06-Crystallography of Organic Compounds

PS-06.04.03 CONFORMATIONAL VARIABILITY OF ALKYNYL LIQUID CRYSTALS. By J. Siripatrasarn*, Department of Chemistry, University of Chiang Mai, Chiang Mai 50201, Thailand, and D. van der Heij, 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-cyanophenyl)-1-trans-4-1-penten-5-vinyl-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 helix/helical structure in which the molecules are arranged head-to-tail while the packing in form II is parallel with an end-to-end 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 the 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/spin elastic ratio \( \frac{k_{33}}{k_{11}} \) of liquid crystals is not related with the length/width ratio \( \frac{L}{W} \) of individual molecules, but with \( \frac{L}{W} \) of molecular ensembles.

Crystal data at \(-110\text{C}: C_{11}H_{12}N_{2}O, M=280.4, \)

(1) Orthorhombic, \( P2_{1}2_{1}2_{1} \), \( a=10.0863(1) \), \( b=25.7093(3) \), \( c=5.8657(4) \), \( V=1619.32(5) \), \( Z=2 \), \( R=0.028 \), 1822 observed reflections \( \theta_{\text{max}}=30.0^\circ \).

(2) Triclinic, \( P1 \), \( a=6.1370 \), \( b=23.2464 \), \( c=8.8669 \), \( \alpha=90.07(1) \), \( \beta=111.19(1) \), \( \gamma=94.36(1) \), \( V=270.2 \), \( Z=2 \), \( R=0.052 \), 1294 observed reflections \( \theta_{\text{max}}=30.0^\circ \).


Dihydriodizines are of interest on account of their analgesic 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 \( \text{H}_{2}\text{SO}_{4} \). The compound crystallized in orthorhombic space group \( \text{P}2_1\text{P}2_1\text{P}2_1 \) with \( a=31.346(4) \), \( b=26.183(4) \), \( c=7.255(5) \). The intensities were collected with Enraf-Nonius CAD-4 diffractometer using Cu K\( \alpha \) radiation filtered with graphite monochromator. The structure was solved by direct methods and was refined to a final \( R=0.039 \) for non-hydrogen atoms using 1197 reflections with \( I>3\sigma(I) \). The programs SHELX86 and SHELX76 were used. The sulphate and the triazine rings are bridged through N\( \cdots\)O hydrogen bonds. The oxygen atom of the water forms O\( \cdots\)O bonds with sulphate anions of two neighboring units and O\( \cdots\)H-N hydrogen bonds with NH-groups of the two triazine rings of two other neighboring units. The six-membered homocyclic ring is planar and the triazine ring is in half-chair conformation. The dihedral angle between the rings is \( 88.6^\circ \).

PS-06.04.05 MOLECULAR AGGREGATION OF CATIONIC SURFACANTS AND AROMATIC COMPOUNDS. T.Kitamura*, H.Uekusa and Y.Ohashi, Department of Chemistry, Tokyo Institute of Technology, Japan; N.Imura and H.Hirata, Niigata College of Pharmacy, Japa.

It has been found that some cationic surfactants such as cetyl-, 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 \( \text{CTAB} \), \( \text{CTAB}-\text{cyanophenol} \), \( \text{CTAB}-\text{picrusol} \), \( \text{CTAB}-\text{acetic acid} \), \( \text{CTAB}-\text{iodo-phenol} \), \( \text{MTAB}-\text{iodophenol} \), \( \text{LTAB}-\text{iodophenol} \), \( \text{DTAB}-\text{iodophenol} \) and \( \text{CTAB}-\text{hydroquinone} \). In order to analyse the rod-like micelles, the structures of the above crystals were determined. Crystal data are summarized in Table I. It is found that the aromatic compound and the surfactant molecules make an elementary 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 I 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.

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<th>Table 1. Crystal data</th>
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Fig. 1. Model of Crystal Types

The phenomenon of RABH (Resonance Assisted Hydrogen Bond) has been so far studied essentially in the intra- and intermolecular HB of the O=C-C=O group (Bertolasi et al. 1989). J. Am. Chem. Soc., 111, 4917; Gilli et al. (1991). Acta Cryst., B47, in the press). It should be, however, generalizable to other heteroconjugated systems such as the O=C-C=NR enamidine fragment.

Accordingly we have undertated the crystal structure determination of molecules containing the enamidine fragment (class A, 4 compounds) and related diketohydrazone (class B, 11 compounds) and ketoketohydrazone (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 distances (Fig. 1).

Class A: B(119) = 0.78, A(12) = 1.80 A, Fig. 1
Class B: B(119) = 0.78, A(12) = 1.80 A, Fig. 2
Class C: B(119) = 0.78, A(12) = 2.92 A, Fig. 3
Class D: B(119) = 0.78, A(12) = 2.74 A, Fig. 4

The following points are to be remarked:

1) The rather long distance observed for B (2.94 A) is typical of an usual intramolecular N-H-O bond.

2) When HB donor and acceptor atoms are part of a N-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 of the 5-membered ring in C.

3) The de-localization of the N-conjugated systems is greater the shorter the HB is.

4) IR and 1H-NMR spectroscopic data of the amine proton are in perfect agreement with the observed pattern of N-O distances.

5) In conclusion: The behavior observed for the O-H=O HB formed by O=C-C=O p-diketone enols and isolated by us through the RABH model is essentially reproduced by other heterocycles (O=C-C=NR and N=C=C=NR) suggesting that it will hold for all HB forming heteroconjugated systems X-Y=C=C=Z, N-O=O, 1,...

PS-06.44.06 INTRAMOLECULAR N-H-O HYDROGEN BOND ASSISTED BY RESONANCE. By Valeria Ferretti, Valerio Bertolasi, Luca Guidi and Paolo Gilli, Dipartimento di Chimica and Centro di Strutturistica Diffarattometrica, Università di Ferrara, Via Borsari 46, I-44100 Ferrara, Italy.


It is clear that previous theories based on the prominent role of positive and negative charges need to be revised. The new model we suggest is based on the idea that very strong 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 H-bonds (Umemiya, H. & Morokuma, K. (1977). J. Am. Chem. Soc., 99, 1318-1333).

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-O and A: O-H=O-O 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 X 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