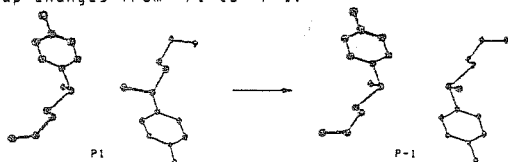


04.4-2 STUDIES OF A SOLID STATE RACEMIZATION REACTION. By R. Norrestam & B.W. Christensen, Chemistry Dept. B and Inst. of Organic Chemistry, The Techn. Univ. of Denmark, DK-2800 Lyngby, Denmark

Certain crystalline organic sulphonium salts, which racemize in the solid state, preserve their crystallinity during the racemization reactions. The reaction rate constants show that the solid state reactions can be almost completely inhibited by cooling down the crystals to below 200 K.

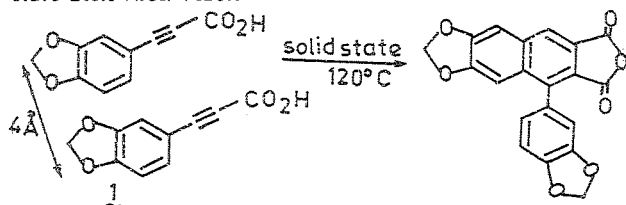
Determinations of the crystal structures by x-ray diffraction techniques of two such salts showed that the final reaction products, the racemates, were ordered. From the structural model of the racemate of one of these salts, the triclinic form (space group P-1) of methyl-butyl-tolyl-sulphonium trinitrobenzenesulphonate, it was possible to derive a well ordered model of the non-racemized specimen (space group P1). The results show that the racemization reaction mainly involves the migration of a sulphonium methyl substituent on one of the two symmetry independent sulphonium ions (the P1 structural model). In this way, the two sulphonium ions become related by inversion symmetry and the space group changes from P1 to P-1.



The results of the studies of 5 intermediate reaction products, using data collected from the same crystal, will be presented.

04.4-3 A NOVEL SOLID STATE DIELS-ALDER REACTION. By Gautam R. Desiraju* and K.V. Radha Kishan School of Chemistry, University of Hyderabad, Hyderabad 500 134, India.

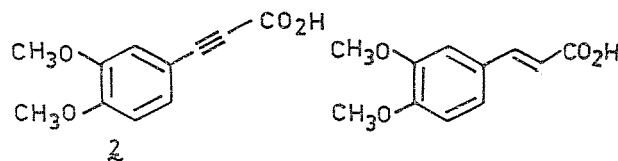
3,4-Methylenedioxy and 3,4-dimethoxy phenylpropionic acids (1 and 2) crystallise with short axes of 4 Å. This highly overlapped packing results in a close approach of triple bonds in adjacent molecules. This orientation of molecules ensures that diene and dienophile components in neighbouring molecules may participate in an intermolecular solid state Diels-Alder reaction.



The crystal structures of acids 1 (P1, Z = 2, a = 3.807, b = 10.297, c = 10.995 Å, α = 84.07, β = 96.46, γ = 98.13°, R = 0.056, 745 reflections) and 2 (P1, Z = 2, a = 3.891, b = 11.361, c = 12.089 Å, α = 112.5, β = 92.53, γ = 96.12°, R = 0.040, 1152 reflections) were solved with the programs MULTAN 80 and SHELXS-86 respectively. The complicating feature in these structure determinations was the presence of

a reflection of intensity around 0.6 F(000) indicating a sheet structure.

The choice of these compounds was a deliberate one, involving an understanding and appreciation of weak intermolecular C-H...O interactions. The crystal structure of 1 was, in fact, predicted to have a 4 Å - short axis on the basis of the 4 Å axis in the related 3,4-methylenedioxy cinnamic acid (Ar-CH=CH-COOH) since, in general, it was expected that for such planar aromatic compounds, a higher C:H ratio would result in a greater tendency for adoption of the 'graphitic' 4 Å-structure. Surprisingly, 3,4-dimethoxycinnamic acid does not adopt the 4 Å-structure. Perhaps, the reduction of two hydrogen atoms in going from the cinnamic to the corresponding propiolic acid, 2, is sufficient to cause a change in the structure type from non-4 Å to 4 Å.

