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Triphenylguanidine Salts: Hydrogen bonding and NLO Properties.

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The calculation of the nonlinear optical (NLO) properties of solids using structural data has been stimulated by the increasing importance of the communications industry and the parallel need for materials having suitable properties. Classical molecular requirements for second-order NLO effects are strongly elongated and conjugated molecules, asymmetrized by interacting donor and acceptor groups. Although they often exhibit extremely large hyperpolarizabilities, some major drawbacks are associated with their dipolar character, e.g. a high tendency towards unfavourable aggregation and small off-diagonal tensor components. It was recognized that octupolar molecules can circumvent the aforementioned disadvantages, since these nonpolar molecules combine excellent (second-order) NLO characteristics with a strict cancellation of all vectorial properties [1].

Several salts have been prepared by acid-base reactions of triphenylguanidine with 1,2,4,5-benzenetetracarboxylic, cyanoacetic, diphenylacetic and trithiocyanuric acids, and their single-crystal X-ray structure analysis has been performed. Using the methodology that we have developed recently [2], we calculated the nonlinear susceptibility tensor components for the non-centrosymmetric salts. An Hirshfeld surface analysis [3] has been performed to study the effect of the various crystalline environments on the triphenylguanidinium cation, namely the effect of the hydrogen bonding motifs.

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CRAFT database for development and testing force fields.

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We collected a database of crystal structures and corresponding thermodynamic data at standard temperature for developing or testing various noncovalent force fields (FF). The FF must correctly predict the molecule-binding energy in crystals. The experimental energy of molecule binding in crystal is $\Delta U^{\exp}_{cryst-vap} = -\Delta H_{sub} - (2 + n_{rot}/2)\cdot RT$, where n_{rot} is the number of free rotational degrees of freedom in the molecule, and ΔH_{sub} is the crystal sublimation energy per molecule. The latter expression is more precise than the conventional (see e.g., [1]) $\Delta U^{\exp}_{cryst-vap} = -\Delta H_{sub} - 2\cdot RT$. The FF-calculated energy of molecule binding in crystal is a difference between the minimized crystal energy per molecule and the minimized energy of the separate molecule in vacuum, $\Delta U^{calc}_{cryst-vap} = U_{cryst} - U_{vap}$. The less is $\left|\Delta U^{calc}_{cryst-vap} - \Delta U^{\exp}_{cryst-vap}\right|$ and geometric deviations from experimental crystal structure, the better the FF. Minimization of these deviations gives interaction parameters for the "in-vacuum" FF of any functional form. In the same way one can calculate thermodynamic potential, which describes the mean-force energy difference between molecule in crystal and in water, $\Delta U^{\exp}_{cryst-aq} = \Delta U^{\exp}_{cryst-vap} - \Delta G_{sol}$, where $\Delta G_{sol} = -RT\ln k_H$ is the free energy of solution of the molecule in water expressed via experimental Henry's law constant, k_H. The potential $\Delta U^{\exp}_{cryst-aq}$ can be used for creating FF with implicit account of water environment [2]. We constructed a database that contains crystallographic structures and corresponding "in-vacuum" ($\Delta U^{\exp}_{cryst-vap}$) and "in-water" ($\Delta U^{\exp}_{cryst-aq}$) thermodynamic data extrapolated to a unified temperature (T=298K). Exploring of available thermodynamic and structural databases allowed us to collect the "in-vacuum" data for about a hundred and the "in-water" data for about sixty molecules. The resulting database CRAFT ("Crystals for Force Field Development and Testing") has been used for developing the empirical "in-water" force field FFSol [2] and testing the "in-vacuum" quantum-mechanical polarizable force field QMPFF3 [3]. This database is presented on the Internet page http://www.craftdb.info. It includes references to crystal structures (taken from the CSD database [4]), molecular properties (n_{rot}, etc.) and corresponding basic thermodynamic data (H_{sub}, k_H, etc.), as well as the resulting values $\Delta U_{cryst\text{-}vap}$, $\Delta U_{cryst\text{-}aq}$ at various conditions. Literature references are provided for all basic thermodynamic data, and the full path of calculation is provided for all calculated data. The major sources of data for sublimation enthalpy is the compilation of Chickos et al. [5] and for Henry's law constant the compilation of Sander [6].

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Structural study of five novel spiro-1,2-oxaphosphetanes.

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Carbonyl olefination of aldehydes and ketones by phosphorus ylides, the Wittig reaction [1], is a reference synthetic method for the regio- and stereodefined construction of carbon-carbon double bonds [2]. Despite being intensively studied for almost 60 years, the mechanism of this basic transformation in organic synthesis is still under debate. Most investigations