

## 06-Crystallography of Organic Compounds

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**PS-06.04.03 CONFORMATIONAL VARIABILITY OF ALKENYL LIQUID CRYSTALS.** By J. Siripitavananon\*, Department of Chemistry, University of Chiang Mai, Chiang Mai 50002, Thailand, and D. van der Helm, Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK 73019, USA; M. Schadt, Central Research Units, F.Hoffmann-La Roche and Co.Ltd, CH-4002 Basel, Switzerland.

The compound 1-(4'-cyanocyclohexyl)-trans-4-(1-penten-5-yl)-cyclohexane is a member in a series of compounds showing liquid crystal properties. The compound crystallizes in two different crystal forms. The structure determinations by single crystal X-ray diffraction show different molecular conformations and different molecular packing for the two crystal forms. The molecular packing in form I is a herringbone structure in which the molecules are arranged head-to-tail while the packing in form II is parallel with an head-to-head and tail-to-tail arrangement of the molecules. All 41 possible molecular conformations involving the four aliphatic bonds of the molecule have been investigated by molecular mechanics. The two conformations found in the two crystal forms correspond to the conformations with the lowest calculated energy. The argument is made that another low-energy conformation found in these molecular mechanics studies might not be suitable for liquid crystal formation. Our results support earlier findings reported by one of us which indicate that the bend/splay elastic ratio  $k_{33}/k_{11}$  of liquid crystals is not related with the length/width ratio (L/W) of individual molecules, but with L/W of molecular ensembles.

Crystal data (at  $-110^{\circ}\text{C}$ ):  $\text{C}_{18}\text{H}_{29}\text{N}$ ,  $M_r = 259.4$ , (I) Orthorhombic,  $P2_12_12_1$ ;  $a=10.886(1)$ ,  $b=26.709(3)$ ,  $c=5.5657(8)\text{\AA}$ ,  $V=1618.3\text{\AA}^3$ ;  $z=4$ ;  $R=0.038$ , 1562 observed reflections ( $\text{CuK}\alpha$ ,  $2\theta_{\text{max}}=150^{\circ}$ ) (II) Triclinic,  $\bar{P}1$ ;  $a=6.137(1)$ ,  $b=23.256(4)$ ,  $c=5.989(1)\text{\AA}$ ,  $\alpha=90.07(1)$ ,  $\beta=111.19(2)$ ,  $\gamma=94.38(1)^{\circ}$ ,  $V=794.2\text{\AA}^3$ ;  $z=2$ ;  $R=0.052$ , 2949 observed reflections ( $\text{CuK}\alpha$ ,  $2\theta_{\text{max}}=150^{\circ}$ ).

**PS-06.04.04**

**THE STRUCTURE OF A TRIAZINE DERIVATIVE** By G.D.Nigam\*, Dept. of Physics, S.Karak & C.R.Saha, Dept of Chemistry, Indian Institute of Technology, Kharagpur 721302 India and S.Srinivasan, Dept. of Physics, Indian Institute of Technology, Madras, India.

Dihydrotriazines are of interest on account of their antimalarial and anticancer properties. The copper (II) complex of the title compound was prepared by refluxing Cu (N-ethyl biguanide) with salicylaldehyde. The product was reacted with  $\text{H}_2\text{SO}_4$  (6N) to give the compound ( $\text{C}_{11}\text{H}_{17}\text{N}_5\text{O}\cdot\text{SO}_4\cdot\text{H}_2\text{O}$ ). The compound

crystallized in orthorhombic space group  $Fdd2$  with  $a = 31.346(1)$ ,  $b = 26.838(6)$ ,  $c = 7.295(5)\text{\AA}$  and  $Z = 16$ . The intensities were collected with Enraf-Nonious CAD-4 diffractometer using  $\text{Cu K}\alpha$  radiation fitted with graphite monochromator. The structure was solved by direct methods and was refined to a final  $R = 0.039$  for nonhydrogen atoms using 1191 reflections with  $I > 3\sigma(I)$ . The programs SHELX86 and SHELX76 were used. The sulphate and the triazine rings are bridged through N-H...O hydrogen bonds. The oxygen atom of the water forms O-H...O bonds with sulphate moieties of two neighboring units and O...H-N hydrogen bonds with NH-groups of the two triazine rings of two other neighboring units. The six-membered homocycle ring is planar and the triazine ring is in half-chair conformation. The dihedral angle between two rings is  $88.5^{\circ}$ .

