

PS06.00.24 THE X-RAY ANALYSIS OF AN ENAMINONE WITH A BULKY SUBSTITUENT. María Jesús Diáñez, María Dolores Estrada, Amparo López-Castro and Simeón Pérez-Garrido. Instituto de Ciencias de Materiales de Sevilla y Departamento de Física de la Materia Condensada, C.S.I.C.-Universidad de Sevilla. Apartado 1065, 41080 Sevilla, Spain

The structure of 2,3,4-tri-O-benzoyl-N-(2,2-diethoxycarbonylvinyl)- β -L-ramno-pyranosylamine has been studied to determine its conformation, which has aroused interest as an "enaminone" as well as for the bulky substituent. X-ray crystallography results on a few other polarized ethylenes and related compounds have been reported (Diáñez et al., 1985 and 1988). Crystal data are: $C_{35}H_{34}NO_{11}$, $M_r=644.7$, orthorhombic, $P2_12_12_1$, $a=12.300(2)$, $b=29.422(5)$, $c=9.736(2)\text{\AA}$, $V=3523.4\text{\AA}^3$, $Z=4$, $D_m=1.21$, $D_x=1.22\text{Mgm}^{-3}$, $\lambda(\text{MoK}\alpha)=0.7169\text{\AA}$, $\mu=0.085\text{mm}^{-1}$, $F(000)=1356$, $T=293\text{K}$. The structure was solved by direct methods and isotropic refinement by full-matrix least squares methods for non-H atoms (H atoms were included with Uiso but not refined) to a final $R(F)=0.10$ and $R(F^2)=0.08$ for 1589 observed reflections with $I \geq 2\sigma(I_0)$. The resonance system, with distances 1.374 for N-C, 1.386 for C=C, 1.443 and 1.449 for C-C bonds, 1.198 and 1.200 for the two C=O and 1.342 and 1.346 \AA for the C-O bonds, revealed a limited electron delocalization in the carbonylvinylamino group. This group has the Z configuration and is planar (maximum deviation 0.093 \AA) and one of the ethoxycarbonyl group is tilted -0.7° . The C-C distances in the pyranose ring are in the range 1.486-1.546 \AA and the glycosidic C-O linkage are C5-O1=1.428 and O1-C1=1.442 \AA . The exocyclic C-O lengths have a mean value of 1.427 \AA , C-CH₃, 1.514 and C-N, 1.459 \AA . The interior and exterior ring angles are consistent with the expected high degree of tetrahedrality. The molecular conformation of the pyranose ring is a chair 1C_4 with puckering parameters $\theta=10^\circ$, $\phi=91^\circ$, $Q=0.57\text{\AA}$. The substituents confirms the β -L configuration. Packing of the molecule is governed by van der Waals forces. There is one intramolecular H-bond [N1-H...O11=2.546 \AA] which reflects the chelated structure.

PS06.00.25 THE FOLDED CONFORMATION-THE RESULT OF PI-PI-INTERACTIONS? Michael Bolte, Institut fuer Organische Chemie Johann Wolfgang-Goethe-Universitaet Marie-Curie-Str.11 60439 Frankfurt am Main Germany

The so-called folded conformation by which an aromatic ring shields a heterocycle is a well known phenomenon. It was first discovered by NMR (Kopple & Marr, 1967) and later on by X-ray crystallography (e.g. Lin & Webb, 1973) for diketopiperazines. But it can also be found for hydantoines (Fujiwara, Bose, Manhas & van der Veen, 1979), 1,4-dihydropyridines (Iwasaki, Watanabe & Maeda, 1987) and dihydrooxazinones (Bolte, 1995).

We have determined the crystal structures of several bis-lactim ethers, which are important intermediates of a synthetic route to enantiomerically pure amino acids (Schoellkopf, 1983).

Some bis-lactim ethers with aromatic side chains, for which the folded conformation was expected, show this conformation while others do not.

Since the understanding whether a small organic molecule adopts the folded conformation could also be very helpful for the conformational analysis of biomacromolecules like proteins it is necessary to know the reasons for the appearance of this conformation. The careful and attentive inspection of all these crystal structures leads to the conclusion that the main reason whether a molecule adopts the folded conformation are steric interactions. We do not deny that there are attractive pi-pi-interactions between heterocycle and aromatic residue, but more important, and decisive, are steric forces.

References: Bolte, M., (1995). Acta Crystallogr. C51, 2587-2593. Fujiwara, H., Bose, A.K., Manhas, M.S. & van der Veen, J.M. (1979). J. Chem. Soc. Perkin Trans. 2, pp. 653-658. Iwasaki, F., Watanabe, T. & Maeda K. (1987). Bull. chem. Soc. Jpn. 60, 1255-1259. Kopple, K.D. & Marr, D.H. (1967). J. Am. Chem. Soc. 89, 6193-6200. Lin, C.-F., & Webb, L.E. (1973). J. Am. Chem. Soc. 95, 6803-6811. Schoellkopf, U., (1983). Top. Curr. Chem. A109, 65-83.

