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Computational investigations of the influence of polymorphism on the lattice dynamics of molecular organic crystals

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The teraHertz range (60 GHz - 4 THz = 2-130 cm⁻¹) is a relatively unexplored, but information-rich part of the vibrational spectrum of molecular crystals. The motions in this frequency range are at lower energies than most of the internal vibrations of molecules (e.g., bond stretching and angle bending), but correspond instead to translations and librations of molecules. Thus, spectroscopic and computational investigations of this frequency range are a source of information on the intermolecular interactions in molecular crystals. Lattice dynamics calculations are being developed within the crystal structure modelling program DMAREL[1-2], for the use of elaborate model intermolecular potentials. Such calculations have been performed to characterise the measured teraHertz spectra of several molecular organic crystals, correlating regions of the spectra to distortions of certain intermolecular interactions. One of the systems studied is the polymorphic pharmaceutical molecule carbamazepine, whose basic hydrogen bonding - amide dimers - remains unchanged between polymorphs (Figure).

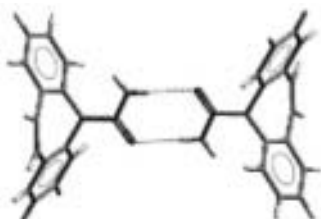


Figure. Hydrogen bonded dimer in the carbamazepine polymorphs.

The calculations show reasonable agreement with observation, providing a molecule level explanation for the observed differences in the spectra of the various polymorphs. An analysis is made of the different types of hydrogen bond vibrations in these dimers (stretching, bending and shearing) and how the energy of these vibrations is influenced by the packing and secondary interactions in the polymorphs. The interactions between aromatic rings in the molecules are found to have an important influence on the hydrogen bond vibrations.

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The packing of methoxy-substituted distyryl-benzenes: questions and answers

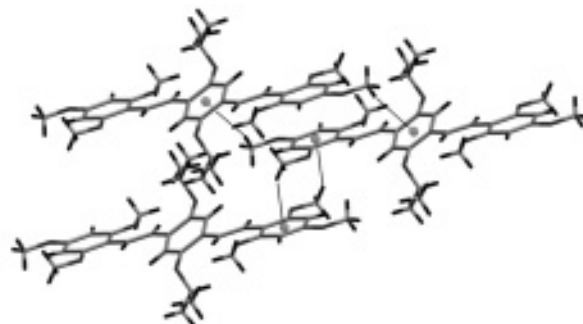
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Distyrylbenzenes can be considered "organic metals" since, when they are doped, they become semiconducting. These materials display a number of interesting properties, such as blue electroluminescence, and in their doped form, their resistance reacts to the atmosphere they are placed in, making them excellent candidates for active materials in an "electronic nose". Since we have been unable to crystallise the doped compounds up to now, we have focussed our attention on the native material to get an idea of the interactions that lead to the packing in the crystal (see Figure). It has become clear that a very large variation exists in how well the differently substituted compounds crystallise: some crystallise easily, while others do not crystallise at all. From a careful study of the packing of seven materials, combined with a literature survey, a set of rules could be deduced that explains the packing of methoxy-substituted distyrylbenzenes.

The relevant factors are (1) the volume of the side chain, since the molecules must form a lattice that can accommodate it without strain, and (2) the intermolecular interactions that are possible within this lattice. Two clearly discernible packing strategies exist for these materials, one of which involves CH-*n*(O) interactions between hydrogen atoms of methoxy group and oxygen atoms of another; the other involves -OCH₃ ... π interactions between a hydrogen atom of a methoxy group and the π -cloud of an aromatic ring.



We have been able to rationalise the seemingly random preference for one strategy over the other by taking intramolecular interactions into account. A macroscopic property, namely the melting point, could be linked with the observed structures for the compounds studied, providing evidence that it is indeed these interactions that are responsible for the observed structure.

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[4] Vande Velde, C.M.L., Geise, H.J. & Blockhuys, F. *Cryst. Growth Des.* 2006, 6, 241-246.