**PS-06.04.05 MOLECULAR AGGREGATION OF CATIONIC SURFACTANTS AND AROMATIC COMPOUNDS**

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It has been found that some cationic surfactants such as cethyl-, myristyl-, lauryl- and decyltrimethylammoniumbromide (CTAB, MTAB, LTAB and DTAB, respectively) exhibit very high viscoelasticity even in very dilute solutions when some aromatic compounds are added to the solution. An electron microscopic study revealed that such high viscoelasticity is caused by the entanglement of enormously elongated rod-like micelles. Recently single crystals were obtained from solutions containing the surfactant and aromatic compounds. The crystals obtained are CTAB[I], CTAB/m-cyano-phenol[II], CTAB/p-cresol[III], CTAB/acridine[IV], CTAB/o-iodo-phenol[V-C], MTAB/o-iodophenol[V-M], LTAB/o-iodophenol[V-Lo, V-Lm polymorphism], DTAB/o-iodophenol[V-D] and CTAB/ hydro-quinone[VI]. In order to analyse the rod-like micelles, the structures of the above crystals were determined. Crystal data are summarized in Table 1. It is found that the aromatic compound and the surfactant molecules make an elemental pattern, and that these patterns stack as flat layers or pleated layers (Fig. 1). As a result, the aggregation modes can be classified into three types. The layers are stacked in an antiparallel way in Type 1 and 3. In Type 2 pairs of antiparallel sheets alternate with other antiparallel pairs having a different orientation to form stacks. Such a characteristic structure seems to be closely related to the structure of micelles.

Table 1. Crystal data

| Type  | a/Å       | b/Å        | c/Å        | $\beta^{\circ}$ | $V/\text{\AA}^3$ | Z          |
|-------|-----------|------------|------------|-----------------|------------------|------------|
| I     | 52.072(7) | 7.260(2)   | 5.638(1)   | 93.78(1)        | 2128.8(8)        | $P2_1/a$ 4 |
| II    | 33.767(3) | 7.470(1)   | 5.575(1)   | 107.076(7)      | 1344.2(6)        | $P2_1$ 2   |
|       | 32.863    | 7.470      | 5.575      | 92.19           |                  |            |
| III   | 32.303(3) | 7.4737(5)  | 5.5743(5)  | 92.19(1)        | 1344.8(3)        | $P2_1$ 2   |
| IV    | 32.066(2) | 7.4014(7)  | 5.5898(4)  | 91.602(8)       | 1326.1(2)        | $P2_1$ 2   |
| V-C   | 17.482(4) | 8.409(3)   | 40.052(5)  | 90.0            | 5888(2)          | $Pna2_1$ 8 |
| V-C*  | 17.231(2) | 8.5132(6)  | 39.167(4)  | 90.0            | 5745(1)          | $Pna2_1$ 8 |
| V-M*  | 17.288(3) | 8.292(6)   | 37.337(13) | 90.0            | 5351(1)          | $Pca2_1$ 8 |
| V-Lo* | 17.239(4) | 8.286(1)   | 35.308(16) | 90.0            | 5043(3)          | $Pca2_1$ 8 |
| V-Lm* | 8.250(5)  | 32.969(28) | 9.066(5)   | 94.51(5)        | 2458(3)          | $P2_1/n$ 4 |
| V-D*  | 8.302(3)  | 30.349(3)  | 9.020(2)   | 95.52(2)        | 2262.0(9)        | $P2_1/n$ 4 |
| VI    | 8.3546(9) | 52.182(2)  | 7.170(8)   | 109.210(8)      | 2951.7(5)        | $P2_1/n$ 4 |

