monoclinic, $P2_1/a$, a=17.282(3), b=10.669(4), c=19.927 (3) Å, ß=102.99(1)°, Z=2, D_c=1.187 g/cm³, room temperature, R=0.084, R_w=0.086 (unit weights for all observed reflecions) for 1255 independent observed reflections ($I>3\sigma(I)$).

A cyclohexane solution of the mixture of A and B in molar ratio 1:1 was prepared. The single crystal A_2B were obtained by slowly evaporating the solution at room temperatutre in two weeks. The structure was solved by direct methods. All of hydrogens were found in subsequent differential Fourier maps.

Molecular complex crystals which have been known for a long time, are composed of two or more distinct species that are arranged, not in statistical disorder, but in mutually identical positions in all cells in the crystal. In general, the formation of a molecular complex is due to the fact that the packing of a biomolecular crystal comes out to have a better density than the packing of its components, or most frequently, the molecules are capable of producing hydrogen bonds (A.I. Kitaigorodsky, "*Molecular Crystals and Molecules*", volume 29 of "*PHYSICAL CHEMISTRY*", ACADEMIC PRESS New York and London,121-130, (1973)). But this is not the case with the A_2B crystal. There is no the possibility of producing hydrogen bonds in A_2B crystal. The calculated densities of A_2B, A and B crystals are 1.187, 1.194 and 1.191 g/cm³, respectively. That is to say, The crystal A_2B, at least, has no better density. The packing energies (kcal/mol), however, by calculating with "OPEC" program are -68.251 (B), -72.902 (A), and -198.454 (A_2B corrected value). The value of A_2B is the lowest when compared with ones of the pure A crystals and the pure B crystals. Maybe, that is why only A_2B was formed from the mixture solution of A and B with the molar ratio 1:1.

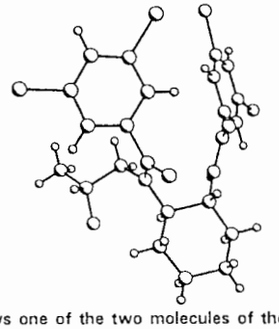
The bond lengths, angles and conformation of A in A_2B crystal are similar to those of A in pure A crystal, and the bond lengths and angles of B in A_2B crystal are similar to those of B in pure B crystal, it is noteworthy that the conformations of B in A_2B and pure B crystals are different. The phenyl rings in the terminals of butadiene chain and the C=C double bond plane are almost located in the same plane (dihedral angle 1.8°), the phenyl rings in the butadiene chain are nearly perpendicular to the C=C double bond plane (dihedral angle 85.7°). The corresponding dihedral angles in the pure B crystal are 33.1° and 74.1°, respectively. Another salient feature of A_2B crystal is the "extra long" C-C single bond length (1.63(1)Å) between the bridge-head carbon atoms of the molecule A component, which is comparable to those of Dewar benzene (1.63Å) (M. J. Cardillo and S. H. Bauer, *J. Am. Chem. Soc.*, **92**, 2399 (1970) and derivatives of bis-norcaradiene (1.622 -1.85Å) M. Pierrot and J. Estienne, "Structure and Properties of Molecular Crystals", edited by M. Pierrot, Elsevier Science Publishers B. V., pp. 51-55, (1990)). We thank Professor Xu Xiaojie (Department of Chemistry, Beijing University) for his help in calculating with "OPEC" program.

PS-06.03.13 X-RAY CRYSTAL STRUCTURE OF A SYNTHETIC CHIRAL "SELECTOR" DERIVED FROM 1R,2R-DIAMINOCYCLOEXANE by °*Cirilli M., §Cirilli R., §Gasparrini F., °Gavuzzo E., §Villani C. from §Dipartimento Studi di Chimica e Tecnologia delle Sostanze Biologicamente Attive, Università La Sapienza, P.le A. Moro 5,Roma and °Istituto di Strutturistica Chimica-CNR, Via Salaria Km. 29.400, Roma.

Only recently the right sort of emphasis has been placed on consequences of stereochemistry in biological processes and therefore on the problem of separating enantiomers. The direct chromatographic separation of enantiomers represent an additional tool for solving stereochemical problems. This technique is based on the preferential interaction of one enantiomer of a raceme compound with a chiral discriminating agent (*selector*) immobilized on an inert support. Proteins, polysaccharides, cyclodextrins, synthetic polymers as well 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,R)-1,2-diaminocyclohexane (DACH). One of these CSPs containing the N,N'-(3,5-dichlorobenzoyl) derivative of (R,R)-1,2-DACH, is particularly effective in the separation of the enantiomers of a large number of 1,2-aminoalcohols (pharmacologically active as β-blockers) in the form of oxazolidin-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 stereo selective interactions between a soluble model of CSP and the enantiomers of a Propranolol by a combination of physicochemical techniques (1D and 2D NMR, FT-IR, UV and CD spectroscopy, X-ray crystallography) with computational methods.

