

1.3 Crystal Packing Calculations on Nonlinear Optical Molecules

(G. Knöpfle)

The optimization of the nonlinear optical properties of organic molecules requires the optimization of both the nonlinear optical response of the molecules and the arrangement of the molecules in the crystals. However, since most organic substances crystallize centrosymmetrically, the search and optimization of organic crystals exhibiting large second-order nonlinear optical susceptibilities is a very time consuming procedure. This search could be made much more efficient if we were able to predict the structure and properties of an organic crystal from the structure and properties of its constituent molecules.

As a first step towards such a prediction, geometries of the nonlinear optical crystals 2-cyclooctylamino-5-nitropyridine (COANP) and 4-dimethylaminobenzaldehyde-4-nitrophenyl-hydrazone (DANPH) were calculated by minimization of the crystal lattice energy which is evaluated using the empirical atom-atom potential method. Although organic molecular crystals are held together mainly through Van der Waals forces, the inclusion of a special potential describing the hydrogen bond interaction is required in order to locate a potential energy minimum near the experimentally observed structure. Electrostatic interactions on the other hand are only of minor importance.

On the basis of this atom-atom potential method a general search procedure was applied to COANP and DANPH yielding the most closely packed structures for the most frequently populated space groups with only a limited amount of input information. The application of this search procedure showed that the experimentally observed crystal structure can be found with the molecular conformation the hydrogen bonding pattern and the "correct" space group as the only input information. In addition, however, different hypothetical structures with different space group symmetry can be obtained with densities and lattice energies that are very close to the corresponding values of the experimentally observed structure. These different structures often show very similar molecular packing motifs. This leads us to the conclusion that highly probable packing patterns can be predicted. The main problem is, however, that the same pattern can occur in different space groups yielding structures which are so close in energy that a final decision towards one of the competing arrangements cannot be made on the basis of the atom-atom potential method.