

04.5-3 STRUCTURE-ENERGY RELATIONSHIPS OF WERNER CLATHRATES. By L.R. Nassimbeni, D.R. Bond, M. Moore and S. Papanicolaou, Department of Physical Chemistry, University of Cape Town, Rondebosch, South Africa.

We have synthesised and determined the structures of a series of compounds of general formula:  $\text{Ni}(\text{NCS})_2(\text{C}_5\text{H}_4\text{NR})_2(\text{C}_5\text{H}_4\text{NR}^1)_2 \cdot n\text{G}$   $\text{C}_5\text{H}_4\text{NR}$  is a substituted pyridine and G is an organic guest molecule.

Cmpd	R	R <sup>1</sup>	n	Guest
1	R = 4-Me, R <sup>1</sup> = 4-Ph		1	CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OH
2	R = R <sup>1</sup> = 4-Me		1	p-cymene
3	R = R <sup>1</sup> = 4-Ph		4	DMSO
4	R = R <sup>1</sup> = 3-Me		1	CHCl <sub>3</sub>
5	R = R <sup>1</sup> = 4-Et		1	o-xylene
6	R = R <sup>1</sup> = 4-Et		1	m-xylene
7	R = R <sup>1</sup> = 4-Et		1	p-xylene
8	R = R <sup>1</sup> = 3,5-Me		-	-

Stoichiometric characterisation of the clathrates was determined by various techniques, including N.M.R., D.T.A. and T.G.A. Host-guest non bonded interactions were studied using atom-pair potentials and the movement of the guest molecules through channels was simulated.

#### 04.5-4 COMPUTATIONAL MODELING OF THE HIGH-PRESSURE STRUCTURE AND THE ELASTIC CONSTANTS OF $\beta\text{-Mg}_2\text{SiO}_4$ .

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Busing and Matsui (Acta Cryst. (1984) submitted) have recently developed a model for simulating crystal structures under hydrostatic pressures or normal and shearing stresses and a way of calculating elastic constants and their pressure derivatives. They have successively applied the method to  $\alpha$ - and  $\gamma$ - $\text{Mg}_2\text{SiO}_4$  and succeeded in reproducing both the experimental structures and the observed elastic properties reasonably well (Phys. Chem. Minerals (1984) submitted). In this paper we present the results for  $\beta\text{-Mg}_2\text{SiO}_4$ , which is an intermediate phase in the high-pressure transformation of  $\alpha\text{-Mg}_2\text{SiO}_4$  to  $\gamma\text{-Mg}_2\text{SiO}_4$ .

$\beta\text{-Mg}_2\text{SiO}_4$  is orthorhombic, space group Imma, consisting of  $\text{Mg}^{2+}$ ,  $\text{O}^{2-}$  and separate  $\text{Si}_2\text{O}_7^{6-}$  ions. The potential energy for our model includes Coulomb and repulsive interactions between non-bonded atoms and bond angle bending and bond distance stretching energy terms for the  $\text{Si}_2\text{O}_7^{6-}$  ions. The repulsive potentials used were the same as those for  $\alpha$ - and  $\gamma\text{-Mg}_2\text{SiO}_4$ . The net charges on the Si and O atoms in the  $\text{Si}_2\text{O}_7^{6-}$  ions and the covalent bond potentials were adjusted so as to reproduce both the experimental atmospheric-pressure structure and elastic constants well.

#### 04.5-5 A NEW SCHEME FOR MODELLING INTERMOLECULAR FORCES IN CRYSTAL STRUCTURES: A SIX-SITE TRANSFERABLE POTENTIAL SCHEME FOR THE AZABENZENE MOLECULES.

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Work on modelling intermolecular forces in molecular crystals has been dominated by the isotropic atom-atom potential, which assumes that the molecule is a superposition of spherical charge distributions. This is certainly a useful first approximation, but the model lacks the ability to improve on this assumed orientation dependence. We have recently developed a method of incorporating explicit orientation dependence into the site-site potential in a general and practically convenient form for packing analysis of molecular crystals.

This new approach has been applied to the azabenzene family, to account quantitatively for the wide variety in their crystal structures, in terms of the change in the intermolecular potential when a nitrogen atom is substituted for a CH group in the aromatic ring. The six-site potential model was of the form,

$$U(\mathbf{R}, \Omega) = \sum_{i,k} \exp[-\alpha_{ik}(\Omega_{ik})(R_{ik} - \rho_{ik}(\Omega_{ik}))] - A_{ik} A_{ik} / R_{ik}^6 + U_e$$

where atoms i and k are of type  $\iota$  or  $\kappa$  (C or N) respectively. A variety of different short anisotropic expansions for  $\alpha_{ik}(\Omega_{ik})$  and  $\rho_{ik}(\Omega_{ik})$  were investigated. The simple electrostatic model, and the justification for expecting the site-site potentials to be transferable, were derived from a distributed multipole analysis of the ab-initio (SCF) wavefunctions of the molecules. We found a very successful model which required specific forms of anisotropy in the repulsive potential, to represent the anisotropic effect of the bonded hydrogen atoms and the nitrogen lone pair electron density. The eleven potential parameters for the repulsion and dispersion interactions were obtained by fitting to the observed crystal structures of benzene, pyrazine, pyrimidine and s-tetrazine, and the resulting potential scheme could 'predict' the crystal structures of not only these molecules, but also pyridine and s-triazine, within a few percent.

These results can be compared with the recent work on these molecules by Williams and Weller (J. Amer. Chem. Soc. (1983) 105, 4143) which demonstrated that the traditional atom-atom approach is incapable of accounting for these crystal structures unless an extra charged site is added to represent the nitrogen lone pair. Thus both studies show that the anisotropic lone pair electron density has a major effect in determining these crystal structures. The new approach to modelling the intermolecular potentials of organic molecules can not only take lone pairs in its stride, but can very adequately account for a CH group as a single anisotropic unit. Its main attraction is in its flexibility, which will enable the accuracy of the potentials to be extended with our increasing knowledge of intermolecular interactions.