PS06.00.26 STRUCTURE OF FIVE GUANIDINE DERIVATIVES AND A STUDY ON BINDING OF THESE MOLECULES WITH CALF THYMUS DNA. Kulandavelu Subramanian, Sudha Lakshmanan, Dept. Of Physics, Anna University, Madras-600025, India, Gertraud Koellner and Thomas Steiner, Institute for Crystallography, Freie University Takustrasse 6, D-14159, Berlin, Germany

Spectrophotometric and spectrofluorometric methods were used to study the interaction of five Guanidine derivatives with Calf thymus DNA. The variation of the interaction with different concentration of DNA, keeping the Guanidine concentration constant, was examined. Based on these studies an effort has been made to elucidate the relationship between molecular structure and DNA binding efficiency of these compounds. The half reciprocal plot of the absorption titration data resulted in an intrinsic binding constant (K) of 1.5×10^4 , 0.5×10^4 , 0.8×10^4 , $0.7 \times 10^4 \text{M}^{-1}$ in base pairs for Guanidine(I), Guanidine(II), Guanidine(III), Guanidine(IV) and Guanidine(V) respectively. Hypochromism was suggested to be due to strong interaction between the electronic sites of the binding chromophore and that of the DNA bases. In addition to the decrease in intensity, a small red shift, extensive broadening were also observed in the spectra. The fluorescence data were analysed to construct the binding isotherms and from these isotherms, binding constants were estimated. A plot of r/C_f Vs r gave the binding constant of 4.6×10^4 , $5.14 \times 10^4 \text{M}^{-1}$ for Guanidine(II) and guanidine(III). For Guanidine(I), Guanidine(IV) and Guanidine(V) the Scatchard plots are not linear and this shows that the binding is co-operative. Guanidine(I): $P2_1/c$, $a=7.970(2)$, $b=14.544(3)$, $c=16.502(4)\text{\AA}$, $\beta=100.58(2)^\circ$, $Z=4$, $R=0.0453$, $wR=0.1607$. Guanidine(II): $P1$, $a=7.96(1)$, $b=9.979(2)$, $c=12.033(2)$, $a=86.48(2)$, $\beta=80.29(2)$, $\gamma=77.44(2)^\circ$, $Z=2$, $R=0.0583$, $wR=0.1885$. Guanidine(III): $P2_1/c$, $a=9.211(4)$, $b=14.671(4)$, $c=11.533(4)\text{\AA}$, $\beta=111.14(4)^\circ$, $Z=4$, $R=0.0652$, $wR=0.075$. Guanidine(IV): $Pbca$, $a=14.928(3)$, $b=14.999(2)$, $c=18.952(2)\text{\AA}$, $Z=8$, $R=0.068$, $wR=0.073$. Guanidine(V): Aba_2 , $a=14.978(3)$, $b=16.709(3)$, $c=18.847(3)\text{\AA}$, $Z=8$, $R=0.0529$, $wR=0.0592$.

PS06.00.27 STRUCTURE OF TWO QUINOLONES AND A STUDY ON LASING EFFICIENCY OF THESE COMPOUNDS. Sudha Lakshmanan, Kulandavelu Subramanian, Dept. Physics, Anna University, Madras-600025, India, Gertraud Koellner and Thomas Steiner, Institute for Crystallography, Freie University Takustrasse 6, D-14159, Berlin, Germany

The crystal and molecular structure of two dyes namely (i) 5-(amino)-8-methyl-quinolone monohydrate and (ii) 5-(isopropylamino)-8-methyl-2-quinolone are carried out to understand the dependent of the lasing efficiency on the molecular conformation of these dyes. Quinolone ring system is essentially planar. The crystal structures are stabilised by O-H...O, N-H...O, N-H...N, and C-H...O interactions. Absorption and fluorescence spectra were recorded with these compounds and compared with those of commercial dye. Lasing activity of these compounds has been studied with the help of three dimensional structure of the molecules.

Quinolone (I) [$C_{12}H_{14}N_2O$]: Space group $P2_1/n$ $a=14.117(5)$, $b=8.628(2)$, $c=8.766(2)\text{\AA}$, $\beta=93.91^\circ(1)$, $Z=4$, $V=1065.2(5)$, $D_x=1.26\text{Mgm}^{-3}$, $\mu=0.62\text{mm}^{-1}$. Of the 1692 measured reflections 1573 were observed [$I > 3\sigma(I)$]. The final R-factor $R=0.0631$ and $wR=0.1825$. Quinolone(II) [$C_{13}H_{16}N_2O \cdot H_2O$]: Space group $P\bar{1}$, $a=8.094(2)$, $b=11.647(2)$, $c=13.644(3)\text{\AA}$, $a=96.52(3)$, $\beta=92.87(3)$, $\gamma=106.21(3)$, $Z=2$, $V=1222.6(5)$, $D_x=1.22\text{Mgm}^{-3}$, $\mu=0.61\text{mm}^{-1}$, $R=0.0651$ and $wR=0.1856$.