160f Force Field Parameter Development for Pyridine, Pyrazine, Pyrimidine, Pyridazine and S-Triazene

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Molecules containing aromatic rings with one, two or three nitrogen atoms are commonly encountered in a diverse range of industrially important substances, such as insecticides, pharmaceuticals, and advanced optical materials. At the present time however force field parameters required for making accurate predictions of properties of these materials in the liquid, supercooled liquid and crystalline states (in the pure or mixed state) are rather limited. Of particular interest in our current force field-based simulations are chromphores containing the s-triazine moiety. However owing to limited experimental data and due to the fact that s-triazine itself is a crystalline solid at room temperature, melting around 354K, parameter development and validation are best carried out using related compounds containing aromatic rings with either one or two nitrogen atoms. Consequently we have undertaken a series of studies aimed at developing high level, condensed phase optimized parameters for this whole series of compounds, using the functional form employed by the successful COMPASS force field, which has previously been found to be capable of yielding predictions of properties such as PVT behavior and heats of vaporization with an accuracy comparable with experiment, over broad ranges of temperature and pressure.

As is customary in COMPASS parameterizations the approach begins with a series of ab initio calculations of optimized structures of the molecules of interest, supplemented by calculations on distorted structures selected to sample the energy surface of the isolated molecule. In addition, owing to the fact that these molecules tend to show quite pronounced shifts in electron density depending on atom environments, additional attention has been paid to correctly representing partial atomic charges. Having established charges and optimized the valence parameters using the ab initio data, we then conduct a series of refinements of the Lennard-Joned nonbonded interactions following standard COMPASS parameterization procedures, which require fitting of the density and heat of vaporization at a single state point (usually room temperature and atmospheric pressure). In this presentation, we will discuss the results of property predictions of the various compounds and related molecules, and will investigate the extent to which parameters can be transferred from the simpler to more complex compounds. Finally, we will conclude by illustrating property predictions when the force field is applied to a series of chromophores of interest.