Dependence of the Conformational Isomerism in 1-*n*-Butyl-3-methylimidazolium Ionic Liquids on the Nature of the Halide Anion

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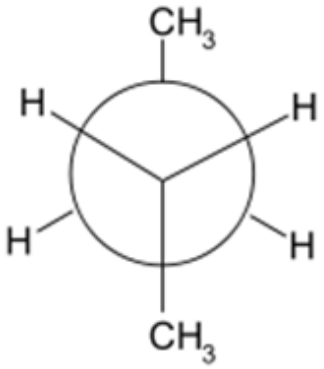
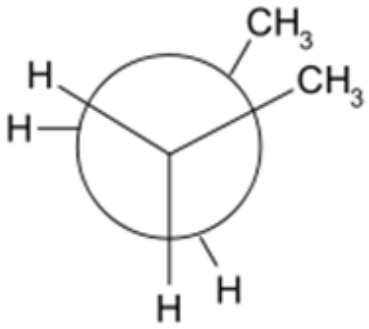
Molecular Conformation

dihedral angle:

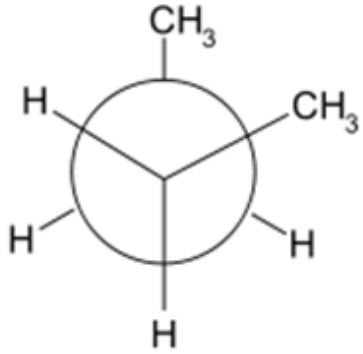
180°

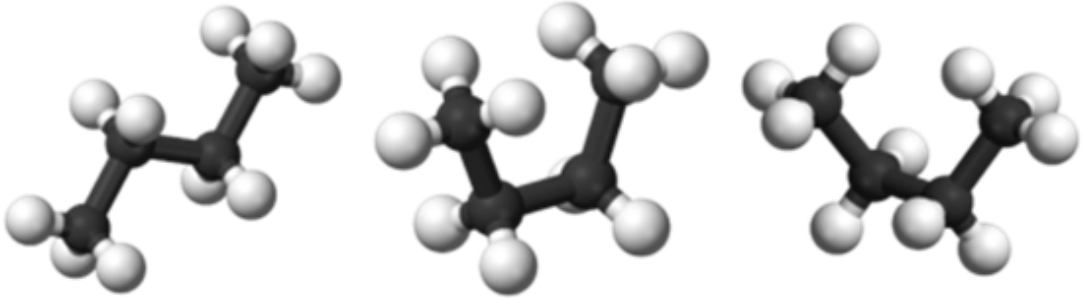


0°

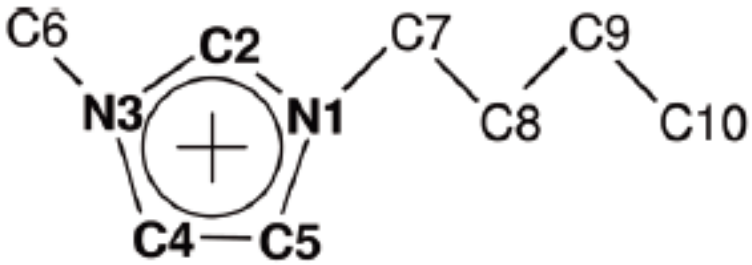


60°

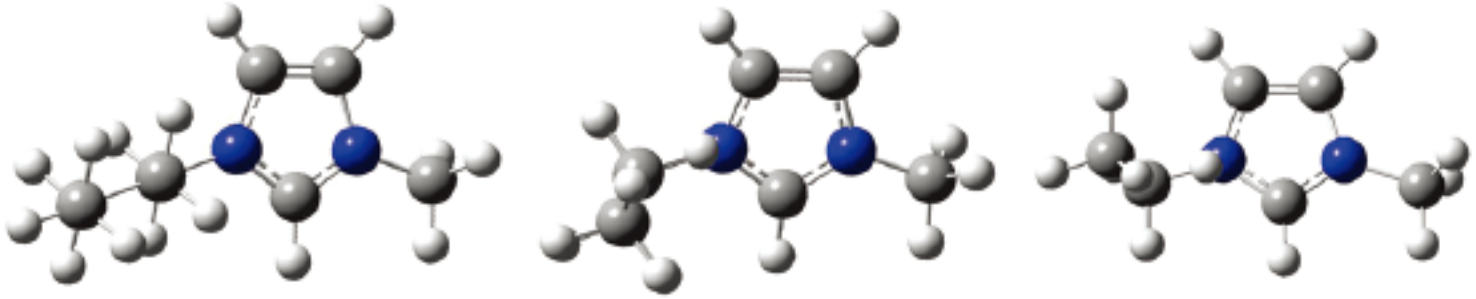




Trans **Eclipsed** **Gauche**



1-*n*-butyl-3-methylimidazolium (C_4mim^+)

