Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

The Position of the Ether Oxygen Atom in Pyrrolidinium-Based Room Temperature Ionic Liquids for the Physicochemical Properties

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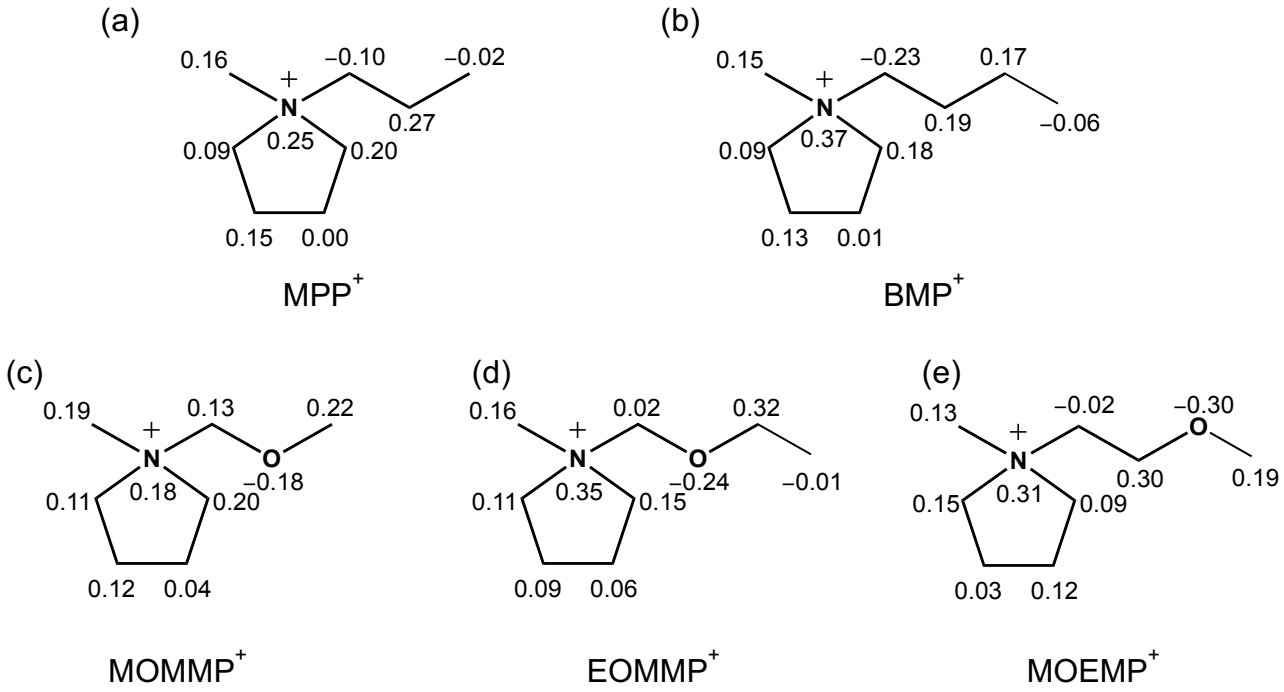

Figure S1. The charge distribution of the cations obtained by the electrostatic potential fitting using Kollman's scheme from the MP2/6-311G(d,p) level. The structures used for the calculation of the charge distribution are exhibited in Figure 2.