Aims of these investigations are: 1) structural determinations on the isolated species (in solution, in the solid state and "in vacuo" by MM calculations); 2) structural determinations on the interacting species (in solution, in the solid state, "in vacuo" by MM calculations 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 $P2_12_12_1$,the cell axis are a=20.71Å, b=21.05Å, c=11.40Å and V=4970.68Å³ with Z=8. The data were collected at room temperature by a rotating anode Rigaku AFC5R 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 4.8% for 2637 reflections with $I>3\sigma(I)$.



The figure shows one of the two molecules of the *selector* contained in the asymmetric unit held togheter by two intermolecular hydrogen bonds.

PS-06.03.14 RENTGENOGRAPHIC AND SPECTROSCOPIC STUDIES OF THE DIFFERENT CRYSTALLINE FORMS OF BIS(1,2:3,4-DIISOPROPYLIDENO-GALACTOPYRANOZO-6-O,6-O'-TIOPHOSPHORYL) DISULFIDE $C_{48}H_{78}O_{24}P_2S_4$. By M.W. Wieczorek[1]*, J. Błaszczyk[1], M.J. Potrzebowski[1], P. Knopik[2], [1]Technical University of Łódź, Institute of Technical Biochemistry, Stefanowskiego 4/10, 90-924 Łódź, Poland; [2]Polish Academy of Sciences, Centre of Molecular & Macromolecular Studies, Sienkiewicza 112, 90-363 Łódź, Poland.

The crystal and molecular structures of three different crystalline forms of bis(1,2:3,4-diisopropylidenogalactopyranozo-6-O,6-O'-tiophosphoryl) disulfide (1a, 1b, & 1c) have been determined - Figure 1.

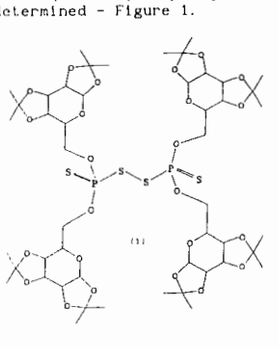


Fig 1 Bis(1,2:3,4-diisopropylidenogalactopyranozo-6-O,6-O'-tiophosphoryl) disulfide (1)
1a (1) · $2C_6H_6$
1b (1) · C_6H_6 + C_6H_{14}
1c (1) · $2CHCl_3$

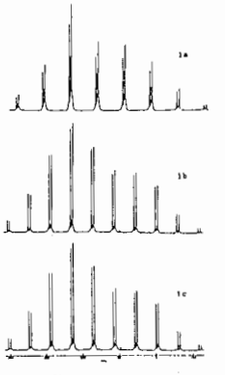


Fig 2 The ^{31}P CPMAS spectra of disulfides 1a,1b,1c

06-Crystallography of Organic Compounds

Three different crystalline forms (1a,1b,1c) of compound 1 belong to different crystallographic systems and space groups, depending upon the solvent used in crystallization. The basic experimental and crystallographic data and information about the crystal forms are presented in Table 1. The high resolution solid state NMR studies have unambiguously revealed that this technique is very sensitive tool to establish molecular packing effect. The shielding parameters for disulfides 1a, 1b, 1c, established from graphical method of Berger and Herzfeld from spinning sideband's intensities were found to be very similar. Hence it was concluded that local geometry of S=P-S--S-P=S skeleton for three forms of disulfides is characterized by almost identical S=P-S angles and P=S, P-S distances.

Table 1. Crystal data and experimental details

	1a	1b	1c
Molecular formula	$C_{48}H_{78}O_{24}P_2S_4$ • 2(C_6H_6)	$C_{48}H_{78}O_{24}P_2S_4$ • C_6H_6 • C_8H_{14}	$C_{48}H_{78}O_{24}P_2S_4$ • 2$CHCl_3$
Crystallization solvent	benzene	benzene/hexane	chloroform
Crystallographic system	trigonal	orthorhombic	monoclinic
Space group	$P3_2$	$P2_12_12_1$	$P2_1$
a (Å)	11.861(1)	10.536(4)	10.4293(8)
b (Å)		25.067(4)	28.206(2)
c (Å)	44.679(3)	28.021(5)	12.105(1)
β (°)			90.696(8)
V (Å^3)	5443(3)	7401(4)	3560.6(7)
Z	3	4	2
Dc (g/cm^3)	1.266(2)	1.249(2)	1.367(2)
μ (cm^{-1})	21.9	2.3	43.5
Crystal dimensions (mm)	regular triangle 0.5, 0.2	0.45, 0.4, 0.3	0.35, 0.35, 0.45
Maximum 2θ (°)	150	50	150
Radiation, λ (Å)	CuKα, 1.54178	MoKα, 0.70930	CuKα, 1.54178
Scan mode	ω/2θ	ω/2θ	ω/2θ
Scan width (°)	0.70+0.14tanθ	1.32+0.35tanθ	0.90+0.14tanθ
hkl ranges	h= 0 14 k= 0 14 l= 0 56	h= 0 12 k= 0 28 l= 0 33	h= 0 13 k= 0 35 l= -15 15
Number of refl. measured:			
total	4367	7192	7873
with I≥3σ(I)	3191	2693	6504
R	0.040	0.067	0.060

