An ONIOM Study of a Guanidinium Salt Ionic Liquid. Experimental and Computational Characterization of *N*,*N*,*N*′,*N*′,*N*″-Pentabutyl-*N*″-benzylguanidinium Bromide

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Dedicated to Professor Gerhard Maas on the occasion of his 60th birthday

The guanidinium salt-based ionic liquid *N*,*N*,*N*′,*N*′,*N*″-pentabutyl-*N*″-benzyl-guanidinium bromide was synthesized and characterized by ^{1}H and ^{13}C NMR spectroscopy in solution and by single crystal X-ray structure analysis. The MO computational hybrid method of Morokuma and coworkers (ONIOM method) is applied to compare experimental and quantum chemical results. Four calculation models for two layer ONIOM calculations are defined based on differences of the area for the high-level layer region. Optimized geometries, interaction energies between the cation and the anion, and atomic charges are compared to data of full-QM calculations for the optimized geometry as well as of an experimental X-ray structure determination. The results indicate that it is mandatory for obtaining reasonable results that the parts of the substituent groups which are directly bound to the amino nitrogen atoms are included into the high-level layer. This least required ONIOM model for guanidinium-type ionic liquids can save computational cost of 90 % compared to the full-QM SCF calculation.

Key words: Guanidinium Salts, Ionic Liquids, X-Ray Crystallography, NMR Chemical Shift Calculations, ONIOM Calculations