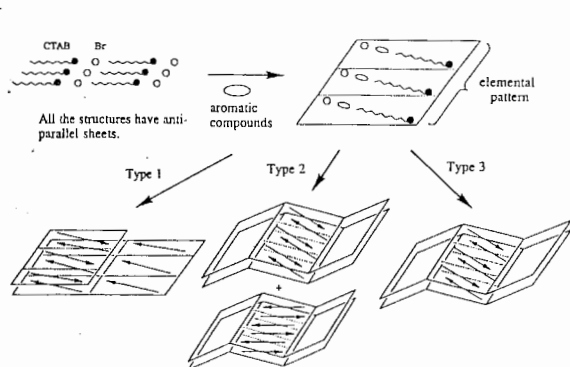
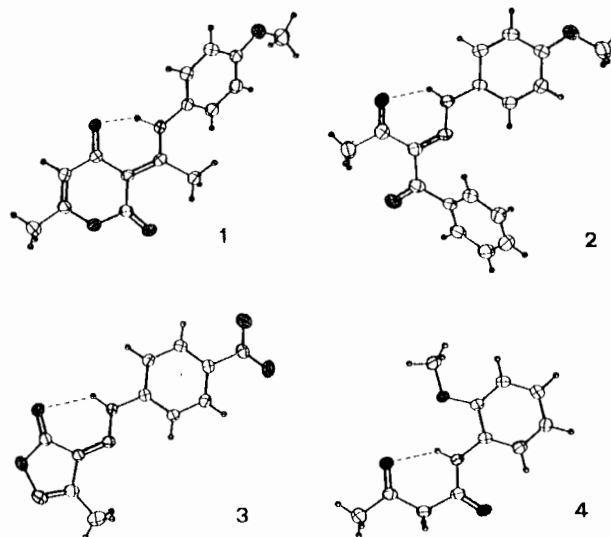


Fig. 1 Model of Crystal Types



**PS-06.04.06 INTRAMOLECULAR N-H...O HYDROGEN BOND ASSISTED BY RESONANCE.** By Valeria Ferretti<sup>\*</sup>, Valerio Bertolasi, Luca Nanni and Paola Gilli, Dipartimento di Chimica and Centro di Strutturistica Diffraattometrica, Università di Ferrara, Via Borsari 46, I-44100 Ferrara, Italy.

The phenomenon of RAHB (Resonance Assisted hb) has been so far studied essentially in the intra- and inter-molecular hb of the O=C-C=C-OH group (Bertolasi *et al.* (1991). *J. Am. Chem. Soc.*, 113, 4917; Gilli *et al.* (1993). *Acta Cryst.*, B49, in the press). It should be, however, generalizable to other heteroconjugated systems such as the O=C-C=C-NH enamionone fragment.

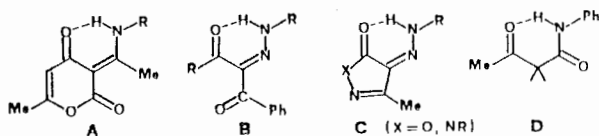
Accordingly we have undertaken the crystal structure determination of molecules containing the enamionone fragment (class A, 4 compounds) and related diketo-hydrazone (class B, 11 compounds) and ketohydrazone (class C, 3 compounds) fragments. As a reference point, the structure of another compound able to form hb but unable to assist it by resonance (D) has been determined. All compounds studied form the expected 6-membered intramolecular N-H...O hb but with different d(N...O) distances.

