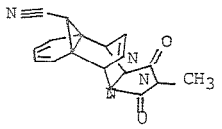
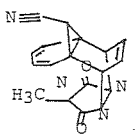
04.4-05 SIMULTANEOUS DOUBLE N-INVERSION IN THE SOLID STATE? By M. Kaftory, Department of Chemistry, Israel Institute of Technology, Haifa, Israel.

The crystal structures of endo(I) and exo(II) adducts of 11-cyano 1,6-methano[10]annulene with 4-methyl-1,2,4-triazoline-3,5-dione have been elucidated by X-ray diffraction methods.



I



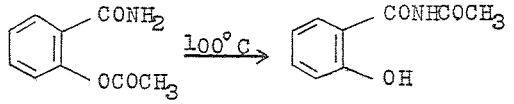
II

The isomer endo is orthorhombic, a=13.318(7), b=9.516(5), c=10.683(6) Å, space group Pnma, Z=4. The molecule occupies the mirror special position. The refinement converged to R=0.064 for 1054 observed reflections. The isomer exo is orthorhombic, a=9.979(5), b=7.031(4), c=9.094(5) Å, space group $Pmn2_1$, Z=2. The molecule occupies the mirror special position. The refinement converged to R=0.058 for 632 observed reflections. Upon heating to ca. 175°C the isomer exo transforms into the isomer endo, as it was proved by powder patterns. Both isomers melt at 195°C. Such a transformation might occur only by a simultaneous double N-inversion and this is the first example for such a process. Yet, there is no clear evidence that the transformation occurs in the solid state, and the possibility of surface melting and transformation in the liquid state can not be excluded.

The isomerisation process involves, in essence, the formation of a chemical bond between the amide nitrogen and the acetyl carbon atom. The conformation of the reactant molecule (I) is such that the amide group and the acetyl group make angles of 40° and 77° respectively with the plane of the benzene ring. The product molecule (II), on the other hand, is virtually planar. Thus the process involves, in addition to the migration of the acetyl group, large conformational changes. This may explain why a single crystal of the reactant breaks up into a polycrystalline product. Within the reactant molecule (I) there is a short contact of 3.27 Å between the reactant centres. Between screw-related molecules of (I) the N...C distance is 3.88 Å, while between glide-related molecules it is 3.91 Å. Thus, while the intra-molecular separation is the smallest, even the inter-molecular separations are within the range in which solid state reactions are known to take place (See for example, Paul and Curtin, Acc. Chem. Res. (1973) 6, 217). The intramolecular process seems to involve the least movement of the atoms, followed by the inter-molecular process involving glide-related molecules. Thus, from structural considerations, while other processes cannot be entirely ruled out, the intra-molecular mechanism appears most likely.

04.4-06 SOLID STATE ISOMERISATION OF O-ACETYLSALICYLAMIDE TO N-ACETYLSALICYLAMIDE. AN X-RAY CRYSTALLOGRAPHIC STUDY OF THE ISOMERS. By V.Mohan Rao and H.Manohar, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012, India.

O-Acetyl salicylamide (I), on heating above 100°C in the solid state, is reported to undergo structural rearrangement to form N-acetyl salicylamide (II).



(I) (II)

The isomerisation has been studied in the solid state (and in solution) employing spectroscopic and thermal techniques (Gordon, Tetrahedron (1967) 23, 863). In an attempt to understand the mechanism of the process at the structural level, crystal structure analyses of I and II have been undertaken.

The crystal data are: (I) Monoclinic, a= 8.155(5), b=8.571(2), c=13.092(3) Å, β=99.54 (5)°, space group $P2_1/c$, Z=4. (II) Triclinic, a=4.566(9), b=10.043(8), c=9.340(9) Å, α=94.45 (7), β=94.23(7), γ=97.22(6)°, space group $P\bar{1}$, Z=2. The structures were solved by direct methods and refined by least-squares procedures using 1604 and 1148 diffractometer data to R-values of 0.076 and 0.062 respectively.

04.4-07 THE CRYSTAL STRUCTURES OF N-SALICYLIDENEANILINES AND THEIR CHROMOTROPIC PROPERTIES. By S.V.Lindeman, V.E.Shklover and Yu.T. Struchkov, Nesmeyanov Institute of Organo-Element Compounds, Academy of Sciences, Moscow, USSR.

Crystals of N-salicylideneanilines possess photochromic or thermochromic properties. We carried out an X-ray study of α_T- and α_2-forms of N-salicylidenepentafluoroaniline (I and II), α-form of N-salicylidene-4-bromoaniline (III) and β-form of N-salicylidene-4-chloroaniline (IV). In all cases the intramolecular hydrogen bond O-H...N is found. In photochromic crystals I-III molecules have a nonplanar structure. The analysis of crystal packing in I-IV and N-salicylideneanilines studied before (e.g. Bregman et al., J. Chem. Soc. (1964) 2086) shows that for thermochromic β-forms the stacking structure is characteristic. In crystals of photochromic α-forms structure patterns may be formally distinguished which can be converted into stacks by small changes of molecular conformation. A possible mechanism of chromotropic interconversions in N-salicylideneanilines is proposed on the basis of intermolecular charge transfer complexes (ICTC). The thermochromic crystals have been considered as an equilibrium mixture of tautomers forming corresponding ICTC (the equilibrium is temperature dependent). In photochromic crystals UV-irradiation causes tautomerisation with the change of molecular conformation and formation of ICTC (although the crystals I and II are already built according to ICTC type).