

06-Crystallography of Organic Compounds

PS-06.04.15 FORMATION OF HYDROGEN-BONDING ADDUCT BETWEEN 1-PHENYL-2-AMINO PYRIMIDINE AND VANILINE, $C_{17}H_{13}N_3O_2$. By I.S. Ahmed Farag and V.B. Rybakov, National Research Centre, Physics department, Cairo, Egypt.

The title compound was prepared by condensation of equimolar quantities of analar vaniline and 1-phenyl-2-amino pyrimidine in absolute ethyl alcohol. Prismatic crystals was obtained with crystallographic data: $a = 12.901(6)$, $b = 19.297(9)$, $c = 6.828(3)$ Å, $\beta = 102.76(2)^\circ$, $V = 1657.9$ Å³, $Z = 4$, F.W. = 291.31. $D_x = 1.17$ g/cm³, space group $P 2_1/n$, $R = 0.038$ and $R_w = 0.036$. The intensity data were collected on an Enraf Nonius CAD-4 computer controlled diffractometer using Mo K_α radiation. The structure was solved by direct method and refined by full matrix least squares using anisotropic temperature factor of all atoms, except for hydrogen atoms, which were treated isotropically. A full discussion was given to explain the occurrence of the condensation process between OH group of vaniline and the heterocyclic N-atom at 5-position of pyrimidine cycle and why this condensation does not take place between the amino group of the pyrimidine compound and the aldehydic group of vaniline to give a schiff base.

PS-06.04.16 CRYSTALS CONTAINING INTERMOLECULAR O-H...O HYDROGEN-BONDED CHAINS ASSISTED BY RESONANCE. By Valerio Bertolasi*, Paola Gilli, Valeria Ferretti and Gastone Gilli, Dipartimento di Chimica and Centro di Strutturistica Diffraattometrica, Università di Ferrara, Via Borsari 46, I-44100 Ferrara, Italy.

We have recently shown [Gilli *et al.* (1993). *Acta Cryst.*, B49, in press] that molecules containing the β -diketone enol fragment $HO-C=C-C=O$ hindered to form intramolecular hbs crystallize by forming h-bonded infinite chains of π -delocalized enolone fragments (intermolecular RAHB: Resonance-Assisted hb). To check whether this is a generally occurring phenomenon we have determined the crystal structures of ten compounds where a β -diketone group is included in a 5- or 6-membered ring. From an analysis of the structures the following general conclusions can be drawn:

- 1) Only one compound is found in the β -diketone form (Fig.1). In the other nine cases the diketone is enolized and forms hbs. This seems to indicate that the enolization process is energetically favoured by the availability of the hb energy.
- 2) The homonuclear resonant β -chain (Figs.2,3) is the preferred packing structure in 8/9 cases, only in the remaining one the chain being interleaved by water molecules (Fig.4).

- 3) O...O distances are in the range $2.59 \leq d(O...O) \leq 2.62$ Å, that is much shorter than the non-resonant hbs [alcohols and carbohydrates: 2.77 ± 0.07 Å (Ceccarelli, C., Jeffrey, G.A. & Taylor, R. (1981). *J. Mol. Struct.*, 70, 255; Kroon, J. *et al.* (1975). *J. Mol. Struct.*, 24, 109)]. Only in one chain the $d(O...O)$ is longer (2.72 Å) because of hb bifurcation.
- 4) The delocalization of the $O=C-C=C-OH$ π -conjugated system is clearly related to the hb shortening.
- 5) IR stretching frequencies, $\nu(OH)$, are decreased from 3600 up to 2450 cm^{-1} confirming the $\nu(OH)$ vs. $d(O...O)$ curve given by Novak [(1974). *Struct. Bonding*, 18, 177]. All data confirm that the intermolecular hb of β -diketone enols is assisted and made stronger by the π -delocalization of the $O=C-C=C-OH$ heterodieneic system in agreement with our previous RAHB model.