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PS-06.03.15 ORDERED AND DISORDERED CYCLOALKANE GUEST MOLECULES IN TRIS(5-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(5-acetyl-3-thienyl)methane (TATM) forms 2:1 inclusion compounds of the host-guest type with cyclohexane, cycloheptane and cyclooctane. The crystal structures of these compounds, studied by X-ray diffraction, show that the cyclohexane inclusion compound crystallizes in two types of triclinic α and β forms with the unit-cells: a = 8.622(2), b = 10.194(2), c = 12.795(2) Å, α = 79.09(1), β = 72.74(1), γ = 84.89(1)°, V = 1053.9(4) Å^3, Z = 2, $P\bar{1}$ for the α-form, and a = 11.637(2), b = 13.669(1), c = 14.263(2) Å, α = 89.38(1), β = 77.00(1), γ = 76.15(1)°, V = 2144(1) Å^3, Z = 4, $P\bar{1}$ for the β-form. In the α-form, the guest molecule is located on a crystallographic center of symmetry, but it is in a general position in the β-form. The unit-cell volumes are roughly in the 1:2 ratio for the α and β-forms respectively. The cycloheptane and cyclooctane inclusion compounds crystallize only in the β-form with the unit-cell dimensions comparable to those of the cyclohexane adduct. All cyclohexane, -heptane and -octane molecules in the β-form are orientationally disordered with respective occupations of 65 and 35%.

PS-06.03.16 CRYSTAL STRUCTURE OF TRIS(5-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.

Tris(5-acetyl-3-thienyl)methane (TATM) forms 2/1 (host/guest) inclusion compounds with cyclohexanone and cyclooctanone, but 1/1 inclusion compound with cyclononanone. The crystal structures of these compounds have been studied by X-ray crystallography. The cyclohexanone clathrate crystallizes in a triclinic unit cell of dimensions a = 8.6479(5), b = 10.2617(4), c = 12.8643(5) Å, α = 78.925(3), β = 72.601(4), γ = 84.466(4)°, V = 1068.2(1) Å^3, Z = 2, $P\bar{1}$ (α-form); the cyclooctanone clathrate crystallizes also in a triclinic unit cell: a = 11.874(2), b = 13.951(2), c = 14.011(2) Å, α = 89.653(1), β = 77.39(2), γ = 75.30(1)°, V = 2187.7(6)Å^3, Z = 4, $P\bar{1}$ (β-form). However, the cyclononanone clathrate has a monoclinic unit cell:, a = 10.994(2), b = 19.464(4), c = 13.417(1) Å, β = 109.40(1)°, V = 2708.1(8) Å^3, Z = 4, $P2_1/c$. The cyclohexanone guest molecule is located on a crystallographic centre of symmetry and thus is orientationally disordered. The cyclooctanone guest molecule although in general position is also orientationally disordered (65/35). Finally, the cyclononanone guest molecule is in general position and ordered. The interactions between the host and the guest molecules are only of the van der Waals type. The relationships between the guest molecules, the stoichiometry and the unit cell dimensions will be discussed in relation to other series of TATM host-guest inclusion compounds.

PS-06.03.17 DIASTEREOMERIC SALTS OF MANDELIC ACID WITH 2-AMINO-2-PHENYLETHANOL AND 1-PHENYL-2-AMINOETHANOL. SALTS WITH VERY UNUSUAL FEATURES. By Sine Larsen[*a], David Kozma[a,b] and Maria Acs[b†], Department of Chemistry[a], University of Copenhagen, Denmark and Department of Organic Chemical Technology[b], Technical University of Budapest, Hungary.

The resolution of racemates via crystallization of diastereomeric compounds is a widely used method to obtain pure enantiomers. Crystal structures and thermochemical properties will be presented for diastereomeric salts formed when the resolution process has been less successful. These examples contribute also to the understanding of the structural and physical chemical background for optical resolution.
The salts investigated are formed by the reaction of mandelic acid with 2-amino-2-phenylethanol and 1-phenyl-2-aminoethanol. Despite the great similarity between the amines their diastereomeric salts have quite different properties. 1-Phenyl-2-aminoethanol cannot be resolved with optically active mandelic acid. A disordered diastereomeric salt precipitates which contains both enantiomers on the four crystallographically inequivalent sites in the structure. This system represents a rare (the first?) example of a solid solution for a diastereomeric salt. Racemic mandelic acid can be resolved with (R)-2-amino-2-phenylethanol if small amounts of water is present. The less soluble diastereomeric salt crystallizes as a hydrate and the water molecule plays an important role for the crystal packing. The more soluble salt is water free and contains four independent cations and anions.These structural differences can be related to the difference between the solubilities The reverse resolution of 2-amino-2-phenylethanol with mandelic acid gives a disordered crystal (solid solution).