

PS11.07.18 INFLUENCE OF INTERMOLECULAR INTERACTIONS IN THE CRYSTAL PHASE ON CONFORMATION OF FLEXIBLE DI- AND TETRAHYDROPYRIMIDINE RINGS. O.V.Shishkin, V.I.Shil'nikov, A.N.Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow Russia

The molecular and crystal structures of derivatives of the 7-aryl-4,7-dihydro-1,2,3-triazolo[1,5-a]pyrimidine and 4-aryl-1,2,3,4-tetrahydro-2-thiopyrimidine which contain flexible six-membered rings have been studied. Results of calculations by AM1 method show that substituents in the phenyl rings do not influence on equilibrium conformation of the di- and tetrahydropyrimidine rings (boat and half-chair respectively). However, experimental data, especially for 4,7-dihydroazolopyrimidine derivatives, indicate considerable change of endocyclic torsion angles. In the case of the nitro group presence in the dihydropyrimidine ring a chair conformation of dihydrocycle has been found in the crystal phase unlike results of quantum-chemical calculations. All these effects can be explained only by differences of intermolecular interactions in the crystals. Analysis of the crystal packing showed that strengthening of some non-bonded interactions in the crystal (for example, hydrogen bond) causes a decrease of puckering of the pyrimidine ring. Dependence between energy of intermolecular interactions calculated by atom-atom potential method and magnitudes of torsion angles has been investigated. Analysis of the non-bonded interaction potential gradient agrees well with molecules deformation in the crystals as compared with the gas phase.

PS11.07.19 A SEMIEMPIRICAL QUANTUM CHEMICAL METHOD TO CALCULATE THE LATTICE ENERGIES OF ORGANIC MOLECULAR CRYSTALS. By Gerhard Raabe, Institut für Organische Chemie, RWTH Aachen, Prof.-Pirlet-Str. 1, D-52056 Aachen, Germany

A semiempirical quantum chemical method based on a perturbative approach [1] is presented which retains the original meaning of the contributions (dispersion, electrostatic, induction, and repulsion energy) to the lattice energy. These components are obtained using the results of the semiempirical MINDO/3 method [2]. Thus the dispersion energy is calculated by means of the London formula employing MINDO/3-FP [3] atom-in-molecule polarizabilities and vertical (Koopmans) ionization potentials. Only the Coulomb part of the electrostatic energy is considered employing MINDO/3 atomic charges which are also used together with the polarizabilities to obtain the induction energy. An approximate method is used to calculate the exchange repulsion energy which includes the repulsive part of the lattice energy via MINDO/3 molecular orbitals and overlap integrals.

Results obtained for several organic compounds including some polymorphs are presented. The choice of the molecular model is discussed, emphasizing the importance of a correct positioning of the hydrogen atoms.

[1] J. N. Murrell, M. Randic, D. R. Williams (1965). *Proc. Roy. Soc.*; **A284**, 566 - 581.

[2] R. C. Bingham, M. J. S. Dewar, D. H. Lo (1975). *J. Am. Chem. Soc.*; **97**, 1285 - 1293.

[3] R. M. Metzger (1981). *J. Chem. Phys.*; **74**, 3444 - 3457.

PS11.07.20 OPTICAL RESOLUTION OF DL-HISTIDINE THROUGH INTERACTIONS WITH A CHIRAL GLYCOLIC ACID. Stephen Suresh and M. Vijayan, Molecular Biophysics Unit, Indian Institute of Science, Bangalore 560 012, India

As part of a programme aimed at studying biologically and evolutionarily important interaction and aggregation patterns, crystals of DL-histidine glycolate and L-histidine glycolate were prepared and analyzed. Crystallization experiments involving DL-histidine and glycolic acid yielded in addition to DL-histidine glycolate, a conglomerate containing crystals of L-histidine glycolate and D-histidine glycolate in an unusual process of chiral separation through interaction with an achiral molecule. The crystal structure of DL-histidine glycolate is made up of alternating layers of unlike molecules as in many other binary complexes involving amino acids. The arrangement of molecules in the structure of L-histidine glycolate is almost identical to that in one of the forms of L-histidine acetate, thus providing another example for the invariance of certain aggregation patterns with respect to changes in the molecules involved. The structure involves packing of columns containing L-histidine molecules and glycolate ions tightly hydrogen bonded to one another. In fact, among the six hydrogen bonds in the structure, five are between unlike molecules within the column. Thus, the histidine-glycolate interactions are much stronger than histidine-histidine interactions, while glycolate-glycolate interactions are non-existent. This points to the high propensity for the occurrence of this type of aggregation involving chiral molecules in association with glycolate ions even in a solution containing molecules of both chiralities. Such aggregates might co-exist in high concentration with those involving both L and D histidine molecules and glycolate ions despite the entropic advantages the latter might have. The crystals obtained from the solution could then be those of L-histidine glycolate, D-histidine glycolate or DL-histidine glycolate, often leading to chiral separation. Thus the observed aggregation of molecules in the chiral complex also appears to provide a structural rationale for chiral separation of histidine in the presence of glycolic acid.