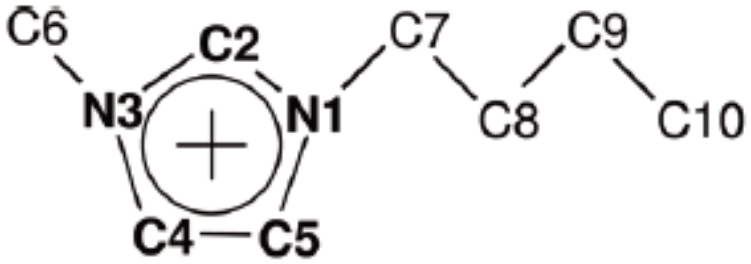


TT *GT* *G'T*

With respect to the N1-C7-C8-C9 and C7-C8-C9-C10 dihedral angle, yielding TT (T-trans) and GT or G'T (G, G'-gauche) isomers

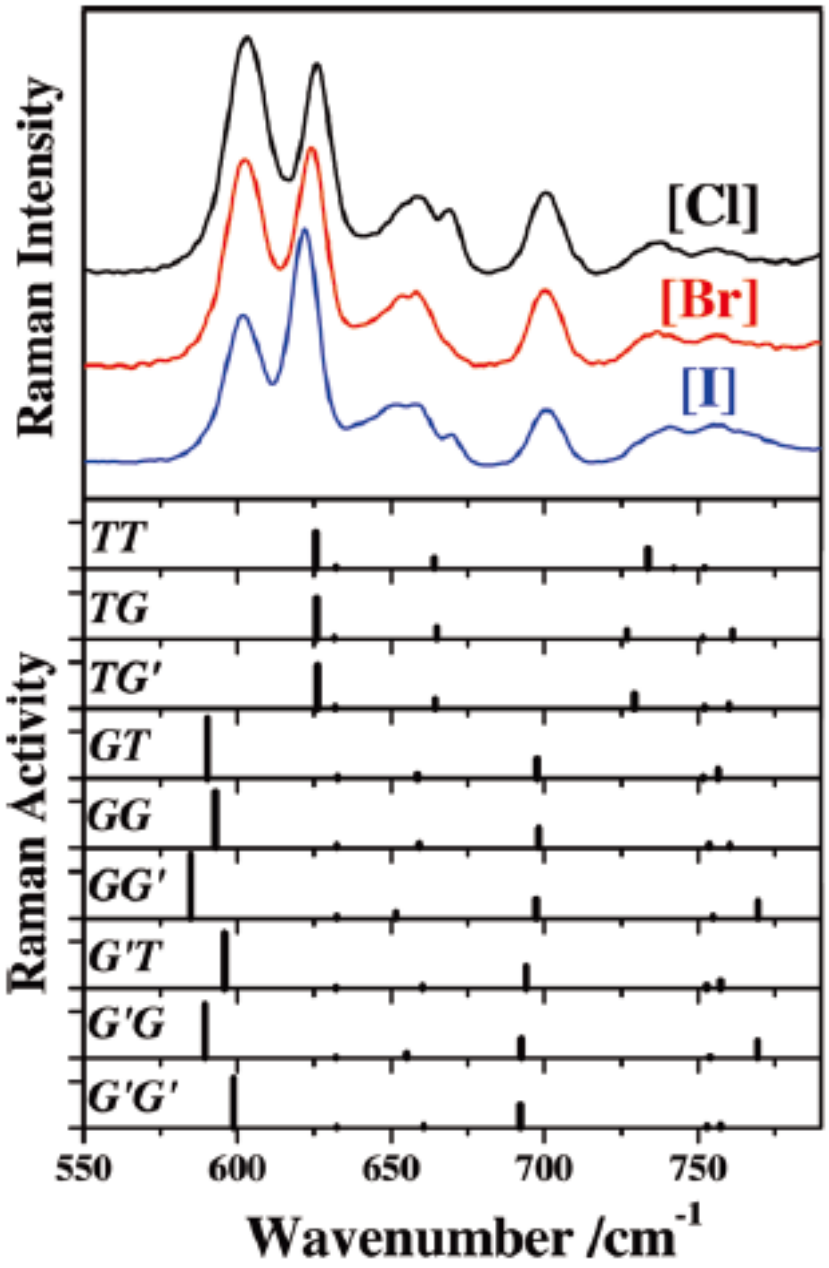
G — dihedral angle is 60°

G' — dihedral angle is –60°



Because the gauche conformation has its mirror image (e.g. G=60° and G'=–60°), when this analysis is applied to the two dihedral angle N1-C7-C8-C9 and C7-C8-C9-C10, nine possible conformers are generated:

TT, TG, TG', GT, GG, GG', G'T, G'G, G'G'



Around 625 cm^{-1}, correspond to trans isomers, such as TT, TG and TG'

Around 600 cm^{-1} correspond to gauche isomers, such as GG, GG', G'G', G'G, GT, G'T

