

06-Crystallography of Organic Compounds

175

(Maurin, Winnicka-Maurin, Paul, Curtin, 1992).

The two title compounds (Figure 1 and 2, respectively), unlike any other mentioned before, form cyclic tetrameric units in crystalline state. The molecules are bonded together by pairs of hydrogen bonds between oxime and carboxyl groups. Seemingly similar

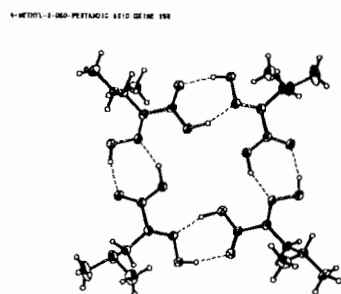


Figure 1

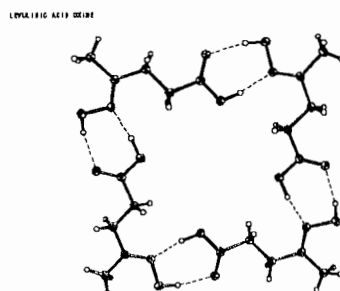


Figure 2

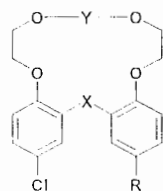
structures differ significantly both in molecular geometries and hydrogen bond dimensions. The dramatic changes in C=N and N-O bond lengths as well as in O...O and O...N hydrogen bond lengths in 4-methyl-2-oxopentanoic acid oxime comparing to levulinic acid oxime and other compounds could be interpreted as the result of resonance interaction between oxime and carboxyl group in the first compound. This reasoning is strongly supported by quantum mechanic calculations done for both title compounds.

References.

- Maurin, J.K., Paul, I.C. & Curtin, D.Y. (1992a). *Acta Cryst.*, **C48**, 0000-0000.
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 Padmanabhan, K., Paul, I.C. & Curtin, D.Y. (1989). *Acta Cryst.*, **B45**, 411-416.

PS-06.03.05 X-RAY STUDY OF DIPHENYLAMINE CONTAINING CROWNS. By Zs. Böcskei¹, V. Németh², B. Ágai², K. Simon¹, ¹Chinoin Pharmaceutical and Chemical Works Ltd, Budapest, POB 110, H-1325, Hungary, ²Department of Organic Chemical Technology, Technical University Budapest, H-1521, Hungary.

Three crowns, **1** (R=H, X=NH, Y=CH₂-CH₂), **2** (R=H, X=NH, Y=CH₂-CH₂-O-CH₂-CH₂), **3** (R=Cl, X=S, Y=CH₂-CH₂-O-CH₂-CH₂) have been analyzed by X-ray crystallography. A water molecule is situated in the middle of crown **2** H-bonded to the N-H group and two oxygen atoms. The conformation of the three macrocycles will be compared.



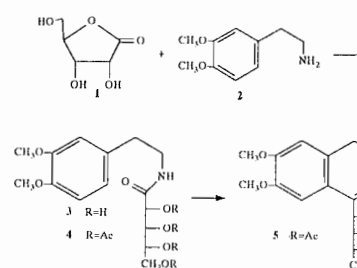
Compound	1	2	3
Formula	C ₁₈ H ₂₀ ClNO ₄	C ₂₀ H ₂₄ ClNO ₅ ·H ₂ O	C ₂₀ H ₂₂ Cl ₂ O ₅
a, Å	11.147	12.463	12.741
b, Å	12.356	12.619	13.516
c, Å	13.743	13.422	12.992
β, °	107.81	102.86	98.10
V, Å ³	1802	2058	2215
Z	4	4	4
S.G.	P2 ₁ /c	P2 ₁ /c	P2 ₁
N _{refl}	2753	1668	1736
R	0.08	0.10	in progress

PS-06.03.06 ENANTIOSELECTIVE SYNTHESIS OF ISOQUINOLINE ALKALOIDS FROM SIMPLE SUGAR. by Z. Czarnocki¹, *Department of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw, Poland*, J.K. Maurin and K. Wieteska, *Institute of Atomic Energy, Solid State Physics Department, 05-400 Otwock-Świerk, Poland*.

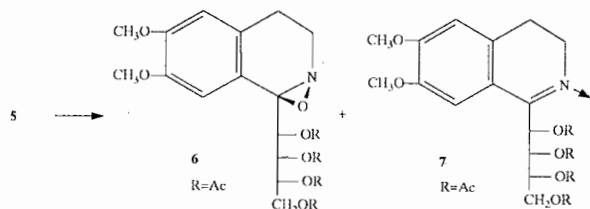
In the course of our study on enantioselective synthesis of isoquinoline alkaloids from various naturally occurring chiral substrates, we launched a project of using a simple sugar - D-ribose as a chiral building block. The synthetic sequence started with a condensation of **1** with 3,4-(dimethoxyphenyl)ethylamine **2** to give an amide **3**, which after acetylation to **4** and Bischler-Napieralski cyclization gave a very unstable imine **5** (Czarnocki 1992).

When **5** was subjected to m-chloroperbenzoic acid (MCPBA) oxidation, compounds **6** and **7** were formed in a relative ratio depending on the temperature (Czarnocki, 1992). The synthetic utility of nitron **7** was further elucidated by its transformation, in several steps, into two isoquinoline alkaloids

Scheme 1



Scheme 2



(R)-calycotomine, and (S)-xylopinine. Both compounds, **6** and **7**, were characterized by spectral means (¹H and ¹³C-NMR) as well as by X-ray structural analysis.