PS11.07.21 THE INFLUENCE OF CRYSTAL PACKING ON THE MOLECULAR STRUCTURE OF MAIN GROUP ELEMENT COMPOUNDS. Edward R.T. Tiekink and Mark A. Buntine Department of Chemistry, The University of Adelaide, Adelaide, S.A. 5005, AUSTRALIA

In a number of recent reviews it has been demonstrated that the molecular structure found in main group element compounds may be dependent on seemingly minor changes in chemistry [1]. Hence, different coordination geometries, coordination numbers or even stoichiometries may be found for compounds with very similar chemical formulae [1]. For example, consider the structures of $\text{Hg}(\text{S}_2\text{COR})_2$ [2]: when $\text{R} = \text{Me}$, a three coordinate T-shaped geometry is found for Hg in a linear polymeric array; for $\text{R} = \text{nPr}$, the Hg atoms are tetrahedral and the structure is comprised of two-dimensional sheets; when $\text{R} = \text{iPr}$, the Hg atoms are again tetrahedral, however, the structure is now a three-dimensional polymer. In the absence of obvious steric and/or electronic effects, it may be concluded that this phenomenon occurs as a result of crystal packing effects. Polymorphs provide an ideal opportunity to examine 'crystal packing' effects on molecular structure. Several organotin systems, including $\text{Ph}_2\text{Sn}(\text{bipy})\text{Cl}_2$ and $\text{Ph}_2\text{Sn}(\text{S}_2\text{CNEt}_2)_2$, which are known to crystallise as polymorphs have been subjected to *ab initio* molecular orbital calculations to investigate their preferred 'gas phase' geometries. Geometry optimisations at the Hartree Fock level of theory, using both the 3-21G and LanL2DZ basis sets, have shown that the distinct structural configurations exhibited by the crystalline polymorphs independently relax to an identical gas-phase geometry. It is

important to recognise that the use of two completely different types of basis set to describe these large organotin systems minimises errors associated with basis set-specific artifacts. The 3-21G basis set is a split valence descriptor, while the LanL2DZ basis set utilises a double zeta description for first row elements and an effective core potential (ECP) for heavier atoms. Calculated gas-phase stabilisation energies range from 400-1200 kJ mol⁻¹, depending on the system under study. More significantly, predicted stabilisation energies from each basis set description agree to within, at worst, 40 kJ mol⁻¹. Detailed results of this study will be presented.

[1] E.R.T. Tiekink: *Main Group Chemistry News*, **3**, 1995, 12 - 16; *Appl. Organomet. Chem.* **5**, 1991, 1 - 21; *Main Group Met. Chemistry*, **15**, 1992, 161 - 186; E.R.T. Tiekink and G. Winter: *Rev. Inorg. Chem.*, **12**, 1992, 183 - 302.

PS11.07.22 INFLUENCE OF FLUORO SUBSTITUTION ON PACKING OF STYRYLCOUMARINS AND THEIR PHOTOBHAVIOUR IN THE CRYSTALLINE STATE. K.

Vishnumurthy¹, K. Venkatesan¹ and T. N. Guru Row^{1,2}, ¹Department of Organic Chemistry, ²Solid State Structural Chemistry Unit Indian Institute of Science Bangalore 560 012, India

The correlation between reactive molecules in crystals and stereochemistry of the photoproducts has been a subject of intensive study(a). Crystals of styryl- coumarins and chloro - substituted derivatives yield centrosymmetric crystals leading to anti-HT photodimers. However, replacement of a hydrogen by fluorine as in 4-(4'-fluoro styryl) coumarin (1) and 4-(2'-fluoro styryl) coumarin (2) produces syn-HH dimers across the styrenic double bond(b). Whereas 4-(3'-fluoro styryl) coumarin (3) and 4-styryl, 6-fluoro coumarin (4) produces anti-HT dimers. The packing modes vary depending upon the position at which fluorine is substituted. In all these structures, there are no significant short intermolecular F...F, F...H, F...C and F...O contacts although in (3) there are a few C-H...F interactions. These observations suggest that long range electrostatic interactions might also play a significant role in these crystals.

(a) V. Ramamurthy and K. Venkatesan; *Chem. Rev.*, 1987, 87, 433.

(b) K. Vishnumurthy, T. N. Guru Row and K. Venkatesan; *J. Chem. Soc., Perkin Trans. 2* (in press).

PS11.07.23 CRYSTAL STRUCTURES OF TEMPO RADICALS SHOWING FERROMAGNETIC INTERACTIONS. H. Yamamoto, H. Yoshikawa, M. Yasui, T. Ishida, T. Nogami and F. Iwasaki, Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo 182, Japan

Some of the 4-arylmethyleneamino-TEMPO radicals (TEMPO = 2,2,6,6-tetramethyl-piperidin-1-oxyl) were revealed to show inter-molecular ferromagnetic interactions, of which **1** ~ **5** and **13** exhibit a ferromagnetic transition (T_c) at an extremely low temperature [T. Nogami, et al. *Chem. Letters*, 29-32 (1994), T. Ishida et al. *Chem. Letters*, 919-922 (1994)]. **6** ~ **11** showed only a ferromagnetic interaction ($\theta > 0$), while **12** showed an antiferromagnetic interaction ($\theta < 0$). The X-ray structure analyses were performed on these crystals at room temperature to investigate whether any systematic intermolecular interactions were demonstrated among these crystals.