As the halide ionic radius decreases, bands at 600 cm^{-1} increases, while band at 624 cm^{-1} decreases, indicates the gauche isomers prefer a stronger, more localized, negative electrostatic field formed by smaller anions

Thermodynamic Parameters calculated by Raman spectra

$$K_{iso} = c_B / c_A \quad (1)$$

$$\Delta_{iso} G^0 = -RT \ln K_{iso} = -RT \ln(c_B / c_A) \quad (2)$$

$$I = Jc \quad (3)$$

$$-RT \ln(I_B / I_A) = \Delta_{iso} H^0 / T - \Delta_{iso} S^0 - R(J_B / J_A) \quad (4)$$

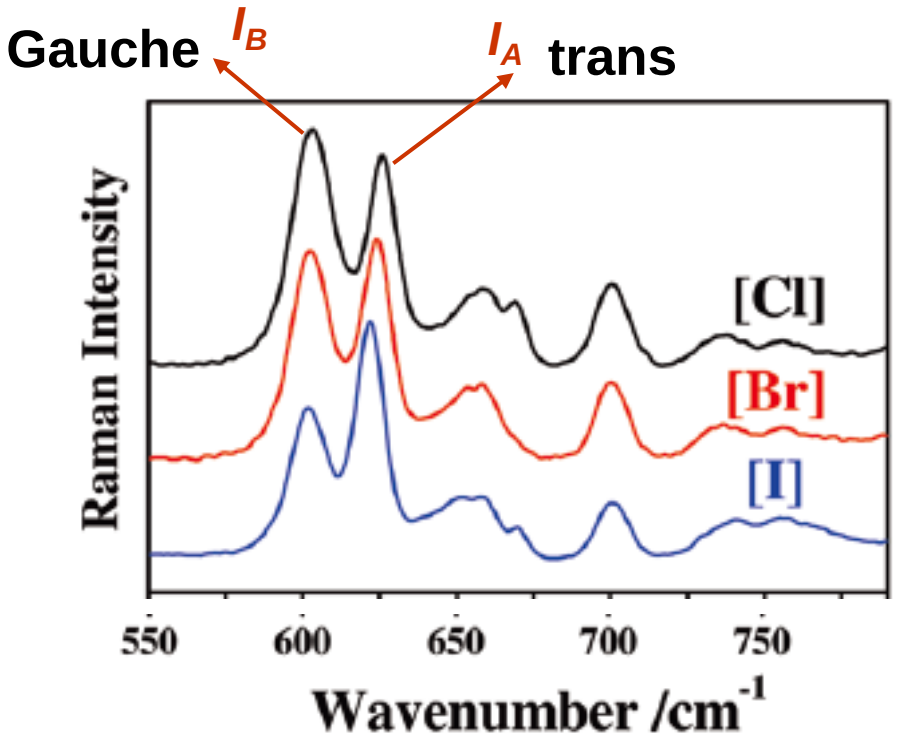
$$\Delta_{iso} G^0 = \Delta_{iso} H^0 - T \Delta_{iso} S^0 \quad (5)$$