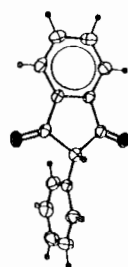


Fig.1. 2-Phenyl-1,3-indandione

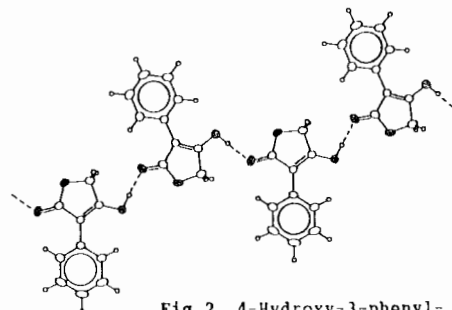


Fig.2. 4-Hydroxy-3-phenyl-2(5H)-furanone

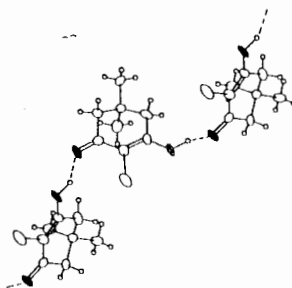


Fig.3. 2-Chloro-5,5-dimethyl-1,3-cyclohexanedione

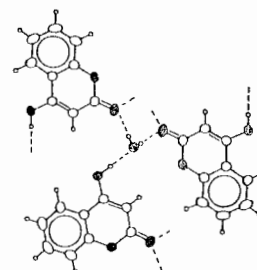


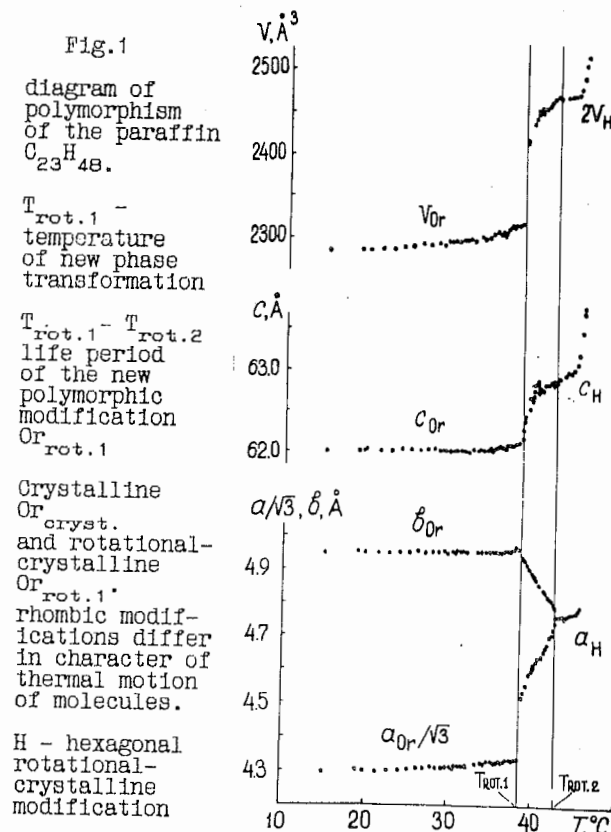
Fig.4. 4-hydroxy-coumarin

PS-06.04.17 NEW PHASE TRANSFORMATION OF THE FIRST ORDER AND NEW POLYMORPHIC MODIFICATIONS OF NORMAL PARAFFINS. By S.K.Filatov*, E.N.Kotelnicova, S.Yu.Chazhengina, St.-Petersburg University, Russia.

By the high temperature X-ray diffraction method there was discovered a jump of volume and some other parameters of normal paraffins C_nH_{2n+2} at temperatures close to the melting point. For homolog $C_{23}H_{48}$ $\Delta V = 4.3\%$ at $T_{rot.1} = 38.5^\circ C$ reflects transition of orthorhombic crystal modification Or_{cryst} to a previously unknown orthorhombic rotational-crystal phase $Or_{rot.1}$, which at $T_{rot.2} = 43^\circ C$ performs a second-order transition to a known hexagonal rotational-crystal modification with melting point at $47^\circ C$. The following model of the process is suggested.

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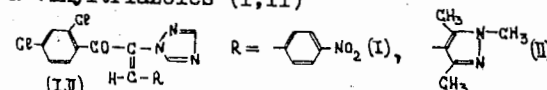
Molecules (aliphatic chains) are packed in the paraffin structure by the principle "a bulge into a hollow", they are located in each other's potential field and perform torsional vibrations around their axes relatively to the fixed equilibrium positions. At heating to $T_{rot.1}$ energy is achieved, at which molecules can escape the potential barrier and take a different orientation. After that molecules continue torsional vibrations, but relatively to positions changing in time and assemblage. The first-order phase transition discovered in paraffins may appear characteristic for other compounds performing transition to rotational-crystal state. The described transformations make paraffins close to liquid crystals.