Ar-CH=N-TEMPO• (Ar: **1** Ph; **2** p-Cl-Ph; **3** p-biPh; **4** p-PhO-Ph; **5** p-PhS-Ph; **6** p-Br-Ph; **7** 3,5-diCl-Ph; **8** 2-Py; **9** 3-Py; **10** 4-Py; **11** Naph; **12** p-F-Ph) Ar-CH₂NH-TEMPO• (Ar: **13** Ph)

For all crystals, two-dimensional O...O networks are constructed, although of which forms are various. In **2**, O atoms arrange to form a pleated sheet with the first and the second nearest

O...O distances of 5.91 and 5.96 Å, respectively. Between sheets the aryl groups of each sheet arrange alternately with face-to-face. Crystal structures of **3**, **6** and **10** belong to the same category as **2**. In **1** and **9**, which are isomorphous, top and bottom lines of the pleats are not straight but zigzag. The nearest aryl groups belonging to the neighboring sheets arrange herringbone-like. The networks of **7** and **12** are constructed with zigzag lines, so that the surface of the sheet is rough in all directions. In **4**, there are no intersheet interactions between aryl groups, because the sheet is almost flat perpendicular to the crystallographic polar axis. This arrangement is quite different from the other crystals. In all these crystals sheet-like arrangement of the N-O radicals are considered to be essentially important for the magnetic interactions. Magnetic interactions may be transferred via intermolecular interactions of side chains, since the intra- and intersheet O...O distances are so long for the direct evidence of the systematic interactions which manifests the magnetic character.

PS11.07.24 CRYSTAL STRUCTURES OF COPPER COMPLEXES SHOWING FERROMAGNETIC INTERACTION. M. Yasui, Y. Ishikawa, T. Nogami, T. Ishida and F. Iwasaki, Dept. of Applied Physics and Chemistry, The Univ. of Electro-Communications, Chofu, Tokyo 182, Japan

We have determined the crystal structures of copper(II) complexes coordinated with pyrimidine derivatives showing ferromagnetic interactions. [Cu(hfac)₂(quinazoline)] (**I**), [Cu(hfac)₂(pyrimidine)] (**II**), [Cu(hfac)₂(4-methylpyrimidine)] (**III**), where hfac is 1,1,1,5,5,5-hexafluoropentane-2,4-dionate, [Cu(NO₃)₂(pyrimidine)₂] (**IV**), and [Cu(NO₃)₂(pyrimidine)(H₂O)₂] (**V**). For **I**, the ferromagnetic transition was observed at about 0.12K [Ishida *et al.*, *Synthetic Metals*, **71**, 1791 (1995)]. The ferromagnetic interaction was observed for **II**, **III**, and **IV**.

X-ray analysis revealed that the crystals of **III** have two modifications, a polymer structure [{"Cu(hfac)₂(4-methylpyrimidine)}_n] (**IIIa**), and a trinuclear complex [{"Cu(hfac)₂}₃(4-methylpyrimidine)₂] (**IIIb**).

All complexes, except for **IIIb**, form one-dimensional polymer structures in which the quinazoline or pyrimidine derivatives play a role of a bridging ligand. For **I**, two bridging ligands coordinate a Cu atom on both axial positions. The hfac ligands coordinate in an equatorial plane. Thus the Cu atom has a distorted octahedral structure. The complex **V** has a similar polymeric structure with two nitrates and two water molecules. In **II** and **IIIa**, which have also one-dimensional polymer structures with a distorted octahedral Cu, two bridging pyrimidine moieties are cis to one another. A Cu atom of **IV** is penta-coordinated with two bridging pyrimidines, one non-bridging pyrimidine and two nitrates. One nitrogen atom of non-bridging pyrimidine is free. The complex **IIIb** has a trinuclear structure. The central Cu atom has an octahedral structure while the terminal Cu atoms have a penta-coordinated square-pyramidal structure. The one-dimensional structure may be related to the ferromagnetic interaction except for **V**.

PS11.07.25 ABILITY OF SOME SPECIFIC NATURAL STRUCTURES TO INTERACT CONCURRENTLY CONTRARY TO DIOXIN. ESR STUDY. Pham The Vung, Nguyen Van Tri, Dinh Pham Thai, Hanoi University of Technology, Ha Van Mao, Dinh Ngoc Lam, Cancer Research Center, Hanoi, Vietnam

On the basis of the ESR experimental results, some new active natural complexes (symbolized XD*) present in special vegetable produces have been revealed. The nucleus structure of these complexes can show an electron Spin combination almost similar to the one of Dioxin (2,3,7,8- TCDD). However, it is especially remarkable that the Spin combination of XD* occupies a quintuplet ground state (S = 4/2) with a deeply negative exchange ener-