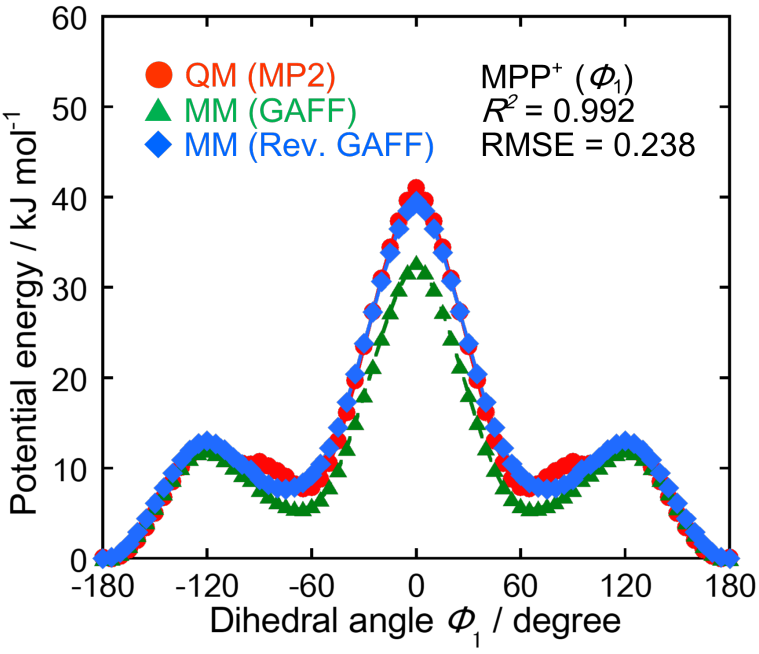

Figure S2. Energy profiles for the dihedral angle (Φ_1) of MPP^+, obtained by the QM (MP2), original MM (GAFF) and revised MM (revised GAFF) calculations shown with red, green and blue lines, respectively. The coefficient of determination (R^2) and the root mean square error (RMSE) were estimated by the difference between QM (MP2) and MM (revised GAFF) profiles.

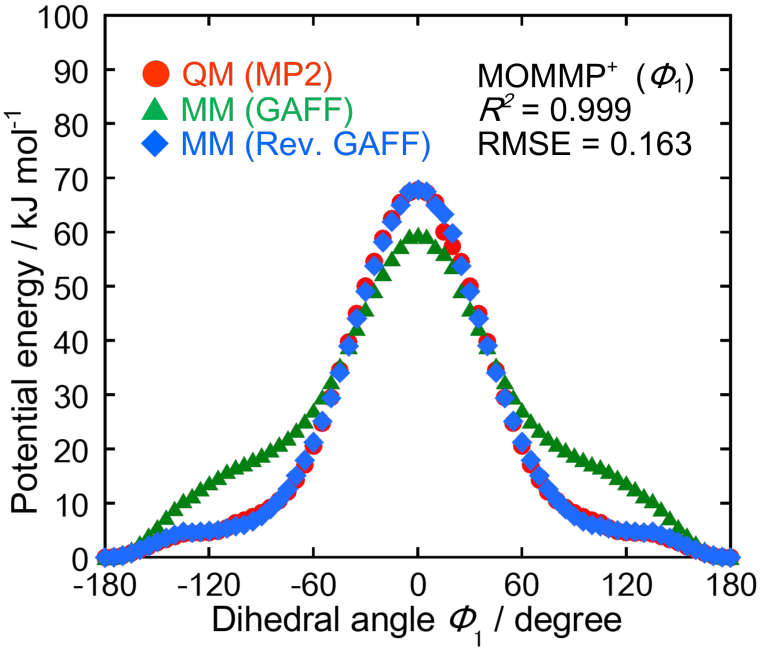

Figure S3. Energy profiles for the dihedral angle (Φ_1) of MOMMP$^+$, obtained by the QM (MP2), original MM (GAFF) and revised MM (revised GAFF) calculations shown with red, green and blue lines, respectively. The coefficient of determination (R^2) and the root mean square error (RMSE) were estimated by the difference between QM (MP2) and MM (revised GAFF) profiles.