06-Crystallography of Organic Compounds

The observation of only one diastereoisomer of **6** is noteworthy and indicates highly stereospecific character of the oxidation step. This observation may be of great significance and we plan to utilize compound **6** as a chiral precursor in the synthesis of natural products.

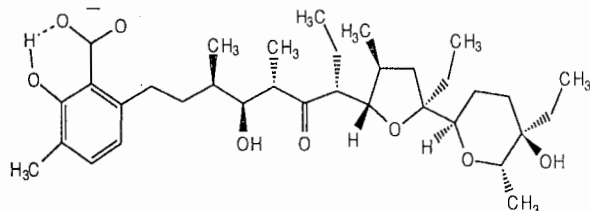
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- Bhat, K.L., Chen, S-Y. & Joulic, M. (1985) *Heterocycles*, **23**, 691-734; *Aldrichimica Acta*, **22** (2), 49,(1989).
 Czarnocki, Z. (1992) *J. Chem. Research (S)*, 334-335.
 Czarnocki, Z. (1992) *J. Chem. Research (M)*, 2801-2819.

PS-06.03.07 COMPLEXATION OF GUANIDINIUM AND AMIDIUM CATIONS WITH THE POLYETHER ANTIBIOTIC LASALOCID. Xiuqi Shui*, Drake S. Eggleston, Nelson Troupe and John W. Westley, SmithKline Beecham Pharmaceuticals, Box 1539, King of Prussia, PA 19406, USA

Studies directed toward the complexation of guanidinium and amidinium groups by organizable recognition sites are expected to be of value for a number of reasons. Among these is the potential for crystallization of otherwise recalcitrant natural products and peptides. As one approach to that goal, complex formation with the highly crystalline naturally occurring ionophore lasalocid A, which has previously been shown to be of value in the complexation and resolution of asymmetric amines (Westley, Evans & Blount, 1977, *J. Am. Chem. Soc.* **99**, 6057-6061), has been investigated for a variety of target molecules. Circular dichroism studies in various polar and nonpolar solvents have confirmed complex formation and several complexes of general formula I have been crystallized. Details of these studies where R = various molecules incorporating guanidinium and amidinium groups and comparisons of the recognition motifs will be presented.

R⁺



PS-06.03.08 CRYSTAL STRUCTURES OF CIS- α -NITROSTILBENE AND THE ADDUCT: TRANS-STILBENE. (CIS- α -NITROSTILBENE)₂

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Crystal structure of *cis*- α -nitrostilbene (I) and that of *trans*-stilbene. (*cis*- α -nitrostilbene)₂ (II) have been determined by X-ray diffraction at room temperature.

Crystal data:

I. formula: C₁₄H₁₁NO₂
 monoclinic, space group: P2₁/n
 a=5.839(2) b=16.034(4) c=24.851(5) Å
 β = 90.95(2)^o
 V=2326.3(9) Å³ Z = 8 D_x = 1.286 Mg/m³
 R = 0.034 wR = 0.043

II. formula: C₁₄H₁₂·(C₁₄H₁₁NO₂)₂
 monoclinic, space group: P2₁/n
 a=15.755(4) b=5.771(1) c=18.809(3) Å
 β = 101.84(2)^o
 V=1763.7(6) Å³ Z = 2 D_x = 1.251 Mg/m³
 R = 0.045 wR = 0.050

The unit cell of I contains two independent molecules. The two molecules have similar bond lengths, bond angles and geometry. The nitro group is close to coplanar with the central C=C bond with the two phenyl rings twisted at about 70^o and 30^o from this plane. The central C=C bond length is 1.329(4) Å.

The unit cell of II contains one molecule of *cis*- α -nitrostilbene and half a molecule of *trans*-stilbene per asymmetric unit. The geometry, bond lengths and angles of the *cis*- α -nitrostilbene are close to those found in I. The central C=C bond length is 1.323(4) Å. The nitro group is close to coplanar with the C=C bond with the two phenyl rings twisted at 70^o and 30^o. The *trans*-stilbene molecule is planar with a central C=C bond length of 1.330(4) Å. The crystal is packed with the *trans*-stilbene molecules wedged between layers of molecules of *cis*- α -nitrostilbene. The efficient packing accounts for the stability of II.

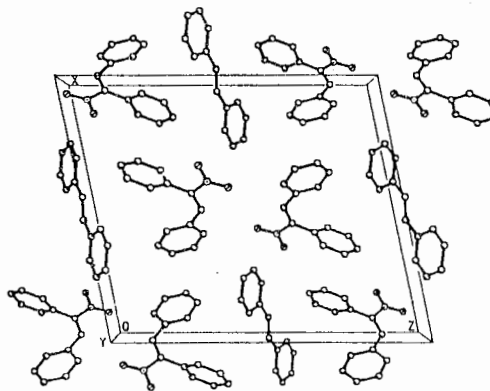


Fig. 1. Crystal packing of II.

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GUEST/HOST-COMPOUNDS WITH ³ NETWORKS OF HYDROGEN BONDED OLIGOMERIC BORATE ANIONS AND BORIC ACID MOLECULES

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The crystalline pentaborates NMe₄[B₅O₆(OH)₄]·0.25 H₂O, NEt₄[B₅O₆(OH)₄], NPhMe₃[B₅O₆(OH)₄] and pipH[B₅O₆(OH)₄] form a series of unique, closely related inclusion compounds with ³ host structures assembled by hydrogen-bonded pentaborate [B₅O₆(OH)₄]⁻ ions (Figure 1 a). The organic cations and water molecules occupy as guest species large straight channels of rectangular cross-section (Figure 1 b).