Benzene quadrupolarity and arene-arene interactions

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We are interested in employing benzenes as lateral synthons in crystal engineering. We recently synthesized a series of perfectly dipole-aligned crystals [1] (Figure 1). Such crystals are important in developing high performance organic NLO crystals. The benzene-benzene T-contact plays a critical role in stabilizing the crystal energy [2].

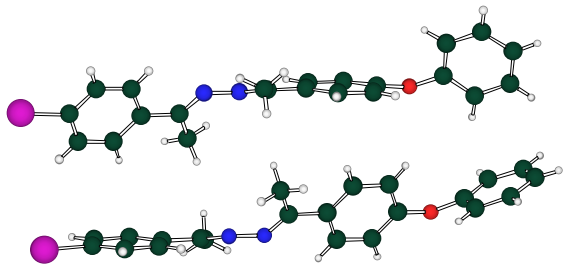

Figure 1. Triple T-contacts in phenoxy-iodo substituted azine crystal

This study focuses on the benzene-benzene intermolecular interaction. We studied the quadrupole-quadrupole interaction and Coulomb interaction of benzene dimer. The quadrupole moment tensor components are calculated using restricted Hartree-Fock theory, RHF, second-order perturbation theory, MP2(full), quadratic CI theory, QCISD, and density functional theory. These levels were employed in conjunction with double- and triple-ξ basis sets. The largest basis set employed is the cc-pVDZ++ basis set. Electron correlation always decreases the independent traceless quadrupole moment Θ_{zz}. It is shown that the quadrupole-quadrupole interaction contributes significantly to arene-arene interactions. Several point charge models of benzene were explored to study the Coulomb interaction of benzene dimer. The model with charges derived from MP2 NBO analysis reproduces the order of experimental benzene dimer binding energy but not the benzene quadrupole moment. The other models reproduce the benzene quadrupole moment but the interaction energies are too large compared with the experimental benzene dimer binding energy. Structures and approaches toward a model that reproduces both the quadrupole moment and the experimental benzene dimer binding energy are being explored.

References:

[1] M. Lewis and R. Glaser, unpublished results.
[2] Lewis, M.; Wu, Z.; Glaser R. *Arene-Arene Double T-Contacts. Lateral Synthons in the Engineering of Highly Anisotropic Organic Molecular Crystals, Chapter 7 in Anisotropic Organic Materials – Approaches to Polar Order*, Rainer Glaser and Piotr Kaszynski, Editors. ACS Symposium Series, Volume 798. American Chemical Society: Washington, D.C., July **2001**.