06-Crystallography of Organic Compounds

PS-06.04.15 FORMATION OF HYDROGEN-BONDING ADDUCT BETWEEN 1-PHENYL-2-AMINO PYRIMIDINE AND VANILLINE, \( C_{17}H_{13}N_{3}O_2 \) by I.S. Ahmed Farag and V.B. Rybakov, National Research Centre, Physics department, Cairo, E.gypt.

The title compound was prepared by condensation of equimolar quantities of anilin vaniline and 1-phenyl-2-amino pyrimidine in absolute ethanol.

Crystallographic data: \( a = 12.990(6) \), \( b = 19.297(9) \), \( c = 6.828(3) \), \( \alpha = 106.76(2) \), \( \beta = 1657.9 \) \( \text{Å}^3 \), \( Z = 4 \), \( F.W. = 291.31 \). \( D_x = 1.17 \text{g/cm}^3 \), space group \( P 2_1/n \), \( R = 0.038 \) and \( R_w = 0.036 \). The intensity data were collected on a Macor Nonius CAD-4 computer controlled diffractometer using Mo K\( \alpha \) 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 aliphatic group of vaniline to give a schiff base.

![Fig. 1. 2-Phenyl-1,1-indandione](image1)

![Fig. 2. 4-Hydroxy-3-phenyl-215M-furanone](image2)

![Fig. 3. 2-Chloro-5,5-dimethyl-1,1-cyclohexadiene](image3)

![Fig. 4. 4-hydroxy-coumarin](image4)

PS-06.04.16 CRYSTALS CONTAINING INTERMOLECULAR O-H-O HYDROGEN-BONDED CHAINS ASSOCIATED BY RESONANCE.

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We have recently shown Gilioli et al. (1993), Acta Cryst., B49, in prebend that molecules containing the \( \beta \)-diketone enal fragment \( \text{CHO-C-C-C=O} \) can be characterized by an intramolecular H-bond to form an infinite chain of molecules.

![Fig. 1.](image1)

To check whether this is a generally occurring phenomenon we have determined the crystal structures of 10 compounds where a \( \beta \)-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 can be found in the \( \beta \)-diketone form (Fig. 1). In the other nine cases the diketone is hydroxylated and forms H-bonds. This seems to indicate that the hydroxylation process is energetically favored by the availability of the H-bond energy.

2) The hydrogen-bonded \( \beta \)-chain (Fig. 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).


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 \( C_{23}H_{46} \), AV=4.3% at \( T_{\text{cr}1}=38.5^\circ \) reflects transition of orthorhombic crystal modification or to a previously unknown orthorhombic rotational-crystal phase or \( T_{\text{cr}1} \) which at \( T_{\text{cr}2}=13^\circ \) performs a second-order transition to a known hexagonal rotational-crystal modification with melting point at \( 47^\circ \). The following model of the process is suggested.

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

\[
\text{Cl} - \text{O} - \text{C} - \text{CH}_2
\]

\[
\text{R} = \text{CH}_2\text{NO}_2(1), \text{O}_2\text{CH}(2)
\]

Crystal (I). Mono-monoclinic, \(a = 0.974(4), b = 20.341(2), c = 8.567(1)\) Å, \(\beta = 91.07(1)\)°, space group \(P2_1/b\). \(\text{F}_{20}(3), \text{Z} = 4\). Crystal (II) is triclinic, \(a = 7.634(7), b = 10.576(4), c = 11.705(2)\) Å, \(\alpha = 65.91(1), \beta = 92.50(1), \gamma = 72.13(1)\), space group \(P1\), \(\text{Z} = 2\).

It was determined that the substitution of the 4-nitrobenzene cycle in (I) for the bulk pyrazole cycle in (II) alters the molecular structure as a whole by rotation of the fragment containing the carbonyl group and the benzene ring by 164°. As a result a C-H intermolecular contact occurs in (II) equal to 3.46 Å, stabilizing the trisole 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 (1) AND 2, 4, 6-TRIBROMOPHENYL-THIOUREA (II).** By Mo Zhihua*, Zhou Zhonghui, Fan Wengi 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 found that their biological activities depend upon N-substituted groups in thioureas. 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 graphite monochromator Mo Kα radiation. A total of 1665 unique reflections (20(1) and 2348 for (II)) were collected in a range of 2θ < 42°. All calculations were performed on PDP11/44 computer with SDP program package. The reflections for E2sin(θ)/λ (3000 and 3200, respectively) were used in the measurements and refinement. Both the structures were solved by direct methods. The crystallographic data are as follows: crystal (1) is monoclinic, space group \(P2_1/1\). \(a = 0.977(1), b = 0.992(1), c = 0.9128(1), \beta = 91.076(1)\) Å, \(V = 8.3100(7)\) Å³, \(Z = 4\), \(D = 1.482, M = 186.6, \mu = 0.325\) mm⁻¹, the final R = 0.029, Rw = 0.031. Crystal (II) is orthorhombic, space group \(P2_1/b2_1/c2_1\). \(a = 0.9997(7), b = 3.7576(4), c = 3.7576(3)\) Å, \(V = 2.1986(3)\) Å³, \(Z = 4\), \(D = 1.482, M = 186.6, \mu = 0.325\) mm⁻¹, the final R = 0.047, Rw = 0.047. The max. \(\Delta F\) are 0.258 Å⁻¹ and 0.300 Å⁻¹, respectively.

06-05 - Conformation Analysis

**PS-06.05.01 THE X-RAY ANALYSIS OF TWO NEW N-VINYLTRIAZOLES.** By Malcaevu S.T., Kramer M.E., Stupnchuk B.B., Rechter M.A., Zacinchenko V.V.

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