

π - π INTERACTIONS OF MAGNESIUMPHTHALOCYANINE AS EVALUATED BY ENERGY PARTITION ANALYSIS

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Magnesiumphthalocyanine (MgPc) is a near-IR-active photoconductor used for laser printers. Our recent structure analysis revealed that the MgPc molecule is not flat in the solid state, but the central Mg atom is projected upward, forming a pyramidal structure. On top of the Mg atom along the stacking axis, the azamethine nitrogen atom is located with a distance of only 2.70 Å. The present arrangement is quite indicative of an appreciable interaction along the stacking axis through the formation of a five-coordinate Mg-complex. Therefore, the Mg-N interaction along the molecular stack has been investigated by energy partition analysis based on semi-empirical MO calculations. The Mg-N bond energy along the molecular stack is found to be roughly one-third of the Mg-N bond in the molecular plane and approximately one-half of the Mg-O bond of the six-coordinate MgPc-complexes: MgPc/(H₂O)₂(NMP)₂ and MgPc/(2-methoxyethanol)₂. These results indicate the formation of five-coordinate MgPc complexes along the stacking axis, showing considerable π - π interactions thorough the central Mg atom.

Keywords: PHTHALOCYANINE, ELECTRONIC STRUCTURE, INTERMOLECULAR INTERACTIONS

CHARGE DENSITY ANALYSIS AND COMPARISON OF THE INTERMOLECULAR INTERACTIONS IN RACEMIC AND OPTICALLY ACTIVE p-FLUOROMANDELIC ACIDS

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Crystallization of racemates normally leads to either a racemic compound or a conglomerate. Pure optically active compounds can be separated from the racemic mixture by various techniques. Having crystals of both forms makes it possible to study the difference in intermolecular interactions made by the exact same compound in different crystal environments. The para substituted fluoromandelic acid shows very different physico chemical properties in the racemic (rac-PFMA) and the optically active (oa-PFMA) crystals. The melting point (mp) and density are significantly higher in oa-PFMA (mp=425.8(5)^o K, ρ =1.508 g/cm³) than in rac-PFMA (mp=408.9(5)^o K, ρ =1.481 g/cm³). It is noteworthy that the racemic mixture of p-fluoromandelic acid crystallizes as a racemic compound instead of forming a conglomerate by spontaneous resolution. Though the crystal quality of oa-PFMA is higher than the crystal quality of rac-PFMA. A data set of rac-PFMA has been collected at 122.4 K using a Nonius KappaCCD diffractometer. Data were collected up to a resolution of 1.02Å⁻¹ in (sin θ / λ) with Rint=0.0389 (redundancy = 35). The multipole refinement and topological analysis of rac-PFMA is performed with VALRAY[1]. The topological properties of oa-PFMA reported earlier[2] will be compared to those of rac-PFMA. The differences found in the properties will be used in a comparison with the differences found in the physico chemical properties.

[1] R. F. Stewart et al. VALRAY98 Users Manual, July 1998.

[2] H.O. Sorensen, C. Flensburg and S. Larsen (1999). Acta Crystallogr., A55S,514.

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ROTATIONAL DISORDER OF FULLERENES: ANALYSIS OF STRUCTURAL DATAI.S. Neretin¹ Y.L. Slovokhotov¹ Y. Kubozono² S. Kashino²¹Institute of Organoelement Compounds Vavilov St., 28 MOSCOW 119991 RUSSIA ²Department of Chemistry, Faculty of Science, Okayama University, Okayama, Japan

The rotational disorder is one of the main hindering factors in the structural studies of fullerene derivatives. It is especially vital for the molecular complexes and ion-radical salts, where the fullerene molecule is chemically unmodified. In certain cases, a disorder may be resolved as two overlapping orientations with some common atoms. We discuss the factors determining the presence/absence of disorder in a series of fullerenes, endohedral metallofullerenes, and fluorofullerenes. The model of gum cavity is proposed, reckoning that at the equilibrium orientation of fullerene molecule all of its atoms are in shallow potential minima. Then, at different orientation, energetic penalty function is defined as the van der Waals volume of those parts of molecule which protrude over the surface of the normally oriented molecule. For the C₆₀ fullerene, the model confidently reproduces both of the known frequently occurring types of disorder, viz. rotation by 60^o around the 3-fold axis (leading to ordered poles and disordered belt) and rotation by 90^o around the 2-fold axis, yielding in an octahedral-like pattern of six characteristic crosses of disordered atoms, while the positions of 48 atoms are nearly common for the both orientations. In the case of C₇₀, four types of disorder are predicted, none of them being very favourable. For C₈₀ with icosahedral symmetry, which exists only in a form of endohedral metallofullerene, rotation by 36^o around a 5-fold axis leads to disordered poles and ordered belt. Molecular mechanics calculations for several crystal structures and series of isomorphous structures were performed in order to confirm the consistency of a model.

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Keywords: FULLERENES, ROTATIONAL DISORDER, MODELLING

MOLECULAR INTERACTIONS IN THE STRUCTURES OF ETHYL 5-AMINO-4,6-DICYANO-[1,1]BIPHENYL-3-CARBOXYLATE METHYL DERIVATIVES

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A series of 2-, 3- and 4- derivatives of ethyl 5-amino-4,6-dicyano-[1,1]biphenyl-3-carboxylate was recently synthesized using the method described by Milart and Sepiol, 1990. The compounds have penta-substituted benzene ring with both electron-donating and electron-withdrawing functional groups strongly affecting their molecular geometry. The structures of three methyl derivatives were determined and analysed: m-CH₃, a=7.2689(1), b=23.0979(3), c= 9.6300(2)Å, β = 99.139(1)^o, P₂/n, V=1596.3(2)Å³, D_x=1.270 Mg/m³; o-CH₃, a=11.7807(6), b=7.5228(11), c=17.939(1)Å, β =93.570(3)^o, P₂/n, V=1586.7(2)Å³, D_x= 1.278 Mg/m³; p-CH₃, a=17.0505(7), b=3.9919(2), c=22.662(1)Å, β =93.169(1)^o, P₂/c, V=1540.1(2)Å³, D_x=1.317 Mg/m³. A presence of the potential proton donors and acceptors and the overall shape of the molecules influence packing in the crystal structure, though the architecture of the hydrogen bonds of NH...N type, which form centrosymmetric dimers, is similar. Conformation of the molecules, and especially the value of dihedral angle between the benzene rings, varying from 43.94(5) for p-CH₃, 53.05(6) for m-CH₃ to 67.15(14)^o for o-CH₃, clearly depends on the methyl substituent position and different weak intermolecular interactions. The results obtained are compared to the structures of ethyl 5-amino-4,6-dicyano-[1,1]biphenyl-3-carboxylate itself and its derivatives with strong electron-withdrawing substituents, NO₂ and CN.

Keywords: BIPHENYL DERIVATIVES, INTERMOLECULAR INTERACTIONS, HYDROGEN BONDS