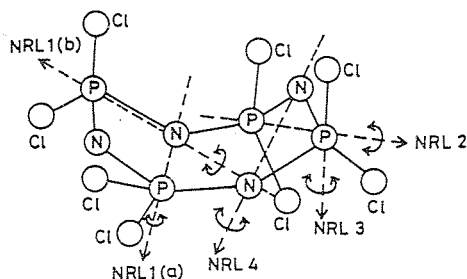


These are examples of systematic crystal structure prediction or crystal engineering and the technique is expected to be useful in designing organic materials for a particular property or reactivity pattern.

04.4-4 INTRAMOLECULAR MOTION AND CONFORMATIONAL ISOMERIZATION: STRUCTURE OF OCTACHLOROCYCLOPHOSPHAZENE : By G. S. Murthy, T. N. Guru Row and K. Venkatesan, Department of Organic Chemistry, Indian Institute of Science, Bangalore-560012; Physical Chemistry Division, National Chemical Laboratory, Poona - 411008, India.

The thermally induced solid-state transformation of octachlorocyclophosphazene (P₄N₄Cl₈) from boat (K-form) to chair form (T-form) by heating the K-form to about 70°C has been reported earlier and their crystal structures determined (Hazekamp, R; Michelsen, T & Vos, A.; Acta Cryst, 1968, B24, 707-713). In the K-form the molecule occupies the special position 4 in the space group P4₂/m whereas in the T-form it is at 1 in the same space group. The possible correlation between the thermal motion and conformational isomerization has been investigated in the structure of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate (Young, Q.C; Richardson, M. F. & Dunitz, J.D; J. Am. Chem. Soc, 1985, 107, 5535 - 5537). The title compound turns out to be another favourable case for temperature variable crystallographic studies. K-form: a=b=10.845(1), c=5.965(1)Å, Z=2; R-factor; 0.032 for 25°C data, 0.037 for 40°C data and 0.028 for 55°C. T-form: a=b=15.320(2), c=5.992(1)Å; Z=2; R-factor 0.065. Based on observations at different temperatures under polarizing microscope, differential scanning calorimetry and rotation photographs the transformation is found to be single crystal to single crystal and the DSC measurements show it to be a second order in nature and irreversible. Molecular motion was analysed

for the K-form in terms of T and L tensors for the rigid-body motions of the molecule as a whole as well as for the internal motions. The nonrigid-body librations analysed are NRL1, NRL2, NRL3 and NRL4 (Fig.). Incorporation of NRL2 and NRL4 produce good agreement between the observed and calculated U_{11} 's reducing the R-value to 3.5% from 23.0% for the 25°C data and 2.3% from 21.9% for the 40°C data. The librational amplitudes NRL2 and NRL4 which correspond to the motions of N and PCl_2 groups respectively increase with temperature. The relevance of these observations to the conformational isomerization in the molecule is discussed.



04.4-5 PHASES AND THERMAL DECOMPOSITION CHARACTERISTICS OF HYDRO-SODALITES $Na_6+x[AlSiO_4]_6(OH)_x \cdot nH_2O$. By Ch. Buhl, J. Felsche and S. Luger, Department of Chemistry, University of Konstanz, West Germany.

Reinvestigation of the hydro-sodalite system does not verify the solid solution character of the series in respect to a steady variation in properties of the samples. Thermoanalyses of carefully prepared pure phases reveal an antagonistic volume/concentration effect of hydrate water in the two end-member series $Na_6[AlSiO_4]_6(OH)_2 \cdot nH_2O$, $0 \leq n \leq 4$ ('basic series') and $Na_6[AlSiO_4]_6 \cdot nH_2O$, $0 \leq n \leq 8$ ('non-basic series'), however. Thermogravimetry and X-ray diffraction heating experiments confirm partial collapse of the sodalite framework upon dehydration of phases of the basic hydro-sodalites which is the common behaviour of framework compounds in decomposition or ion exchange experiments. Contrary, phases of the non-basic sodalite hydrate series $Na_6[AlSiO_4]_6 \cdot nH_2O$ show significant expansion of the alumino-silicate framework when $0 \leq n \leq 8$ are released at temperatures of 350-450 K under open system conditions. This antagonistic effect on the sodalite type host lattice is discussed in terms of hydrogen bonding, which has been verified by supplementary neutron diffraction analyses for the non-basic hydro-sodalites, distinctively.