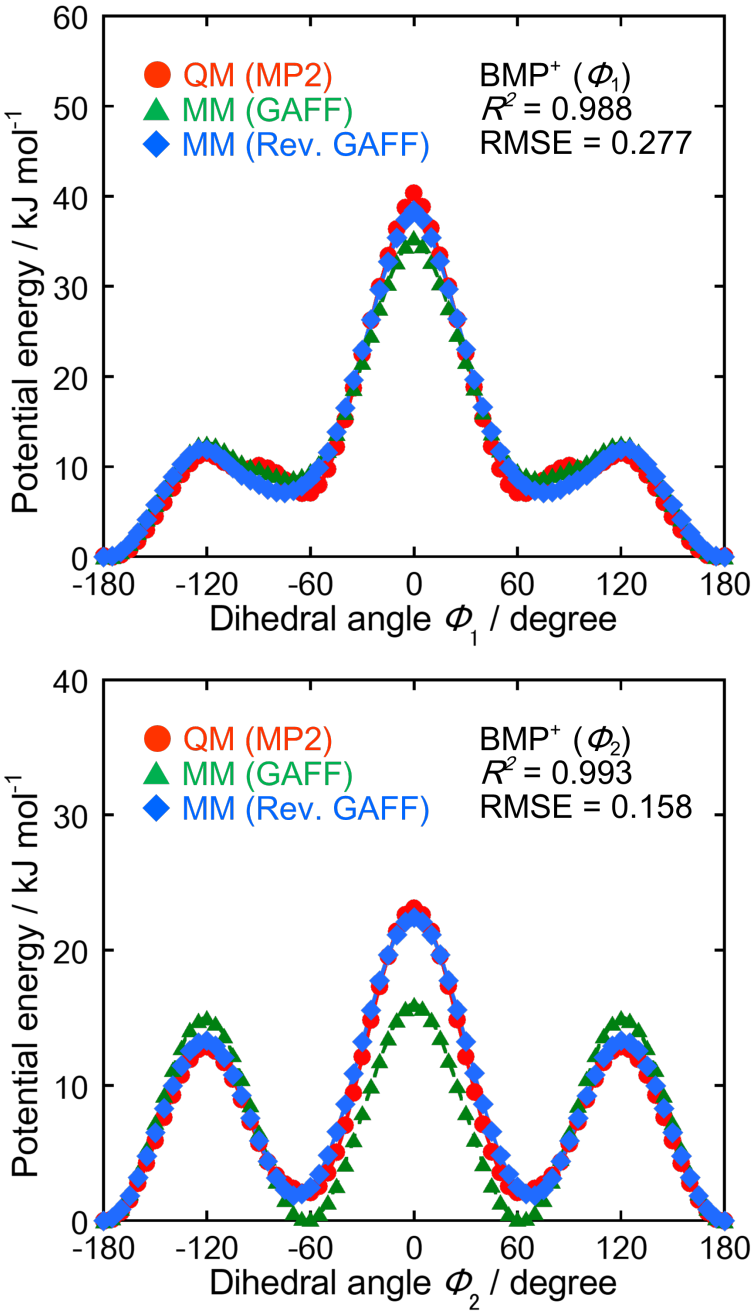

Figure S4. Energy profiles for the dihedral angles (Φ_1 and Φ_2) of BMP^+, obtained by the QM (MP2), original MM (GAFF) and revised MM (revised GAFF) calculations shown with red, green and blue lines, respectively. The coefficient of determination (R^2) and the root mean square error (RMSE) were estimated by the difference between QM (MP2) and MM (revised GAFF) profiles.