k_{iso} — equilibrium constant

c_A, c_B — concentration of each isomer

I_A,I_B — Raman band intensity for A and B isomers

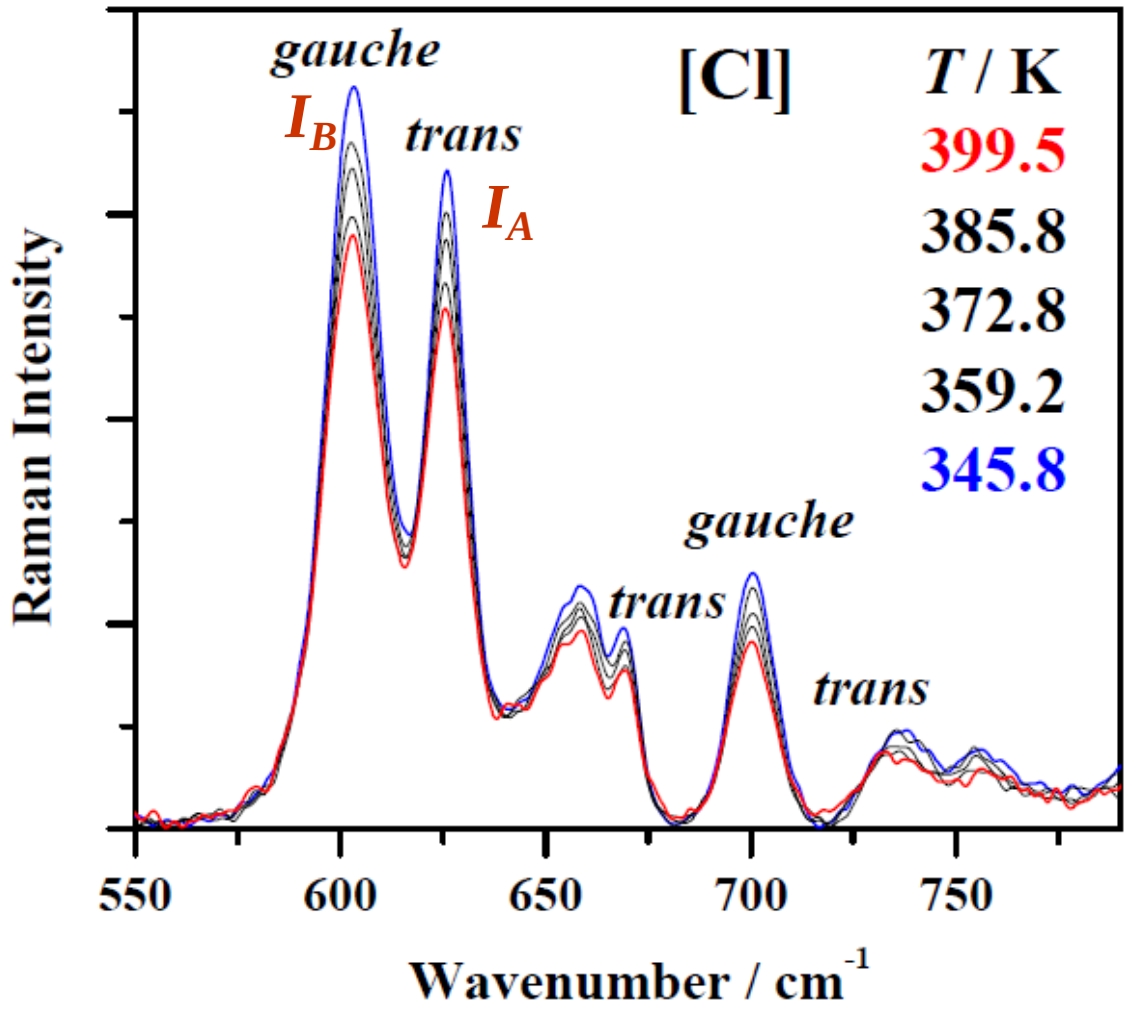
J_A, J_B — Raman scattering coefficient for A and B isomers



