## 06-Crystallography of Organic Compounds



### PS-06.04.12 FLUORINE ATOM IN AN H-BOND SYSTEM, CAN WE DRAW BASIC RULES ABOUT ITS BEHAVIOR?

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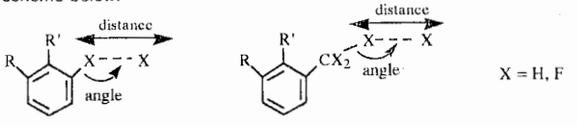
The fluorine atom is the smallest and the most highly electronegative member in the halogen family[1]. Since fluorine does not behave in the same way as the other halogen atoms when it is in a compound, it is difficult, if not impossible, to predict its behavior.

The purpose of our work is to study the behavior and the influence of a fluorine atom when it is interacting with a hydrogen atom in an adjacent molecule. In this work we selected some small organic compounds and investigated the H---F distance and the linearity of the X-H---F (X=C, N) group of atoms to see if there are any basic rules of behavior that could be identified. Our study includes three main groups of molecules. The first group includes molecules that have only C,H and F atoms. The second contains molecules that have only C and H atoms, and the third includes molecules that have C,H,F and in addition, O and/or N atoms. A description of the distances and the angles that we investigate at are shown in the scheme below.




This work will include examples from each of the three groups above that we studied in order to answer the question in the title of this abstract.

1. Pauling, L., *J. Am. Chem. Soc.*, 51, 1010 (1929).
*(Supported by NIH grants GM44360 and CA10925)

### PS-06.04.13 PYRIDINIUM PICRATE—THE CRYSTAL AND MOLECULAR STRUCTURES OF PHASES I AND II. CORRECTION OF THE STRUCTURE REPORTED FOR PHASE I. STUDY OF THE PHASE TRANSFORMATION.

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Pyridinium picrate, $C_5H_6N^+.C_6H_2N_3O_7^-$, is a simple organic salt which almost fifty years ago was reported to exist in two crystalline phases, one phase being stable below 70°C and the other between 70°C and the melting point of 165°C (Kofler, A. (1944). *Z. Elektrochem.* **50**, 200-207). The crystal structure of the lower-temperature Phase I has been reported at room temperature, studied by two-dimensional methods (Talukdar, A. N. & Chaudhuri, B. (1976). *Acta Cryst.* B**32**, 803-808). We were led to reinvestigate the system by a number of unusual features in Kofler's description of the phase behaviour. Single crystals of Phase I were grown from solution and those of Phase II from the melt. We have determined the structure of both phases, including analysis of the thermal motion of the picrate ions, which was found to be appreciably larger in Phase II than in Phase I. To our surprise (because there were no obvious indications of error), the reported crystal structure of Phase I was wrong; the error was caused by confusion between a centre and two-fold screw axis in projection down [010], thus being similar to those corrected in the 1950's for the structures of ß-selenium (Marsh, R. E., Pauling, L. & McCullough, J. D. (1953). *Acta Cryst.* **6**, 71-75) and *p*-nitroaniline (Donohue, J. & Trueblood, K. N. (1956). *Acta Cryst.* **9**, 960-965). The packing units in the two phases of pyridinium picrate are nearly identical and consist of hydrogen-bonded cation-anion pairs. These are packed in stacks, with the ion-pairs superimposed in parallel array in Phase I whereas those in Phase II are antiparallel; the transition between the two phases cannot therefore be expected to be single crystal to single crystal, as indeed it is not. Differential scanning calorimetry and variable-temperature powder X-ray diffraction photography show that the phase transition is first order and occurs at 110°C. Kofler appears to have been misled by a colour change in the Phase I crystals at 70°C, which we have also observed but cannot explain. The DSC measurements give $\Delta H_{trans}$ = 6.8 kJ/mol and $\Delta H_{fus}$ = 31.2 kJ/mol. Remarkably, the transition has proved not to be reversible under our experimental conditions; for example, Phase II crystals remain unchanged after 24 hours at 80°C. We do not have an explanation for the lack of reversibility other than giving it the conventional description of 'large hysteresis'. We have also measured cell dimensions as a function of temperature for both phases, and this makes possible a prediction of the approximate form of the P-T phase diagram.

The details of the structure determinations (both at 298 K) are: *Phase I* (stable up to 383 K): $M_r$ = 308.22, λ(Mo Kα) = 0.71069 Å, F(000) = 632, yellow laths, monoclinic, μ(Mo Kα) = 0.95 $cm^{-1}$, $P2_1/c$, $a$ = 12.132 (2), $b$ = 3.791(1 ), $c$ = 26.634(3) Å, ß = 92.54 (5)°, V = 1223.8 $Å^3$, Z = 4, $D_m$ =1.62 (flotation at 298 K), $D_x$ = 1.67 g $cm^{-3}$, $R_{int}$ = 0.0167 (based on 25 pairs of equivalent reflections), $R_F$ = 0.0435, $R_W$ = 0.0387 (based on 1645 independent reflections with F > 3σ(F)). *Phase II* (stable above 383 K): $M_r$ = 308.22, λ(Mo Kα) = 0.71069 Å, F(000) = 632, yellow prisms, triclinic, μ(Mo Kα) = 0.90 $cm^{-1}$, $P1bar$, $a$ = 10.130 (2), $b$ = 8.968(2 ), $c$ = 7.232(1) Å, α = 86.43 (5)°, ß = 80.29 (5)°, ß = 89.89 (5)° (this cell is reduced); V = 646.3 $Å^3$, Z = 2, $D_m$ = 1.60 (flotation at 298 K), $D_x$ = 1.58 g $cm^{-3}$, $R_F$ = 0.0671, $R_W$ = 0.072 (based on 1478 independent reflections with F > 3σ(F)).

### PS-06.04.14 THE BIOLOGICAL NONEQUIVALENCE OF POLYMORPHS AND THE STRUCTURAL MEMORY OF THEIR SOLUIONS.

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The polymorphism of crystals is a new perspective trend in drug design. The examples of biological inequivalence of the polymorphs of the substances used as drugs are discussed and some possible explanations of such difference in biological activity are given. One of the most obvious explanations is the difference between the molecular agglomerates which are present in crystals. The cooperative effect of molecular packing can fasten the detailes of molecular conformation. Sometimes after dissolution of a substance such agglomerates or some fragments of them occur in the solution at least temporarily.

Specifically two crystal forms of 6-methyluracil considerably differ in the antioxidant effect of their solutions. X-ray data show that the cyclic dimers formed by a pair of NH...O=C bonds occur in both of them. However, in the form I the dimers are united by single H-bonds and wavy layers arise as a result. In the form II the dimers are joined into ribbons using pairs of H-bonds. It is very likely that hydrated dimers predominate in the solution of the crystals I, but rather long fragments of ribbons occur in the solution of the crystal II. Slightly different molecular conformations are to exist in the agglomerates of this two types. Thus, we obtain a probable explanation of the biological inequivalence of two polymorphs.

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