06.05 - Conformation Analysis

PS-06.05.01 **THE X-RAY ANALYSIS OF TWO NEW N-VINYLTRIAZOLES.** By Malinovsky S.T., Krimer M.Z., Stynghach E.P., Rechter M.A., Zavorotnik V.E. Institute of Chemistry, Academy of Sciences of Moldova. Kishinev, 277028, Moldova.

Among N-vinyltriazoles derivatives some compounds with strong fungicide activity are known. In order to understand the dependence between the activity of these molecules and their structure we have carried out X-ray investigations.

In this paper we give the results of X-ray analysis of two representatives of N-vinyltriazoles (I,II)



Crystal (I) is monoclinic: $a=9,874(1)$, $b=20,341(2)$, $c=8,567(1)$ Å, $\gamma=91,10(1)^\circ$, sp. gr. $P2_1/b$, $R=0,028(835 \text{ ref.})$. Crystal (II) is triclinic: $a=7,634(1)$, $b=10,578(1)$, $c=11,702(2)$ Å, $\alpha=85,91(1)$, $\beta=82,50(1)$, $\gamma=72,13(1)^\circ$, sp. gr. $P\bar{1}$, $R=0,029(1648 \text{ ref.})$. It was determined that the substitution of the 4-nitrobenzene cycle in (I) for the bulky pyrazol cycle in (II), alters the molecular structure as a whole by rotation of the fragment containing the carbonyl group and the chlorobenzene ring by 164° . As a result a C1-N intermolecular contact occurs in (II) equal to 3.46 Å, stabilizing the triazol cycle position. At the same time the Z-configuration is well preserved in (I) and (II).

PS-06.05.02 **CRYSTAL AND MOLECULAR STRUCTURES OF P-CHLOROPHENYL-THIOUREA (I) AND 2,4,6-TRIBROMOPHENYL-THIOUREA (II).** By Mao Zhihua*, Zhou Zhonghua, Den Wengli and Hong Zhou, Department of Chemistry and Center of Analysis and Measurement, Sichuan University, Chengdu, Sichuan, China; Shan Shuxiang, Department of Biological Engineering, Sichuan University, Chengdu, Sichuan, China.

Thiourea and its derivatives have important significance in medicine and biology, from 1950s to now, scientists have been studying their anti tuberculosis activity and toxicity in rats and insects, and found that their biological activities depend upon N-substituted groups in thiourea. The biological activity of some of them are notable and have a widely useful future. Therefore we determined the crystal structures of the title compounds and studied their molecular structures. A colorless bright crystal for (I) and a pale yellow one for (II) both with suitable sizes were used for the measurements. Diffraction data were collected in $\omega/2\theta$ mode on a ENRAF NONIUS CAD4 diffractometer using MoK α radiation. A total of 1666 unique reflections for (I) and 2448 for (II) were collected in

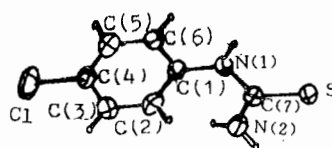


Fig. 1. The perspective view of (I)

a range of $2^\circ \leq \theta \leq 25^\circ$. All calculations were performed on a PDP11/44 computer with SDP program package. The reflections for $I \geq \sigma(I)$ (1330 and 1207 respectively) were used in the measurements and refinements. Both the structures were solved by direct methods. The

crystallographic data are as follows: crystal (I) is monoclinic, space group $P2_1/a$, $a=1.0671(1)$, $b=0.8912(1)$, $c=0.9128(1)$ nm, $\beta=106.85(1)^\circ$, $V=0.8307 \text{ nm}^3$, $Z=4$, $D_c=1.492 \text{ g.cm}^{-3}$, $M_r=186.66$, $\mu=6.325 \text{ cm}^{-1}$, the final $R=0.029$, $R_w=0.031$; Crystal (II) is orthorhombic, space group $Pcab$, $a=0.9997(2)$, $b=0.7876(4)$, $c=2.7920(3)$ nm, $V=2.1984 \text{ nm}^3$, $Z=8$, $D_c=2.35 \text{ g.cm}^{-3}$, $M_r=388.92$, $\mu=84.325 \text{ cm}^{-1}$, the final $R=0.047$, $R_w=0.047$. The max. $\Delta\rho$ are 0.258 e/\AA^3 and 0.530 e/\AA^3 respectively.