

06-Crystallography of Organic Compounds

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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	$C_{18}H_{18}O_2P_2S_4 \cdot 2(C_6H_6)$	$C_{18}H_{18}O_2P_2S_4 \cdot C_6H_6 \cdot C_8H_{14}$	$C_{18}H_{18}O_2P_2S_4 \cdot 2CHCl_3$
Crystallization solvent	benzene	benzene/hexane	chloroform
Crystallographic system	trigonal	orthorhombic	monoclinic
Space group	$P\bar{3}_2$	$P2_12_12_1$	$P2_1$
a (Å)	11.861(1)	10.526(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
D _c (g/cm ³)	1.286(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 2 θ (°)	150	50	150
Radiation, λ (Å)	CuK α , 1.54178	MoK α , 0.70930	CuK α , 1.54178
Scan mode	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Scan width (°)	0.70+0.14tan θ	1.32+0.35tan θ	0.90+0.14tan θ
hkl ranges	h=0 14 k=0 14 l=0 55	h=0 12 k=0 29 l=0 33	h=0 13 k=0 35 l=-15 15
Number of refl. measured:			
total	4367	7192	7873
with I \geq 3 σ (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, $\alpha = 79.09(1)$, $\beta = 72.74(1)$, $\gamma = 84.89(1)^\circ$, $V = 1053.9(4)$ Å³, $Z = 2$, $P\bar{1}$ for the α -form, and $a = 11.637(2)$, $b = 13.669(1)$, $c = 14.263(2)$ Å, $\alpha = 89.38(1)$, $\beta = 77.00(1)$, $\gamma = 76.15(1)^\circ$, $V = 2144(1)$ Å³, $Z = 4$, $P\bar{1}$ 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, $\alpha = 78.925(3)$, $\beta = 72.601(4)$, $\gamma = 84.466(4)^\circ$, $V = 1068.2(1)$ Å³, $Z = 2$, $P\bar{1}$ (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, $\alpha = 89.653(1)$, $\beta = 77.39(2)$, $\gamma = 75.30(1)^\circ$, $V = 2187.7(6)$ Å³, $Z = 4$, $P\bar{1}$ (β -form). However, the cyclononanone clathrate has a monoclinic unit cell; $a = 10.994(2)$, $b = 19.464(4)$, $c = 13.417(1)$ Å, $\beta = 109.40(1)^\circ$, $V = 2708.1(8)$ Å³, $Z = 4$, $P2_1/c$. 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).