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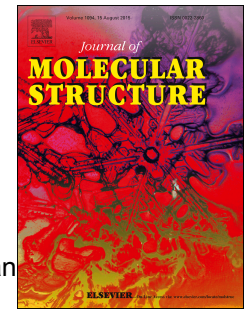

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DFT and Vibrational Spectroscopy study of 1-Butyl-3-methylimidazolium trifluoromethanesulfonate ionic liquid

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Abstract

Structural and vibrational characterizations for the 1-butyl-3-methylimidazolium trifluoromethanesulfonate ionic liquid ([BMIM][OTF]) were performed combining the experimental Raman spectrum with density functional theory (DFT) calculations based in the hybrid B3LYP/6-311++G** level of theory. Structurally, the trifluoromethanesulfonate anion, [OTF] is linked to 1-butyl-3-methylimidazolium cation, [BMIM] by a bidentate coordination by means of two different S-O---H hydrogen bonds. The [OTF] anion plays a very important role in the structure and stability of [BMIM][OTF], as observed by the strong increase in the dipole moment value when the anion is added to cation. Intramolecular H and halogen bonds evidence the high stability of ionic liquid, as supported by NBO and AIM calculations. Very good correlations were observed between the predicted infrared and Raman spectra with the corresponding experimental ones. The different Mulliken charges observed on the O atoms of O---H bonds support the asymmetric bidentate coordination of [OTF] anion with the [BMIM] cation. The [OTF] anion increase the reactivity of [BMIM][OTF], as compared with [BMIM][NO_3]. In addition, the [OTF] anion reduces drastically the electrophilicity and nucleophilicity indexes of cation evidencing the strong influence of anion on the properties of cation. The vibrational analyses have revealed a very important shifting of one of the two antisymmetric modes of [BMIM][OTF] towards lower wavenumbers due probably to an asymmetric of S=O---H bond interaction which is no observed in the anion. The complete vibrational assignments were performed for ionic liquid, cation and anion and the harmonic scaled force constants were reported at the same level of theory.

KEYWORDS: 1-butyl-3-methylimidazolium trifluoromethanesulfonate, vibrational spectra, conformations, molecular structure, descriptor properties, DFT calculations.

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