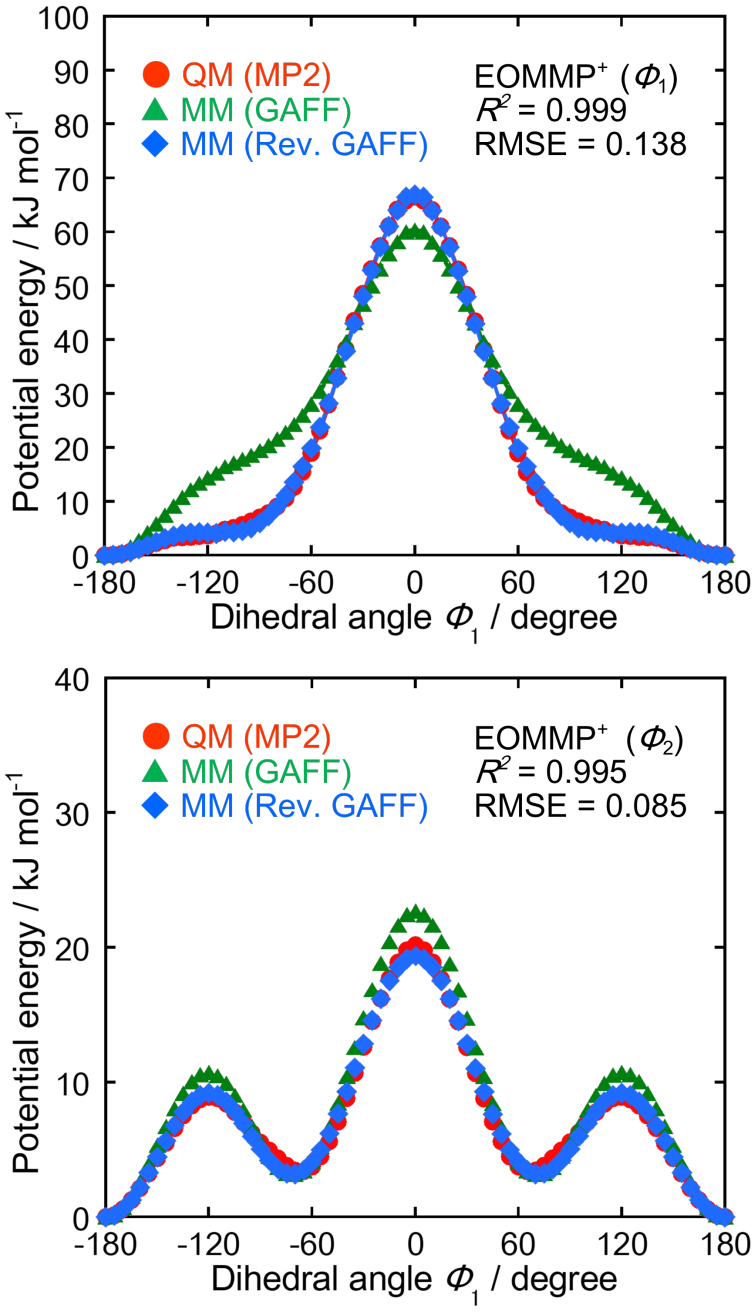

Figure S5. Energy profiles for the dihedral angles (Φ_1 and Φ_2) of EOMMP$^+$, obtained by the QM (MP2), original MM (GAFF) and revised MM (revised GAFF) calculations shown with red, green and blue lines, respectively. The coefficient of determination (R^2) and the root mean square error (RMSE) were estimated by the difference between QM (MP2) and MM (revised GAFF) profiles.

