Conclusive evidence for the decisive effect of intermolecular interactions on molecular conformation in the solid state is provided by an analysis of the phase relationships between isomeric crystals of \( (\text{Py} \cdot \text{C}_4\text{H}_6\text{Me})\text{Re} \text{CO}_3 \text{Br}_2 \text{I} \). This is interpreted as further evidence in support of the conjecture that molecular shape is not an inherent property of small molecules, but more likely the result of environmental pressure. The stable form of I in solution and in molecular mechanics is the lateral isomer which on refluxing in toluene converts to the diagonal isomer [1]. Both isomers have been isolated as single crystals and studied crystallographically [2]. The diagonal isomer now has the lower triclinic symmetry and undergoes a phase transition above 100°C into the monoclinic form of the lateral isomer. The thermally induced isomerisation in solution is therefore seen to be linked to an intramolecular interaction, whereas in the crystal it is driven by an intermolecular interaction. The intermolecular interaction is readily identified by noting that the sequence of events described here is restricted to compounds with small substituents, compatible with a characteristic packing in sheets in the triclinic crystal, stabilised by polar interactions that operate only if the molecule has the diagonal conformation. This novel result has an important bearing on the old question of conformational changes between solution and crystal.


**PS11.03.09 CRYSTALLOGRAPHY AND KINETICS: STRUCTURE CORRELATIONS IN THE LIGHT OF MARCUS RATE-EQUILIBRIUM THEORY.** Valeria Ferretti, Paola Gilli, Valerio Bertolasi and Gastone Gilli, Dipartimento di Chimica e Centro di Strutture Dinamiche, Università di Ferrara, via L. Bersani 46, 1-44100 Ferrara, Italy

Systematic comparison of crystal structures containing the same molecular fragment leads to structure correlations, that is intercorrelations of fragment geometrical parameters in its configuration space. Structure correlations are supposed to map minimum-energy pathways in the fragment PES (Potential Energy Surface) (Dunitz, "X-ray Analysis and the Structure of Organic Molecules", Cornell, Ithaca, 1979; Bürgi & Dunitz, Acc. Chem. Res. 1983, 16, 153).

The exact relationship between crystal structure correlations and chemical kinetics (or chemical equilibrium) is a complex physical-chemical problem which has been seldom treated (see, for instance, Bürgi in "Perspectives in Coordination Chemistry", VCH, Basel, 1992; Ferretti, Gilli, Bertolasi & Gilli, Cryst. Rev. 1996, in press). In this communication an interpretation is attempted which makes use of the Marcus rate-equilibrium theory (Marcus, Discuss. Faraday Soc. 1960, 29, 21; J. Phys. Chem. 1968, 72, 891) to relate crystal structure correlations with the kinetic concepts of activation energy barriers, reaction pathways and distances of the reactants from the transition state as well as with thermodynamic standard free energies of chemical reactions.

**PS11.03.10 INFLUENCE OF DOPING ON LOW-FREQUENCY DIELECTRIC RELAXATION OF (VDF-TrFE) COPOLYMER.** T.B. Frolova, N.D. Gavrileova, K.A. Verkhovskaya, Moscow State University, Moscow, Russia, Institute of Crystallography RAS, Moscow, Russia

In this paper low-frequency dielectric relaxation of (P(VDF-TrFE) 70/30, pure and doped with rododine R6G, in frequency range 20Hz-20kHz and temperature region 80-400K were investigated. The region of 310 K for the pure copolymer is the region of anomalies of dielectric permittivity and other electrophysical properties. We connect the existence of these anomalies with the structural changes in the amorphous phase of copolymer. After doping by R6G the region of anomalous behavior shifts to 100-110K. Besides, doping results in increasing of values of dielectric permittivity of copolymer (from 80 to 400). The results are used to test the "universal law" of dielectric response.

1. K.A. Verkhovskaya, N.D. Gavrileova, T.B. Frolova, I.A. Smirnova "Low-frequency dielectric dispersion and pyroeffect in ferroelectric copolymer of vinylidene fluoride with trifluoroethylene all phase transitions"//RAN (ser. phys.)- in printing.