04. ATOMIC SCALE MECHANISM AND CHEMICAL PROPERTIES

04.3-9 ON THE VALIDITY OF STRUCTURE CORRELATION METHOD (SCM). By V. Bertolasi, F. Belluoli, V. Ferruzzi and G. Gilli - Istituto Chimico, Universita di Ferrara, Italy.

SCM is an attempt of obtaining information on reaction paths and transition state geometries from crystallographic data (Bürgi & Dunitz, Acc. Chem. Res., 16, 153, (1983)). It assumes that observed deformations of the reaction centre in different crystal environments can be arranged in a logical sequence to map the path of a chemical reaction. The central question is if the observed path actually maps the true reaction coordinate, i.e., if it follows the corresponding valley on the energy hypersurface. Few attempts were done to check this correspondence (Bürgi, Lehn & Wipff, J. Am. Chem. Soc., 86, 1956, (1974)).

We have studied the system C(sp²)–N(sp³) (1). This is planar owing the partial double bond character of the C-N bond in crystal environment, however, it is often deformed from planarity, the deformation being described by the torsion angle around C-N (\(\tau\)) (\(-180^\circ < \tau < 180^\circ\)) and the out-of-plane bending of the amino nitrogen (\(\chi_N\)) (ranging from 0° for planar sp² to 60° for tetrahedral sp³ nitrogen). Deformation data for several crystal structures have been collected and an energetic model, based on molecular mechanics considerations, has been proposed (Gilli & Bertolasi, Acta Cryst. A37, C85 (1981)). Proper choice of the parameters in the force field give rise to the energy map \(E = f(\tau, \chi_N)\) shown in the figure, when experimental points (A=anilines, B=naphthylamines, D=enamines and N=amidines) are reported on the energy surface they are seen to distribute themselves along paths of relative minimum according to the basic principles of the SCM method.

04.4-1 GAS-SOLID PHOTOOXIDATION: PHOTOOXIDATION OF THIOKETONES IN THE CRYSTALLINE STATE. By P. Arjunan, V. Ramamurthy and K. Venkatesan, Department of Organic Chemistry, Indian Institute of Science, Bangalore-560012, India.

Reactions of organic compounds are more selective when performed in the solid state than in the solution phase. For example aromatic thio­ ketones are known to undergo oxidation readily in solution to the corresponding S-oxides and/or ketones. However among the large number of diaryl thio­ ketones investigated by us only a few exhibited photoactivity in their crys­ talline state. With the aim of finding out the reactivity-molecular packing relationship, X-ray crystallographic analyses of both stable and reactive thio­ ketones have been examined.