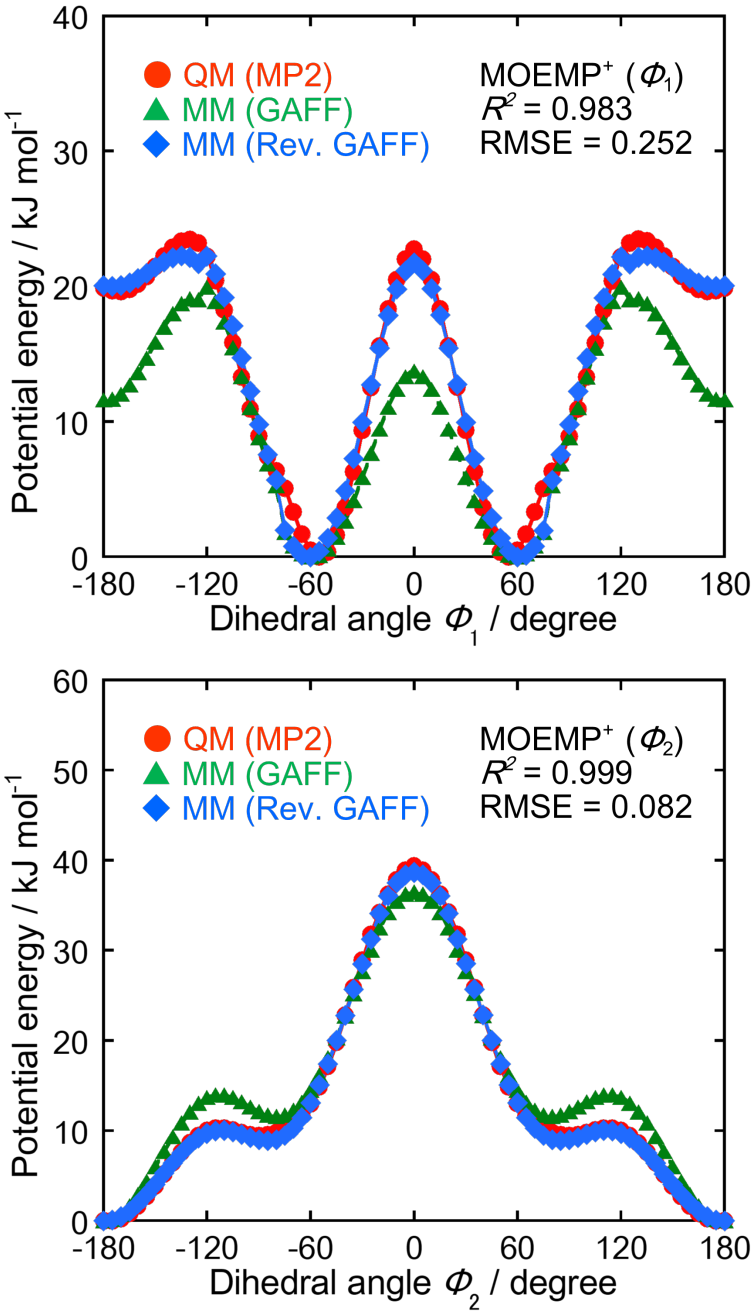

Figure S6. Energy profiles for the dihedral angles (Φ_1 and Φ_2) of $MOEMP^+$, obtained by the QM (MP2), original MM (GAFF) and revised MM (revised GAFF) calculations shown with red, green and blue lines, respectively. The coefficient of determination (R^2) and the root mean square error (RMSE) were estimated by the difference between QM (MP2) and MM (revised GAFF) profiles.

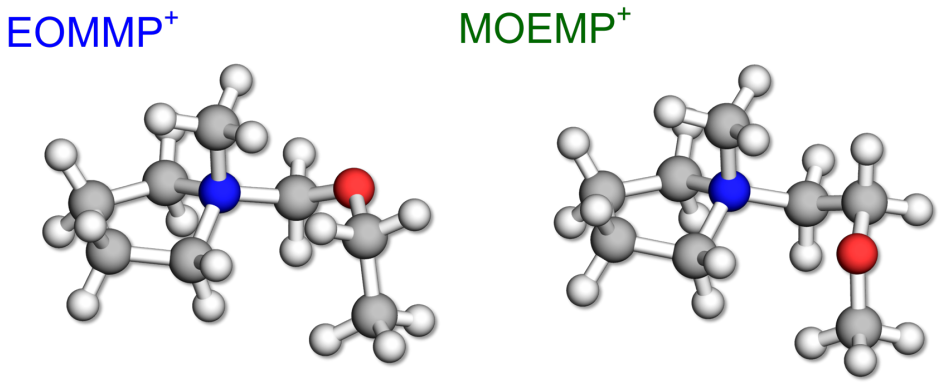

Figure S7. Optimized geometries of $EOMMP^+$ and $MOEMP^+$ at MP2/6-31G(d) level when the dihedral angles Φ are fixed to 60°.

Table S1. Fitting parameter for the density of the pyrrolidinium-based RTILs.

RTILs	a / g cm^{-3}	b / g cm^{-3} K^{-1}	R^2
MPPTFSA	1.695	8.942×10^{-4}	0.99
BMPTFSA	1.656	8.758×10^{-4}	0.99
MOMPTFSA	1.769	9.611×10^{-4}	0.99
EOMMPTFSA	1.719	9.492×10^{-4}	0.99
MOEMPTFSA	1.732	9.328×10^{-4}	0.99

Table S2. Fitting parameter for the viscosity of the pyrrolidinium-based RTILs.

RTILs	η_0 / mPa s	$E_a(\eta)$ / kJ mol^{-1}	R^2
MPPTFSA	5.2×10^3	23	0.99
BMPTFSA	5.9×10^3	25	0.99
MOMPTFSA	4.2×10^3	20	0.99
EOMMPTFSA	4.1×10^3	19	0.99
MOEMPTFSA	5.3×10^3	23	0.99

Table S3. Fitting parameter for the ionic conductivity of the pyrrolidinium-based RTILs.

RTILs	κ_0 / mS cm^{-1}	$E_a(\kappa)$ / kJ mol^{-1}	R^2
MPPTFSA	1.2×10^{-4}	25	0.99
BMPTFSA	1.3×10^{-4}	29	0.99
MOMPTFSA	1.0×10^{-4}	21	0.99
EOMMPTFSA	1.1×10^{-4}	23	0.99
MOEMPTFSA	1.2×10^{-4}	27	0.99

Table S4. Cathodic decomposition potentials at 298 K and calculated LUMO energies of cations.

RTILs	$E_{cathode}$ vs. Ag|Ag(I) / V[a)]	E_{LUMO} / eV[b)]
MPPTFSA	−3.07	−0.23
MOMMPTFSA	−3.00	−0.22
BMPTFSA	−3.21	−0.19
EOMMPTFSA	−3.04	−0.17
MOEMPTFSA	−2.52	−0.15

a) The value indicates the potential that –0.1 mA cm^{-2} of current density was observed, respectively.

b) LUMO energy of cation calculated with the MP2/6-311G(d,p) level using Gaussian09 program.

