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 description, 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.


PSI1.07.22 INFLUENCE OF FLUORO SUBSTITUTION ON PACKING OF STYRYLOUMARINS AND THEIR PHOTOBEBAVIOUR IN THE CRYSTALLINE STATE. K. Vishnumurthy, K. Venkatesan and T. N. Guru Row\textsuperscript{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\textsuperscript{(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\textsuperscript{(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 contacts although in (3) there are a few C-H...F contacts. These observations suggest that long range electrostatic interactions might also play a significant role in these crystals.


PSI1.07.23 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 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)\textsubscript{2}(pyrimidine)\} (III), \{Cu(hfac)\textsubscript{2}(quinoxaline)\} (I), \{Cu(hfac)\textsubscript{2}(pyrimidine)\} (II), \{Cu(hfac)\textsubscript{2}(4-methylpyrimidin)\} (III), \{Cu(hfac)\textsubscript{2}(4,5,5,6-tetrafluoropyrimidine)\} (IV), \{Cu(NO\textsubscript{3})\textsubscript{2}(pyrimidine)\} (V) and \{Cu(NO\textsubscript{3})\textsubscript{2}(pyrimidine)\} (VII). For I, the ferromagnetic transition was observed at about 0.12 K [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)\textsubscript{2}(4-methylpyrimidin)\} (IIIa) and a trinuclear complex \{Cu(hfac)\textsubscript{2}(4-methylpyrimidin)\} (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 IIIb, 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 pentacoordinated square-pyramidal structure. The one-dimensional structure may be related to the ferromagnetic interaction except for V.

PSI1.07.25 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$^{\text{+}}$) 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$^{\text{+}}$ occupies a quintuple ground state (S = 4/2) with a deeply negative exchange energy.
Breaking van der Waals contacts followed by the disruption of hydrogen bonds in NEGH crystals is due to the fact that initial melting involves the disruption of hydrogen bonds as dimers disassociate to form monomers. This activity depends on many factors such as the concentration and the lifetime of the XD* state, the kinetic conditions of the surrounding and the interaction.

This research was supported by the National Basic Research. Program in Natural Sciences and from the 10-50 National Committee.


Hydrochloride salts of N-(1-Naphthyl)-N̈-(3-ethylphenyl) guanidine (NEGH) and an N̈-methyl analog aptiganel (CERESTAT®), which are N-methyl-D-asparte ion channel blockers, have anomalous physical properties. The melting point of crystals of the salts differ by 70°, their densities differ by 0.12g/cm³, and they exhibit significant differences in solubility. In general, high melting points suggest greater stability. Higher melting compounds of analogous composition might be expected to have higher density and lower solubility than the lower melting compounds. In this case the opposite relationships are observed. The higher melting salt is more soluble and less dense than the lower melting salt. Due to the addition of a methyl group in aptiganel there is a larger volume per molecule. However, the increased volume per molecule (66Å³) is greater than might be expected. In the solid state NEGH has an extended conformation with the planar rings well away from each other. The methyl substitution in aptiganel appears to induce or stabilize a conformation in which the rings are oriented toward one another. Due to its extended conformation planar rings of NEGH are sufficiently exposed to interact and contribute to closer packing of the molecules and higher density but not to a greater melting point. Although there were three NH...Cl hydrogen bonds in each structure, those in NEGH are engaged in forming dimers whereas in aptiganel one of the hydrogen bonds links the molecules into infinite chains. This difference in hydrogen bonding provides the explanation for the anomalous relationship between melting points and density and solubility. Upon initial melting only van der Waals forces must be overcome to melt NEGH crystals, while in aptiganel the crystals do not begin to melt until hydrogen bonds between adjacent molecules are broken. The broader melting point observed for NEGH crystals is due to the fact that initial melting involves the hydrogen bonds as dimers disassociate to form monomers.

1Registered trademark of Cambridge Neuroscience.

Chiral Compounds of Industrial Interest

MS11.08.01 CONFORMATIONAL STUDIES OF VITAMINS D DERIVATIVES. King Suwinska and Andrzej Kutner, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland Pharmaceutical Research Institute, Warsaw, Poland.

The fat-soluble vitamins D play essential role in stimulation of intestinal calcium transport, bone calcification, bone calcium mobilization, and phosphate transport as well as stimulation of cell differentiation and inhibition of cell proliferation. Vitamins D2 and D3 were found to exist in two almost equimolar equilibrium conformations in both liquid and solid states. The biologically active form of vitamin D3 1,25-hydroxylated derivative was found to exist in solid state as the beta conformer only. To explain the influence of 1-hydroxy substituent on the conformation of the vitamin D the 1-hydroxy vitamin D2 and 1-hydroxy vitamin D3 was crystallized and the structures of those two compounds were solved. For both compounds only one conformer was found in the solid state. The results of crystal structure determinations were compared with the semi-empirical calculations and will be discussed.


MS11.08.02 STRUCTURAL ASPECTS OF DIASTEREOMERIC DISCRIMINATION. Edward J. Valente, Christopher Miller, Gerard Ruggiero, Department of Chemistry, Mississippi College, Clinton, MS 39058, and Drake S. Eggleston, Department of Physical and Structural Chemistry, SmithKline Beecham, Co., King of Prussia, PA, 19401.

Systems showing two kinds of diastereoselective solubility disparities are described. In the system of warfarin and its derivatives and (+)-quinidine, a pattern in resolution success (= formation of a separable salt) as a function of warfarin substituent position has been found. Warfarin with a single phenyl substituent in the 3'- or 4'-positions and 2',3'-, 3',4'- disubstituted warfarins usually form less-soluble salts between their (+)-(S)-isomers and (+)-quinidine; their diastereomers are oils. The solid state structures of the less-soluble salts show that a single, strong N-H...O interaction linking warfarin enolate anions with protonated quinuclidine of quinidine. Packing motifs are remarkably similar over the range of substituents demonstrating that how a dominant interion interaction may serve as the basis for successful resolutions within a series of related substances. In the system of mandelic acid and its phenyl substituted derivatives and (+)-ephedrine, both less-soluble and more soluble salts can be isolated from 95% ethanol. The uniformly unsolvated salts vary from little to strong solubility disparities in aqueous ethanol, properties which correlate with their temperatures and heats of fusion. Six kinds of packing motifs have been found. These demonstrate a considerable range in packing efficiency while retaining correlations with configuration of the mandelate anion. Interion H-bonding type is one of the important organizing principles. Links between some of the packing group have been found in the form of polymorphs and solid-solid phase transitions in some of the salt phases.

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