Thermodynamic properties for liquid, glass and crystalline states of 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C₆mim][NTf₂]) are reported in a range of temperatures from (5 to 370) K, based on new measurements by adiabatic calorimetry. Mole fraction purities of the samples were determined to be 0.9976 and 0.9942 from fractional-melting experiments. The triple point temperature 272.03 K and the glass transition temperature 184.3 K were observed. It was found that [C₆mim][NTf₂] forms three crystalline phases, α, β, and γ, depending on heating and cooling steps taken. Heat capacities of the crystalline phases differ by <2 % in the temperature range (220 to 260) K, while they are nearly identical below 210 K. The enthalpy of fusion ΔₙαH = 28.09 +/- 0.08 kJ/mol was measured for the α crystal which had the highest heat capacity. For the two other crystals (β and γ) the enthalpies of fusion were both nearly identical to that of the α crystal. The heat-capacity jump at the glass transition was observed to be 171 +/- 3 J/K/mol, and the residual entropy was 755.8 +/- 3.2 J/K/mol. The temperature dependence of vapor pressure for [C₆mim][NTf₂] was determined by an effusion experiment in a range of temperatures from (446 to 494) K. An analysis of the vapor pressure measurements resulted in a calculated enthalpy of vaporization (at 462 K) of 123.4 kJ/mol, and a standard entropy change of 139.5 J/K/mol. By combining the entropy of vaporization with liquid entropy, the entropy in the ideal-gas state was calculated to be 1193 J/K/mol at 462 K.

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