Table X1 Revised general AMBER force field parameters (non-bonded term) for MPP^+

Atom label[a]	Atom type	RESP charge	Van der Waals parameter	
		0.8*q (e)	σ (Å)	ε (kJ mol^{-1})
C1	c3	-0.0378	3.40	0.458
H1	hx	0.0790	1.96	0.066
H2	hx	0.0790	1.96	0.066
C2	c3	-0.0339	3.40	0.458
H3	hc	0.0508	2.65	0.066
H4	hc	0.0508	2.65	0.066
C1	c3	-0.0339	3.40	0.458
H5	hc	0.0508	2.65	0.066
H6	hc	0.0508	2.65	0.066
C4	c3	-0.0378	3.40	0.458
H7	hx	0.0790	1.96	0.066
H8	hx	0.0790	1.96	0.066
N1	n4	0.1449	3.25	0.711
C5	c3	-0.2883	3.40	0.458
H9	hx	0.1359	1.96	0.066
H10	hx	0.1359	1.96	0.066
H11	hx	0.1359	1.96	0.066
C6	c3	-0.2107	3.40	0.458
H12	hx	0.1056	1.96	0.066
H13	hx	0.1056	1.96	0.066
C7	c3	0.1629	3.40	0.458
H14	hc	0.0032	2.65	0.066
H15	hc	0.0032	2.65	0.066
C8	c3	-0.2417	3.40	0.458
H16	hc	0.0773	2.65	0.066
H17	hc	0.0773	2.65	0.066
H18	hc	0.0773	2.65	0.066

[a] Atomic labelling scheme is shown below:

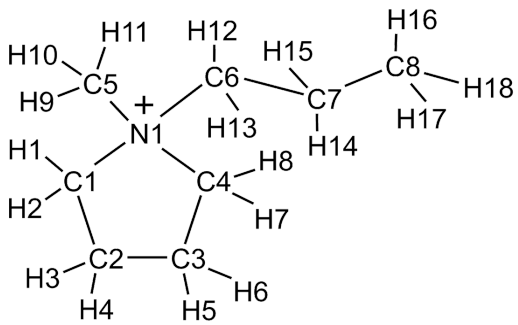

Table X2 Revised general AMBER force field parameters (non-bonded term) for $MOMMP^+$

Atom label[a]	Atom type	RESP charge	Van der Waals parameter	
		0.8*q (e)	σ (Å)	ε (kJ mol^{-1})
C1	c3	-0.0297	3.40	0.458
H1	hx	0.0801	1.96	0.066
H2	hx	0.0801	1.96	0.066
C3	c3	-0.0301	3.40	0.458
H5	hc	0.0502	2.65	0.066
H6	hc	0.0502	2.65	0.066
C2	c3	-0.0301	3.40	0.458
H3	hc	0.0502	2.65	0.066
H4	hc	0.0502	2.65	0.066
C4	c3	-0.0297	3.40	0.458
H7	hx	0.0801	1.96	0.066
H8	hx	0.0801	1.96	0.066
N1	n4	0.0938	3.25	0.711
C5	c3	-0.2514	3.40	0.458
H9	hx	0.1317	1.96	0.066
H10	hx	0.1317	1.96	0.066
H11	hx	0.1317	1.96	0.066
C6	c3	-0.0065	3.40	0.458
H12	hx	0.0922	1.96	0.066
H13	hx	0.0922	1.96	0.066
O1	os	-0.2154	3.00	0.711
C7	c3	-0.0713	3.40	0.458
H14	h1	0.0899	2.47	0.066
H15	h1	0.0899	2.47	0.066
H16	h1	0.0899	2.47	0.066

[a] Atomic labelling scheme is shown below:

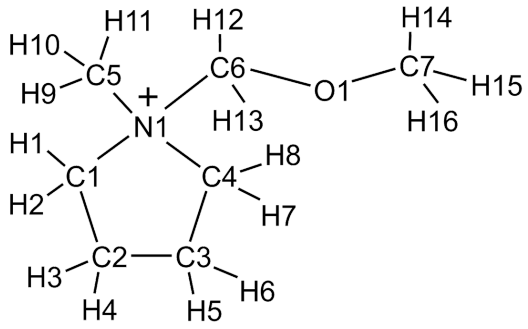

Table X3 Revised general AMBER force field parameters (non-bonded term) for BMP^+

