Crystal Structure and Theoretical Calculation of a Promising "Green" Solvent

Ebru Aktan[1], Melek Canbulat Özdemir[2], Ertan Şahin[3] and Beytiye Özgün[1]

[1]*Gazi University, Faculty of Science, Department of Chemistry, Ankara, Turkey*
[2]*Middle East Technical University,Faculty of Engineering, Department of Environmental Engineering, Ankara, Turkey.*
[3]*Atatürk University, Faculty of Science, Department of Chemistry, Erzurum, Turkey*

Corresponding Author: e-mail: ebruaktan@gazi.edu.tr

Introduction: Ionic liquids (ILs) are salts which contain organic cations and organic or inorganic anions. The unique properties of ILs such as very low vapor pressure, nonflammability, electrochemical and thermal stability have gained them promising applications in a wide variety of fields. They were used as environmental friendly solvents for reactions, catalysts for organic synthesis, electrolytes in dye sensitized solar cells and extracting agents. ILs are promising "green" solvents and they have several advantages compared to traditional organic solvents.

A series of phenyl/alkyl-substituted-3,5-dimethylpyrazolium ILs were synthesized and characterized by Özdemir and Özgün. The crystal structure of one of these ILs was obtained. In this study, we have characterized 1-phenyl-2,3,5-trimethylpyrazolium tetrafluoroborate, by X-ray diffraction techniques and calculated the optimized molecular geometry, vibrational wavenumbers and $^{1}H/^{13}C$ NMR chemical shift values.

Material and method: Diffraction data collections were performed on a Rigaku R-AXIS RAPID-S diffractometer using Mo Ka radiation ($\lambda = 0.71073$ Å) at T=294 K. Integration of the intensities, correction for Lorentz and polarization effects and cell refinement were performed using CrystalClear (Rigaku/MSC Inc., 2005) software. The structures were analyzed using a combination of direct and difference Fourier methods provided by SHELXS97 and were refined as full-matrix least squares against F2 using all data by SHELXL97 computer programs.

The molecular structure of the title molecule in the ground state is optimized by Density Functional Theory (DFT) using B3LYP/6-311G+(d,p) method. ^{1}H NMR and ^{13}C NMR chemical shifts were computed at the B3LYP and WP04 method using 6-311G++(2d,2p) basis set in the solvent $CDCl_3$ by applying GIAO approach.

Results: Crystal data and details of the structure determination for the studied IL are obtained experimentally by X-ray diffraction method and theoretically by DFT and compared with each other.

Discussion: It was observed that the calculated geometrical parameters are very compatible with X-ray diffraction results. The general agreement between experimental and calculated NMR chemical shift values are good. This study can provide useful information to understand and design of new IL compounds, which are eco-friendly.

Keywords: Ionic liquids, "Green" Solvent, Crystal structure, Geometry optimization, Density Functional Theory.