PS11.03.08 MOLECULAR REARRANGEMENT DUE TO CRYSTAL PACKING. Jan C. A. Boeyens, Centre for Molecular Design, Chemistry Department, University of the Witwatersrand, Private Bag 3,Wits, 2050, South Africa

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 $(\eta^5 - C_5H_4Me)Re(CO)_2Br_2(I)$. 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.

1. L. Cheng and N. J. Coville, Organometallics, 1996, in press.
2. J. C. A. Boeyens, L. Cheng, N. J. Coville, D. C. Levendis and K. McIntosh, unpublished results.

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 and Centro di Strutturistica Diffrattometrica, Università di Ferrara, via L. Borsari 46, I-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 physicochemical 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.Gavrilova, 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 rodomine R6G, in frequency range 20Hz-20kHz and temperature region 80-400K were investigated. The region of 310K 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.

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PS11.03.11 NON-TOPOLOGICAL PHASE TRANSITION OF N-2,4-DINITROPHENYL-o-ANISIDINE. K. Takada, K. Taguchi, M. Yasui and F. Iwasaki, Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo 182, Japan

N-(2,4-dinitrophenyl)-o-anisidine (1) has two crystalline modifications, orange and red forms. The orange form transforms to the red form at the wide temperature range, 383~431K, and these transition points are depending on the specimens. During the crystals of the orange form were kept at 393 K for several hours, some orange crystals partially turned to the red form. The red region of these partially changed crystals could be kept in room temperature for long time. X-ray oscillation and Weissenberg patterns of the orange, the red and the boundary parts of these crystals observed by a Weissenberg-type diffractometer with the imaging plates revealed that the b axis of the transformed red form was always coincident with the b axis of the orange form, although powder diffraction rings with preferred orientation were also observed in the red part. Crystal data: Orange form, P2/a, a=21.561(5), b=4.219(1), c=16.749(5)Å, β=122.30(1)°, Z=4, R=0.060 for 1842 reflections. Red form, $P2_1$, a=15.693(2), b=10.981(3), c=3.842(1)Å, β=98.39(2)°, Z=2, R=0.079 for 886 reflections. The molecules of these forms are rotational isomers. In the orange form an intramolecular hydrogen bond is formed between the NH and o-nitro groups, while in the red form the NH group is hydrogen-bonded to the o-nitro and methoxy groups bifurcately, so that the methoxyphenyl group rotates by about 60° during the transformation. In the crystals the molecules are arranged approximately perpendicular to the shortest axes, b for the orange form and c for the red form. However, the diffraction patterns showed that the solid-phase transformation occurred coinciding of the b axes of both forms. This fact suggests that a mechanism of the transformation cannot be understood from topological arrangements. The transformation from the orange to the red forms retaining the b axes should be performed by twisting of the molecules together with an intramolecular rotation of the o-methoxyphenyl group. Such motion needs a large space, so that this rearrangement may occur from defects in the crystals as shown from the wide transition temperatures and the fact of changing to a polycrystalline state.