From IR- and X-ray diffraction heating experiments strong evidence is given for the dynamical nature of interactions between all the non-framework constituents with increasing activation barriers for the hydrogen, oxygen and sodium atoms, respectively. The cubo-octahedral geometry of the sodalite cage in the given 1:1 alumino-silicate matrix controls the corresponding interactions, which result in some new stereochemical features of the aqueous hydroxyl-groupings $[O_nH_{2-n}]^{1-}$ in the basic hydro-sodalite phases with different hydrate water contents ($1 < n \leq 3$).

04.4-6 Al VACANCIES IN $\alpha-Al_2O_3$ FORMED BY DEHYDRATION OF $\alpha-AlOOH$. By K. Hagiya and M. Ohmasa, Institute of Materials Science, University of Tsukuba, Japan.

Many people have so far investigated the dehydration of goethite ($\alpha-FeOOH$) and diaspora ($\alpha-AlOOH$) and established that hematite ($\alpha-Fe_2O_3$) and corundum ($\alpha-Al_2O_3$) are derived from precursor in an orientated manner (topotaxy) with twinning developing during the transformation. Lima-de-Faria (J. Lima-de-Faria, Z. Kristallogr., 1963, 119, 176-203) showed that the products revealed distinct satellite reflections on oscillation photographs in the early stage of the reaction. He thought that the satellite could be derived from the structure with alternation of zones having complete cation distribution and those having incomplete ones. Recently Watari and his coworkers (F. Watari, P. Delavignette and S. Amelinckx, Solid State Chem., 1979, 29, 417-442) have carried out electron microscopic studies on dehydration of goethite and thought that the satellite reflections were not caused by the modulation of cation distribution but by the periodic arrangement of voids in the structure of $\alpha-Fe_2O_3$. The present studies have, therefore, been carried out to elucidate the origin of satellite reflections of the dehydration products.

Single crystals of diaspora from Shokozen, Hiroshima, Japan were selected for experiments. The specimen was heated to 500°C quickly, kept at 500°C for 30 minutes and then quenched in air. Two kinds of diffraction patterns were observed on X-ray photographs. One of them corresponds to the precursor and the other to the product. The latter indicates satellite reflections. Since the validity of the above models can be checked by determination of the ratio of Al to O, averaged structure was determined. Intensities of main reflections correspond to the averaged structure were measured on an automated four-circle diffractometer (Rigaku AFC-5) equipped with RU-200 X-ray generator (operation condition: 50 kV, 120mA), using $MoK\alpha$ radiation monochromatized by graphite. The cell parameters determined are $a=4.752(3)$ and $c=12.989(11)$ Å and the same space group $R\bar{3}c$ as normal $\alpha-Al_2O_3$ was adopted from the extinction rule. In order to avoid the effects of precursor, ω -scanning was employed for intensity measurements. 369 reflections were used for refinement. Least-squares refinement of the site occupancy of Al, atomic positions and anisotropic temperature factors using RFINE2 (L. W. Finger, 1969), yielded $R=0.138$ and $R_w=0.115$. According to the model proposed by Watari et al., the occupancy of the cation must be 1.0, because they interpreted the satellite as diffraction by periodic arrangement of voids and perfect $\alpha-Fe_2O_3$ crystallites from their high resolution electron micrographs. The occupancy of Al was determined to be 0.751(5) from the present determination of the averaged structure. The result suggests that the origin of the satellites is the modulation of the Al occupancy. It must be reasonable to consider that the same phenomena occur in the dehydration product of $\alpha-FeOOH$. We have also determined the amplitude of the modulation and suggested from the result that the feature of the satellites ascribe the modulation to a periodic distribution of Al-deficient layers (M. Ohmasa et al., Acta Cryst., 1984, A40, C-256). In the Al-deficient layers, the electric charge is not neutral and protons could migrate in those layers to compensate the unbalance. Such structure could easily evaporate in the high flux of charged particles (electrons) and in the high vacuum, and would form a periodic arrangement of voids. Two thirds of octahedral sites are occupied in normal $\alpha-Al_2O_3$, and 75% of Al sites are occupied in the modulated $\alpha-Al_2O_3$. The ratio of Al to O in the latter is 1:2. Since this value is same as the ratio of Al to O in $\alpha-AlOOH$, the modulated $\alpha-Al_2O_3$ must be the nucleus of the dehydration product, and behavior of the satellites must be very important to analyze the process of formation of the new phase.