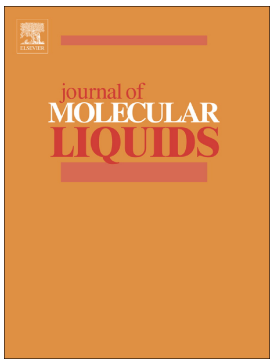

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Quantum Chemical Analysis of Electronic Structure and Bonding Aspects of Choline Based Ionic Liquids

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Abstract:

The gas phase quantum chemical calculation using M06-2X/6-31+G(d,p) level was carried out to understand the electronic structure and weak interactions of choline based ionic liquids (CILs; Cations: choline & N,N-dimethylaminoethanol (DMAE). Anions: Cl^-, HSO_4^- & $H_2PO_4^-$). Based on the MESP analysis, 24 different conformers were generated by arranging anions around cations in "chemically intuitive" locations where the proximity of multiple interaction pattern occurs. Investigation of optimized geometries of CILs illustrates that the presence of folded conformation in choline cation increases the stability of the most stable R1 conformers through strong O/N-H···O hydrogen bonding interactions. Computed interaction energies of ionic pairs were correlated well with the multiple interaction patterns existing in the ionic pairs. Based on the computed interaction energies, the stability order of CILs is as follows: **CS** < **CC** < **CP** < **NP** < **NS** < **NC**. The higher stability of **NC** ion pair is mainly due to the presence of both strong N-H···O and O-H···O hydrogen bonding interactions and higher proximity of folded conformation. The cooperative behavior of CILs is analyzed through the magnitude of red shifting and nature of IR intensity of vibrational bands. The Bader's QTAIM and NCI-RDG analyses were utilized to quantify the nature of non-covalent interactions present in CILs. Our NBO analysis clearly explained the presence of $n_{O/Cl^-} \rightarrow \sigma^*_{O-H}$ interactions in the most stable CIL ion pairs and good correlation is obtained between the hydrogen bond lengths and the stabilization energies. Overall, the present study sheds light on the importance of choosing appropriate anion and cation in preparing task-specific nature of CILs to achieve the desired physicochemical properties.

Keywords: Ionic Liquids, Choline cation, N,N-dimethylaminoethanol (DMAE) cation, hydrogen bonding, task-specific and QTAIM.