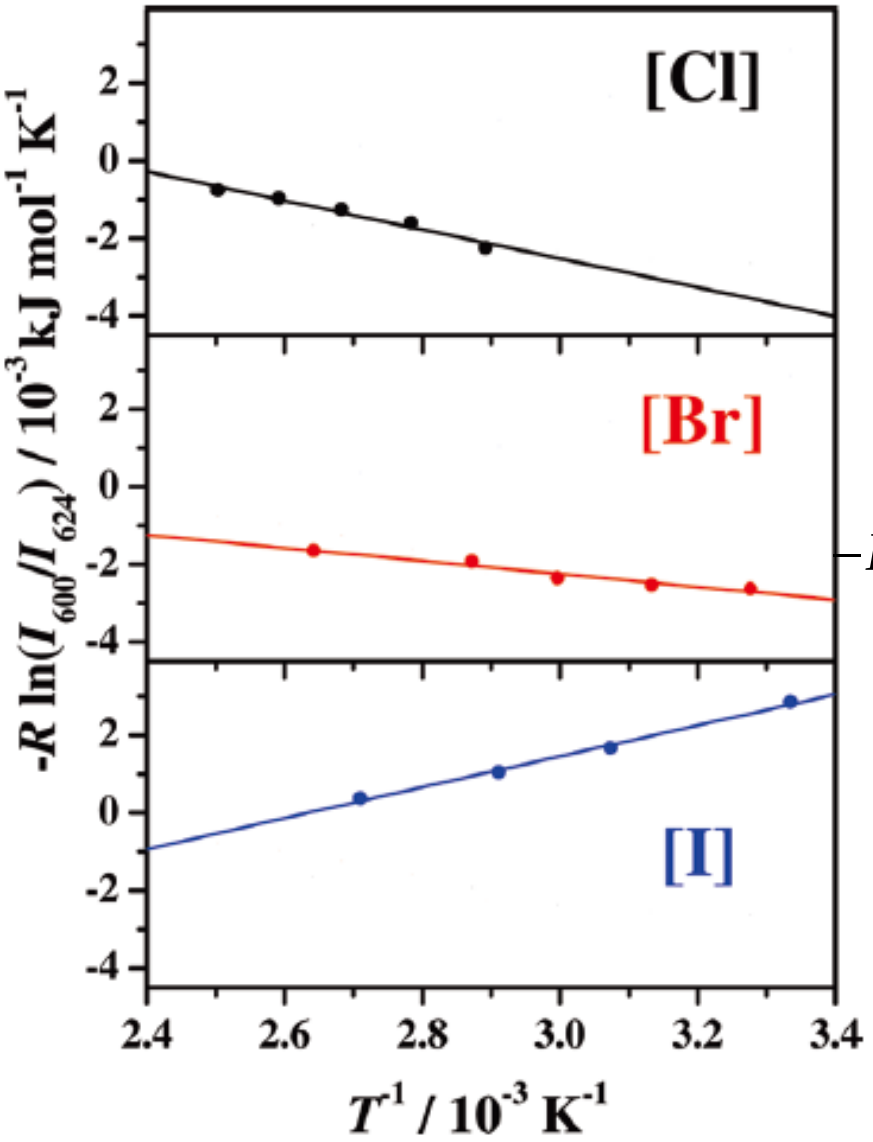
Bands at 600 and 625 cm^{-1} should reflect the relative amounts of the corresponding isomers, and thus allow calculation of the Gibbs free energy of the isomerization process, the intensity can be recognized as I_B and I_A.

$$[A] \longrightarrow [B]$$

trans **gauche**



$$-RT\ln(I_B / I_A) = \Delta_{iso}H^0 / T - \Delta_{iso}S^0 - R(J_B / J_A)$$



$\Delta_{iso}H$ are negative for both bmimCl and bmimBr, but positive for bmimI

$$-RT\ln(I_B/I_A) = \Delta_{iso}H^0/T - \Delta_{iso}S^0 - R(J_B/J_A)$$

$$\Delta_{iso}G^0 = \Delta_{iso}H^0 - T\Delta_{iso}S^0$$

TABLE 1: Gibbs Free Energy $\Delta_{iso}G^{\circ}$, Enthalpy $\Delta_{iso}H^{\circ}$, and Temperature Multiplied Entropy $T\Delta_{iso}S^{\circ}$ for the *TT* to *GT* (or *G′T*) Isomerization Process at 298 K