Atom label[a]	Atom type	RESP charge	Van der Waals parameter	
		0.8*q (e)	σ (Å)	ε (kJ mol^{-1})
C1	c3	-0.0552	3.40	0.458
H1	hx	0.0777	1.96	0.066
H2	hx	0.0777	1.96	0.066
C3	c3	-0.0405	3.40	0.458
H5	hc	0.0520	2.65	0.066
H6	hc	0.0520	2.65	0.066
C2	c3	-0.0405	3.40	0.458
H3	hc	0.0520	2.65	0.066
H4	hc	0.0520	2.65	0.066
C4	c3	-0.0552	3.40	0.458
H7	hx	0.0777	1.96	0.066
H8	hx	0.0777	1.96	0.066
N1	n4	0.2532	3.25	0.711
C5	c3	-0.3186	3.40	0.458
H9	hx	0.1372	1.96	0.066
H10	hx	0.1372	1.96	0.066
H11	hx	0.1372	1.96	0.066
C6	c3	-0.1835	3.40	0.458
H12	hx	0.0847	1.96	0.066
H13	hx	0.0847	1.96	0.066
C7	c3	0.0189	3.40	0.458
H14	hc	0.0199	2.65	0.066
H15	hc	0.0199	2.65	0.066
C8	c3	0.0675	3.40	0.458
H16	hc	0.0183	2.65	0.066
H17	hc	0.0183	2.65	0.066
C9	c3	-0.2230	3.40	0.458
H18	hc	0.0669	2.65	0.066
H19	hc	0.0669	2.65	0.066
H20	hc	0.0669	2.65	0.066

[a] Atomic labelling scheme is shown below:

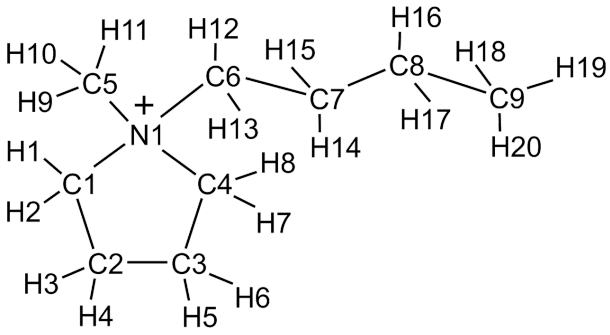

Table X4 Revised general AMBER force field parameters (non-bonded term) for $EOMMP^+$

Atom label[a]	Atom type	RESP charge	Van der Waals parameter	
		0.8*q (e)	σ (Å)	ε (kJ mol^{-1})
C1	c3	-0.0407	3.40	0.458
H1	hx	0.0796	1.96	0.066
H2	hx	0.0796	1.96	0.066
C3	c3	-0.0313	3.40	0.458
H5	hc	0.0495	2.65	0.066
H6	hc	0.0495	2.65	0.066
C2	c3	-0.0313	3.40	0.458
H3	hc	0.0495	2.65	0.066
H4	hc	0.0495	2.65	0.066
C4	c3	-0.0407	3.40	0.458
H7	hx	0.0796	1.96	0.066
H8	hx	0.0796	1.96	0.066
N1	n4	0.1784	3.25	0.711
C5	c3	-0.2663	3.40	0.458
H9	hx	0.1310	1.96	0.066
H10	hx	0.1310	1.96	0.066
H11	hx	0.1310	1.96	0.066
C6	c3	-0.1115	3.40	0.458
H12	hx	0.1087	1.96	0.066
H13	hx	0.1087	1.96	0.066
O1	os	-0.2277	3.00	0.711
C7	c3	0.1432	3.40	0.458
H14	h1	0.0494	2.47	0.066
H15	h1	0.0494	2.47	0.066
C8	c3	-0.2605	3.40	0.458
H16	hc	0.0876	2.65	0.066
H17	hc	0.0876	2.65	0.066
H18	hc	0.0876	2.65	0.066

[a] Atomic labelling scheme is shown below:

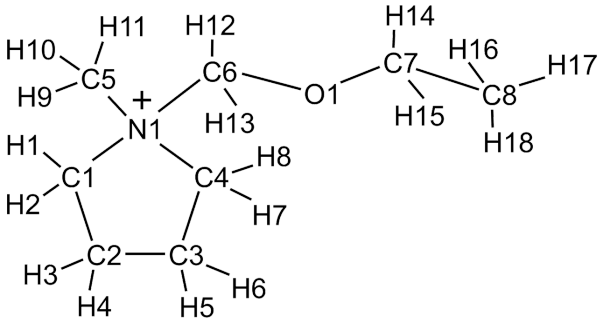

Table X5 Revised general AMBER force field parameters (non-bonded term) for $MOEMP^+$

Atom label[a]	Atom type	RESP charge	Van der Waals parameter	
		0.8*q (e)	σ (Å)	ε (kJ mol^{-1})
C1	c3	-0.0572	3.40	0.458
H1	hx	0.0776	1.96	0.066
H2	hx	0.0776	1.96	0.066
C3	c3	-0.0404	3.40	0.458
H5	hc	0.0529	2.65	0.066
H6	hc	0.0529	2.65	0.066
C2	c3	-0.0404	3.40	0.458
H3	hc	0.0529	2.65	0.066
H4	hc	0.0529	2.65	0.066
C4	c3	-0.0572	3.40	0.458
H7	hx	0.0776	1.96	0.066
H8	hx	0.0776	1.96	0.066
N1	n4	0.2434	3.25	0.711
C5	c3	-0.3171	3.40	0.458
H9	hx	0.1357	1.96	0.066
H10	hx	0.1357	1.96	0.066
H11	hx	0.1357	1.96	0.066
C6	c3	-0.0865	3.40	0.458
H12	hx	0.0748	1.96	0.066
H13	hx	0.0748	1.96	0.066
C7	c3	0.1530	3.40	0.458
H14	h1	0.0128	2.47	0.066
H15	h1	0.0128	2.47	0.066
O1	os	-0.2941	3.00	0.711
C8	c3	-0.0004	3.40	0.458
H16	h1	0.0642	2.47	0.066
H17	h1	0.0642	2.47	0.066
H18	h1	0.0642	2.47	0.066

[a] Atomic labelling scheme is shown below:

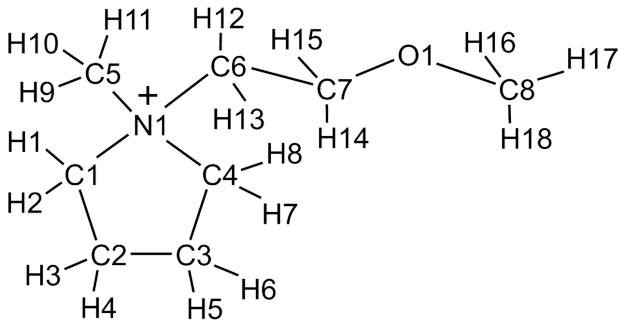

Table X6 Revised general AMBER force field parameters (torsion term) for cations.

Torsion angle	Dihedral parameter			
	No. of paths[a]	Magnitude of torsion $V_n/2$ (kJ mol^{-1})	Phase offset γ (deg.)	Periodicity of the torsion n[b]
hx-c3-n4-c3	1	0.837	0.0	3
c3-n4-c3-c3	1	0.107	180.0	-1
c3-n4-c3-c3	1	-0.115	0.0	-2
c3-n4-c3-c3	1	0.906	0.0	3
n4-c3-c3-c3	1	0.793	0.0	-1
n4-c3-c3-c3	1	-1.543	180.0	-2
n4-c3-c3-c3	1	1.236	0.0	3
c3-c3-c3-c3	1	-2.648	180.0	-1
c3-c3-c3-c3	1	-0.878	180.0	-2
c3-c3-c3-c3	1	0.468	0.0	3
n4-c3-os-c3	1	2.764	0.0	-1
n4-c3-os-c3	1	-8.253	180.0	-2
n4-c3-os-c3	1	2.013	0.0	3
n4-c3-c3-os	1	0.902	180.0	-1
n4-c3-c3-os	1	3.571	0.0	-2
n4-c3-c3-os	1	-1.351	180.0	-3
n4-c3-c3-os	1	1.124	0.0	4
c3-os-c3-c3	1	-0.604	0.0	-1
c3-os-c3-c3	1	0.995	180.0	-2
c3-os-c3-c3	1	0.547	0.0	3

[a] Number of bond paths that the total $V_n/2$ is divided into.

[b] Negative value is not used in the computation but signifies more than one component around a given bond.