Class A:  $2.51 \leq d(\text{N}\cdots\text{O}) \leq 2.56$  Å, Fig.1

Class B:  $2.56 \leq d(\text{N}\cdots\text{O}) \leq 2.61$  Å, Fig.2

Class C:  $2.78 \leq d(\text{N}\cdots\text{O}) \leq 2.92$  Å Fig.3

Class D:  $d(\text{N}\cdots\text{O}) = 2.748$  Å Fig.4



The following points are to be remarked:

- 1) The rather long distance observed for D (2.748 Å) is typical of an usual intramolecular N-H...O bond.
- 2) When hb donor and acceptor atoms are part of a  $\pi$ -conjugated system the hb should be shortened by the resonance. This should happen in classes A, B and C but actually happens only in A and B because of the steric restraints caused by the 5-membered ring in C.
- 3) The delocalization of the  $\pi$ -conjugated systems is greater the shorter the hb is.
- 4) IR and <sup>1</sup>H-NMR spectroscopic data of the aminic proton are in perfect agreement with the observed pattern of N...O distances.
- 5) In conclusion: The behaviour observed for the O-H...O hb formed by O=C-C=C-OH  $\beta$ -diketone enols and interpreted by us through the RAHB model is essentially reproduced by other heterodienes (O=C-C=C-NH and O=C-C=C-N-NH) suggesting that it will hold for all hbs forming heteroconjugated systems A-C-(C=C)-N-DH, N=O,1,...

**PS-06.04.07 A GENERALIZED MODEL FOR THE STRONG O-H...O HYDROGEN BOND.** By Paola Gilli<sup>\*</sup>, Valerio Bertolasi, Valeria Ferretti and Gastone Gilli, Dipartimento di Chimica and Centro di Strutturistica Diffraattometrica, Università di Ferrara, Via Borsari 46, I-44100 Ferrara, Italy.

In spite of the extraordinary wealth of data on the O-H...O hb, the true chemical reasons determining its strength remain widely unknown. So far it was believed that such strong bonds were to be related either to severe intramolecular strain or to systems containing -O-H...O- or =O-H<sup>+</sup>...O= groups (Jeffrey, G.A. & Saenger, W. (1991). *Hydrogen Bonding in Biological Structures*, p.112. Berlin: Springer). It has been recently discovered, however, that there are very strong -O-H...O- bonds (up to  $d(\text{O}\cdots\text{O}) = 2.42$  Å) in non-strained neutral molecules where the two O atoms are connected by a system of  $\pi$ -conjugated double bonds. Such bond has been addressed to as RAHB (Resonance Assisted Hydrogen Bonding) (Gilli, G., Bellucci, F., Ferretti, V. & Bertolasi, V. (1989). *J. Am. Chem. Soc.*, 111, 1023-1028; Gilli, G. & Bertolasi, V. (1990). *The Chemistry of Enols*, Z. Rappoport ed., ch.13. New York: John Wiley; Bertolasi, V., Gilli, P., Ferretti, V. & Gilli, G. (1991). *J. Am. Chem. Soc.*, 113, 4917-4925; Gilli, G., Bertolasi, V., Ferretti, V. & Gilli, P. (1993). *Acta Cryst.*, B49, in the press).

It is clear that previous theories based on the preminent role of positive and negative charges need to be revised. The new model we suggest is based on the idea that very short O-H...O bonds must overcome a very strong O...O repulsion which cannot be compensated by the electrostatic attraction which is known to cause weak or medium range hbs (Umeyama, H. & Morokuma, K. (1977). *J. Am. Chem. Soc.*, 99, 1316-1333). This imply that very strong O-H...O bonds must have a relevant covalent component or, in VB terms, be a mixture of the two canonical forms A: -O-H...O= and B: =O-H...O<sup>+</sup> with the greatest possible contribution of form B. Usually, the contribution of B is small because dissociation of charges enhances its energy with respect to A. Any chemical situation able to make comparable the energies of A and B is then the origin of the short O-H...O bond.

It is easy to show that A and B energy equalization can be produced only by three chemical situations:(i) by