06-Crystallography of Organic Compounds

As small, synthetic molecules are generally used as selector, frequently bonded to silica micro particles. We have recently developed a family of new chiral stationary phases (CSPs) for HPLC applications, based on different derivatives of (R)-1,2-di-amino-cyclohexanone (DACH). One of these CSPs containing the N,N-3,5-dichlorobenzyl derivative of (R)-1,2-DACH, is particularly effective in the resolution of the enantiomers of a large number of 1,2-aminoalcohols (pharmacologically active as &beta; blockers) in the form of azaxolidin-2-ones. It has been shown that the knowledge of the recognition mechanism underlying such separations can lead to the design of improved CSPs. In this respect we are now investigating the origin of the stereoselective interactions between a soluble model of CSP and the enantiomers of x-Propanol by a combination of physico-chemical techniques (NMR, FT-IR, UV and CD spectroscopy, X-ray crystallography) and computational methods.

Aims of these investigations are: 1) structural determinations on the isolated enantiomers (in solution, in the solid state and "in vacuo" by NMR calculations), 2) structural determinations on the interacting species (in solution, in the solid state, "in vacuo" by X-ray crystallography through automatic docking procedures). Here we show some preliminary results on the solid state structure of the selector.

The selector was crystallized from chloroform. The space group is P212121, the cell parameters are a = 20.71 Å, b = 21.06 Å, c = 14.10 Å and V = 4970.6 Å³ with Z = 8. The data were collected at room temperature by a rotating anode Rigaku AFC501 equipped with a four circle diffractometer from Molecular Structure Corporation. The structure was solved by direct methods with the program SIR92 and anisotropically refined to a final R of 0.036 for 5434 reflection with I(303). The figure shows one of the two molecules of the selector contained in the asymmetric unit held together by two intermolecular hydrogen bonds.

**PS-06.03.14 HENTOCRYSOGRAPHIC AND SPECTROSCOPIC STUDIES OF THE DIFFERENT CRYSTALLINE FORMS OF Bпл (1.2.3.4-Disopropylbenzilidene-2,6-diphenylbencenecarbonitrile, 1.2.3.4-BIPYRIDyl) DIAZEPAM and Benzodiazepincarbonitrile.**

*It is not clear if the text is referring to a specific compound.*

*Further details are not provided in the image.*

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PS-06.03.15

**GROUPER AND DISORDERED CYCLOALKANE GUEST MOLECULES IN TRIS-2-ACETYL-3-THIENYL METHANE INCLUSION COMPOUNDS.** By L. Pang and F. Brisse, Département de Chimie, Université de Montréal, C.P. 6128, Succ. A, Montréal, Québec, H3C 3J7 Canada.

Tris(2-acetyl-3-thienyl)methane (TATM) forms 2:1 host/guest inclusion compounds with cyclohexane and cyclooctane, but 1:1 inclusion compound with cyclodextrine. The crystal structures of these compounds have been studied by X-ray crystallography. The cyclohexane clathrate crystallizes in a triclinic unit cell of dimensions $a = 8.6479(5)$, $b = 10.3617(4)$, $c = 12.8463(5)$, $\alpha = 78.925(3)$, $\beta = 72.601(4)$, $\gamma = 84.466(4)$, $V = 1068.21(4)$, $Z = 2$, $P \overline{1}$ (monoform); the cyclodextrine clathrate crystallizes also in a triclinic unit cell: $a = 11.8742(4)$, $b = 13.9512(4)$, $c = 14.0112(4)$, $\alpha = 89.653(1)$, $\beta = 77.392(1)$, $\gamma = 75.301(1)$, $V = 2187.76(1)$, $Z = 4$, $P \overline{1}$ (b-form). However, the cyclodextrine clathrate has a monoclinic unit cell: $a = 9.0944(2)$, $b = 19.4664(4)$, $c = 31.4737(1)$, $\beta = 109.40(1)$, $V = 7708.16(1)$, $Z = 4$, $P \overline{1}$.

The crystallographic data and experimental details are presented in Table 1. The high-resolution solid state NMR studies have unambiguously revealed that this technique is very sensitive to establish molecular stacking effect. The abiding parameters for disulfides 2a, 5b, 1c, established from graphical method of Herber and Helferty from splitting band's intensities were found to be very similar. Hence it was concluded that the local geometry of S-S or -S-F-S interaction for these groups is characterized by almost similar S-S or F-S distances, and S-F distances.

**Table 1.** Crystallographic data for disulfides 2a, 5b, 1c.

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<thead>
<tr>
<th>Molecular formula</th>
<th>$\text{C}_x\text{H}_y\text{S}_z\text{F}_w$</th>
<th>S-S bond length (Å)</th>
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<tr>
<td>2a</td>
<td>$\text{C}_4\text{H}_8\text{S}_2\text{F}_4$</td>
<td>1.591</td>
<td>94.2</td>
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<td>1c</td>
<td>$\text{C}<em>{12}\text{H}</em>{24}\text{S}<em>2\text{F}</em>{12}$</td>
<td>1.591</td>
<td>94.2</td>
</tr>
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**REFERENCES (selected):**

2. V. V. Titushev et al., Zh. Strukt. Khim., 17 (1976), 945.

PS-06.03.16

**CRYSTAL STRUCTURE OF TRIS-3-ACETYL-3-THIENYL METHANE - CYCLOALKANONE INCLUSION COMPOUNDS.** By F. Brisse and L. Pang, Département de Chimie, Université de Montréal, C.P. 6128, Succ. A, Montréal, Québec, H3C 3J7 Canada.

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