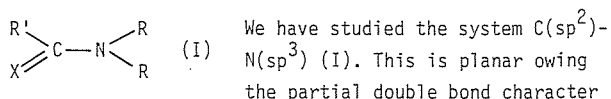


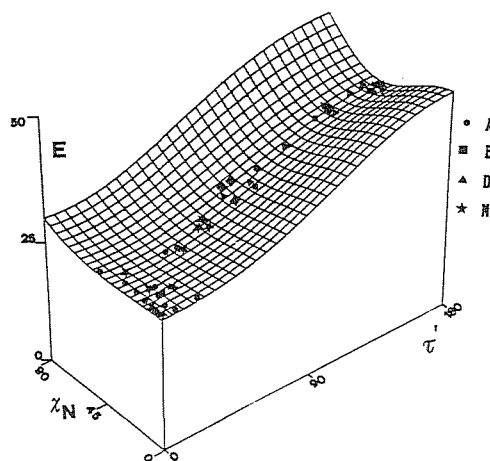
04.3-9 ON THE VALIDITY OF STRUCTURE CORRELATION METHOD(SCM). By *V.Bertolasi, F.Bellucci, V.Ferretti and G.Gilli-Istituto Chimico, Università di Ferrara, Italy.*

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., 98, 1956, (1974)).



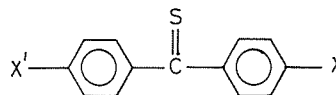
We have studied the system  $C(sp^2)-N(sp^3)$  (I). This is planar owing to the partial double bond character

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 ( $\tau'$ :  $-180^\circ \leq \tau' \leq 180^\circ$ ) and the out-of-plane bending of the amino nitrogen  $\chi_N$  (ranging from  $0^\circ$  for planar  $sp^2$  to  $60^\circ$  for tetrahedral  $sp^3$  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=amides) 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 thioketones are known to undergo oxidation readily in solution to the corresponding S-oxides and/or ketones. However among the large number of diaryl thioketones investigated by us only a few exhibited photoreactivity in their crystalline state. With the aim of finding out the reactivity-molecular packing relationship, X-ray crystallographic analyses of both stable and reactive thioketones have been examined.



	X	X'	Reactivity
I	$N(CH_3)_2$	$N(CH_3)_2$	Nil
II	OMe	OMe	"
III	Phe	H	Yes
IV	H	H	"

The crystal data [ $a, b, c(\text{\AA}), \alpha, \beta, \gamma(^\circ)$ ], space group and the final R-value are : I : 17.029(5), 6.706(5), 14.629(4); 90.0, 113.55(2), 90.0 ;  $P2_1/c$ , 6.1% ; II : 9.810(3), 9.635(3), 15.015(4), 79.11(2), 102.38(3), 107.76(3),  $P\bar{1}$ , 7.4% ; III : 7.443(1), 32.691(3), 11.828(2),  $PbCa$ , 6.8% ; IV : 14.042(2), 5.863(2), 13.403(3), 90.0, 106.40(2), 90.0,  $P2_1/n$ , 4.4% . In addition, crystals of 1-naphthyl phenylthioketone which crystallize in the space group  $P2_12_12_1$  with  $a = 5.873(3)$ ,  $b = 13.677(3)$  and  $c = 15.668(5)\text{\AA}$  undergo photooxidation. The structure has been refined to  $R = 6.9\%$  . The crystal structure of compound IV has been reported by Rindorf and Carlson (Acta Cryst, 1979, B35, 1179). X-ray results of the reactive compounds show that the thiocarbonyl chromophores are stacked, with S...S distance between the closest sulphur atoms varying from about 3.7 to  $3.9\text{\AA}$ . Further, there is a channel along the shortest crystallographic axis in each case with cross-sectional area varying from 4 to  $9\text{\AA}^2$  with the chromophores directed towards the channel. On the other hand the molecular packing of the non-reactive crystalline compounds do not possess these features.