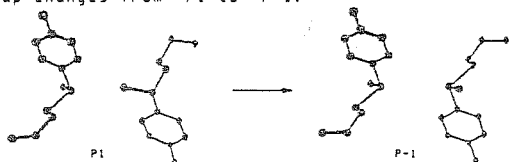


04.4-2 STUDIES OF A SOLID STATE RACEMIZATION REACTION. By R. Norrestam & B.W. Christensen, Chemistry Dept. B and Inst. of Organic Chemistry, The Techn. Univ. of Denmark, DK-2800 Lyngby, Denmark

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.

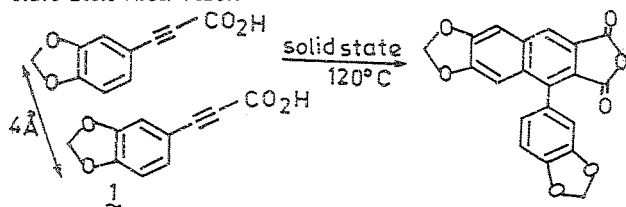
Determinations of the crystal structures by x-ray diffraction techniques of two such salts showed that the final reaction products, the racemates, were ordered. From the structural model of the racemate of one of these salts, the triclinic form (space group P-1) of methyl-butyl-tolyl-sulphonium trinitrobenzenesulphonate, 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.

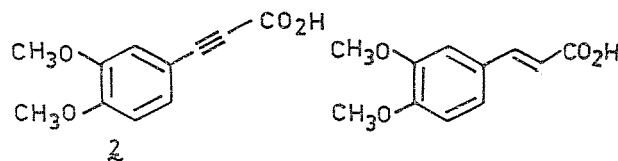
3,4-Methylenedioxy and 3,4-dimethoxy phenylpropionic acids (1 and 2) crystallise with short axes of 4 Å. This highly overlapped packing results in a close approach of triple bonds in adjacent molecules. This orientation of molecules ensures that diene and dienophile components in neighbouring molecules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