

PS06.00.28 Cl-AGGREGATES IN CRYSTALS OF DICHLORO-NAPHTHALENES AND CHLOROBENZENE.

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The halogene atoms form as usual some aggregates (layers, ribbons) in organic crystals; the examples of such aggregates have been described in the previous works of P.M. Zorky. Each Hal atom has four or five nearest neighbours in such formations, and the mean distance Hal...Hal is approximately equal to double vdW radius ($2R_{vdw}$).

In this work the Cl-aggregates in crystals of 2,6-dichloronaphthalene (I), 1,4-dichloronaphthalene (II) and chlorobenzene (III) are considered. In all of them each Cl atom forms as usual two contacts Cl...Cl which are shorter than $2R_{vdw}=3.80\text{\AA}$ and two contacts Cl...Cl which are rather longer than $2R_{vdw}$.

The existence of Cl-layers has been found in a, b and g forms of dichlorobenzene. It was interesting to know what a change of crystal structure occurs in substances with a smaller concentration of Cl. There are two ways of decreasing of Cl concentration: 1) increasing of the carbon part of a molecule, 2) decreasing of the number of Cl atoms. The first of them takes place in I and II; the ribbons of Cl atoms exist in these crystals. The second way is realized in III, where the roads formed by Cl atoms occur.

PS06.00.29 PECULIARITIES OF TETRASYSTEM ORGANIC CRYSTALS. STRUCTURAL CLASS P1, Z = 8(1,1,1,1).

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The so-called polysystem organic crystals, in which chemically identical molecules occupy more than one orbit, specifically multisystem crystals with $k3$ (three or more molecules per asymmetrical unit), are of particular interest. The reasons for their occurrence are yet unknown.

We have considered about ten representatives of the structural class $P\bar{1}$, $Z = 8(1,1,1,1)$ with $k = 4$. In all of them the molecules are arranged in a specific way; their orientations appear to be not arbitrary.

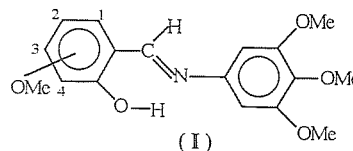
A good example is the crystal structure of chlordiazepoxide, $C_{16}H_{14}N_3OCl$ (CMABOX10). The substance contains two similar but crystallographically non-equivalent H-bonded dimers A - C and B - D; each of them exhibits the presence of local two-fold axis. These two axes skew at 88.1° , the distance between them is 2.40\AA . At the same time the A - C and B - D dimers can be transformed into one another by the third two-fold axis, which skew with each of the axes of the dimers at 44.1° . Thus, in this crystal one can see a tetramer with pseudosymmetry 2 composed of two dimers with the same pseudosymmetry.

In other representatives of this class we have found not only two-fold axes but also axes $2q$ of hypersymmetry; in such cases symmetrically non-equivalent molecules can be transformed into one another by a rotation through 180° and a shift (this shift is small in chlordiazepoxide).

PS06.00.30 PACKING MODES ANALYSIS IN 3,4,5-TRIMETHOXY N(METHOXY MONOSUBSTITUED SALICYLIDENE) ANILINES.

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Structural investigation of the anils of salicylaldehyde, known for their thermochromic and/or photochromic properties, forms part of our study on the interplay in organic solid state between crystal forces and molecular conformation. Systematically varying a substituent position, we are carrying out an investigation of the nature of stacking interactions which involve a subtle and complicated interplay between van der Waals forces, dipole-dipole interactions, intermolecular hydrogen bonding and $\pi - \pi$ interactions of aromatic rings. We report the structures and the packing analysis of four N-(Methoxysalicylidene)-3,4,5-trimethoxyanilines (I) which differ only by the position of the methoxy group at the vanillidene ring.

**PS06.00.31 STERIC AND ELECTRONIC EFFECTS ON CONFORMATIONS OF N-ACYLINDIGO AND N,N'-DIACYLINDIGO DYE MOLECULES.**

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Solid and solution state structures of *N*-mono- and *N,N'*-dichloroacetyl substituted indigo were compared to further understanding of spectral changes in substituted indigos (*J. Chem. Soc. Perkin 2* 1993 165). Steric repulsions between the acyl groups and the chromophore carbonyl groups induce large conformational twisting (8 and 20° respectively) about the central $C=C$ bond of the chromophore; the twisting is offset in the monosubstituted compound by the remaining $N-H...O$ intramolecular hydrogen bond. The near equivalence of the central $C=C$ bond lengths is explained by resonance effects. The inductive effect of the *N*-acyl groups completes the description of the spectral shifts.

More subtle conformation changes were explored in comparing the diacyl series, *N,N'*-diacetylindigo, *N,N'*-bis(chloroacetyl)indigo, and *N*-acetyl-*N'*-chloroacetylindigo. Steric crowding again determines the gross conformation. The *N*-acyl groups form double intramolecular $C-H...O$ hydrogen bond relays with the *N*-acyl $C-H$'s as bifurcated hydrogen bond donors to the chromophore carbonyls and the *N*-acyl carbonyls as acceptors to chromophore aryl $C-H$'s. The relative order of observed $C-H...O$ hydrogen bond distances correlates with $C-H$ acidity and O basicity (*J. Org. Chem.* 1993 58 6493).

Additional structures, including *N*-methoxyacetylindigo, *N,N'*-dimethoxyacetylindigo, and *N,N'*-diethoxymalonylindigo will be presented along with further analysis of the effects of steric interactions, $C-H...O$ hydrogen bonding, and electrostatic interactions on the conformations of indigo dye molecules.