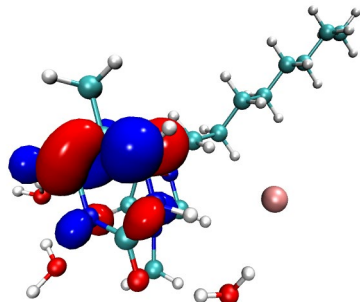
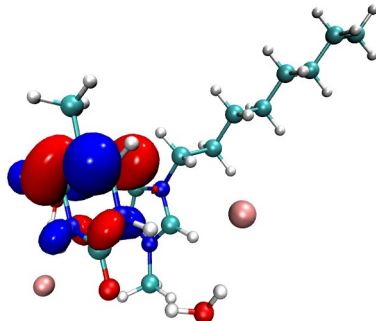
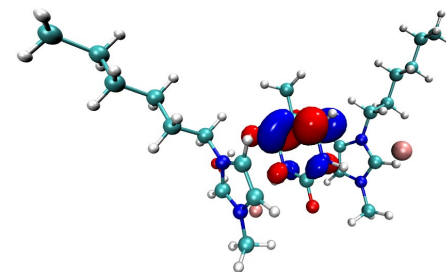


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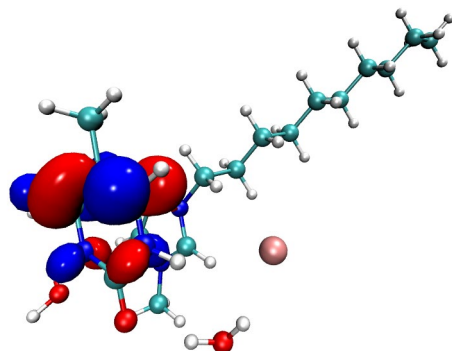
T-1H₂O-2[C₆mim]⁺-2Br⁻1



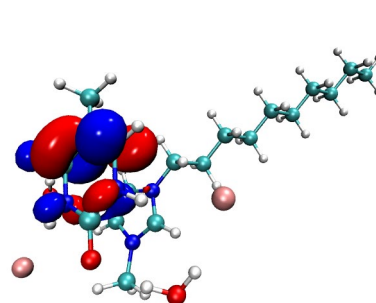
LUMO

T-3H₂O-[C₈mim]⁺-Br⁻1T-2H₂O-[C₈mim]⁺-2Br⁻1T-1H₂O-2[C₈mim]⁺-2Br⁻1

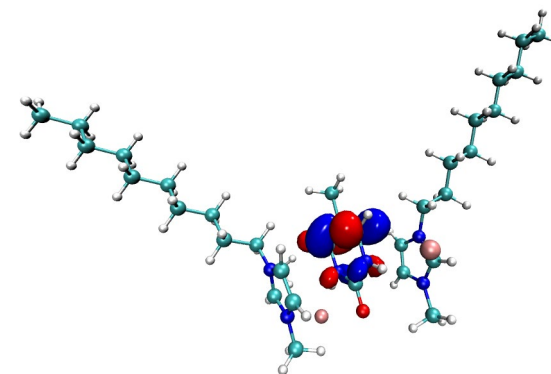
LUMO

T-3H₂O-[C₁₀mim]⁺-Br⁻1

LUMO

T-2H₂O-[C₁₀mim]⁺-2Br⁻1

LUMO

T-1H₂O-2[C₁₀mim]⁺-2Br⁻1

LUMO

LUMO

LUMO

Figure S2. The isosurface maps of the frontier molecular orbitals for the isolated T, micro-hydrated T-4H₂O-Br⁻1, T-3H₂O-[C_nmim]⁺-Br⁻1, T-2H₂O-[C_nmim]⁺-2Br⁻1, and T-1H₂O-2[C_nmim]⁺-2Br⁻1 species calculated at the TD-M06-2X/6-311++G(2d, p)/PCM/water level (isovalues = 0.0 1 a.u.).