	[C_4mim][Cl]		[C_4mim][Br]		[C_4mim][I]	
	Raman	MD	Raman	MD	Raman	MD
$\Delta_{iso}G^{\circ}$/kJ mol^{-1}	0.0(5)	−3.1(3)	0.3(2)	−2.3(3)	2.0(2)	2.4(1)
$\Delta_{iso}H^{\circ}$/kJ mol^{-1}	−3.7(4)	−2.8(2)	−1.6(2)	−2.3(3))	3.9(2)	0.4(1)
$T\Delta_{iso}S^{\circ}$/kJ mol^{-1}	−3.6(3)	0.2(2)	−2.0(2)	0.1(1)	1.9(2)	0.0(0)

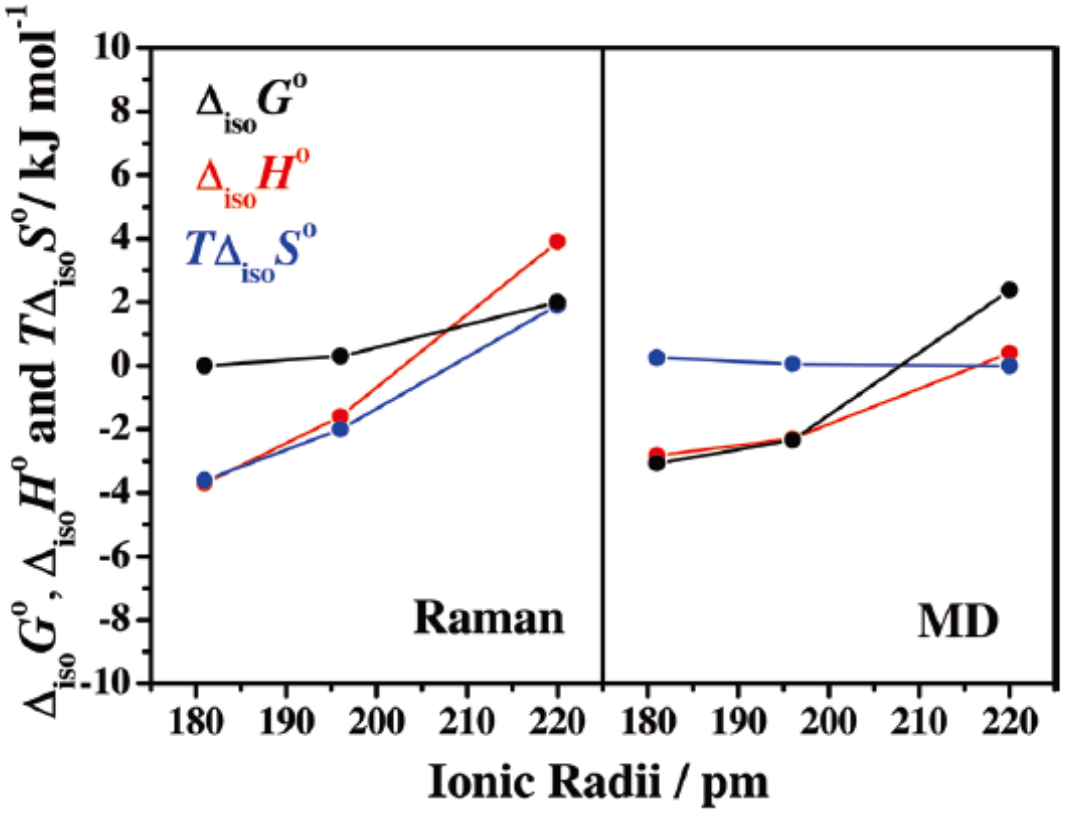
$$[A] \longrightarrow [B]$$

trans **gauche**

$\Delta_{iso}G^{\circ} < 0$ favoured reaction(Spontaneous)

$\Delta_{iso}G^{\circ} = 0$ Neither the forward nor the reverse reaction prevails (Equilibrium)

$\Delta_{iso}G^{\circ} > 0$ disfavoured reaction(Nonspontaneous)



- Δ_{iso}G are close to zero, indicates the trans and gauche isomers coexist in the ionic liquid

- Δ_{iso}G becomes more negative with the decrease of the halide ionic radius, indicates **the gauche isomers are more stable than trans isomers in the existence of smaller halide ions.**