

04.3-3 CRYSTALLOGRAPHIC MAPPING OF PROTON TRANSFER PATHWAYS: COMPARISON BETWEEN THEORETICAL REACTION COORDINATES AND EMPIRICAL CORRELATIONS X-H/H...Y IN HYDROGEN BONDS.

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It has long been recognized that there is a direct correlation between the distance X-H and the strength of the interaction in a hydrogen bond X-H...Y. However, the detailed form of the correlation curve has been much debated in the past, in particular for strong O-H...O bonds. In the present paper it is shown that the general form of the correlation curves appears rather obvious on extending previous empirical diagrams of distances O-H versus H...O. This extended correlation curve has a form which is typical for the reaction path of a proton transfer reaction $X-H+Y \rightleftharpoons X\cdots H\cdots Y \rightleftharpoons X+H-Y$. This is in accord with the general idea that the distribution of experimental points in a series of diffraction studies of different compounds tend to approach the minimum energy reaction path of proton transfer in one particular hydrogen bond.

A detailed comparison is made between the empirical correlation curve and the minimum energy reaction path along the potential energy surface calculated theoretically for different types of hydrogen bonds. Furthermore, comparison is made with the reaction coordinate derived by applying the bond order conservation postulate and Pauling bond orders. By this procedure it is also possible to find a simple functional form for the empirical correlation curves of different types of hydrogen bonds.

04.3-4 MAPPING THE EXPANSION OF COORDINATION AT SILICON FROM 4 TO 5: A MODEL FOR THE S_N2 REACTION AND IRREGULAR REARRANGEMENT PROCESSES. By G. Klebe, Institut für Kristallographie, Universität Frankfurt/Main (FRG)

Crystal structure data of 46 independent molecular fragments containing pentacoordinated silicon with up to three chemically different ligand atoms were analysed to obtain information on the geometric changes that occur during the transformation from tetra- to pentacoordination. A significant correlation is found between bond length and bond angle changes.

The structural changes from tetrahedral to trigonal-bipyramidal coordination can be interpreted in terms of the geometric transformations along the S_N2 reaction pathway occurring with inversion of configuration. They may be taken as a model for the molecular motions of dynamic rearrangements which are observed in chelated coordination complexes of pentacoordinated silicon by NMR spectroscopy in solution. These processes involve bond fission/bond reformation through an intermediate change of coordination from 5+4+5 at silicon.

To overcome the difficulty of comparing bonds to different ligand atoms, standard bond lengths were subtracted from the observed values. The smallest scatter in the regression curve describing the pathway is obtained when reference values are used which are derived by least-squares analysis from a large number of distances taken from differently coordinated silicon compounds (Klebe & Bürgi, Abstract for 13th IUCr-Congress, 1984).

04.3-5 CORRELATIONS OF INTRAMOLECULAR AND LATTICE MOTIONS IN A MOLECULAR CRYSTAL. By O. Scheidsteger and G. Huttner, Fakultät für Chemie, Lehrstuhl für Synthetische Anorganische Chemie, Universität Konstanz, P.B. 5560, D-7750 Konstanz, F.R.G.

Single crystals of trans- $L_2Mo(CO)_4$ (I) transform to crystals of cis- $L_2Mo(CO)_4$ (II) upon heating ($L = 1,3$ -dimethyl-4-imidazoline-2-ylidene; O. Scheidsteger et al., Z. Naturforsch. 38b, 1598 (1983)). This topotactic reaction is analyzed by X-ray and morphological studies. Models for this process from a molecular and from a lattice point of view are given in Figures 1 and 2.

Fig. 1: The molecular isomerization process.

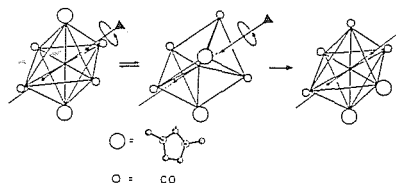
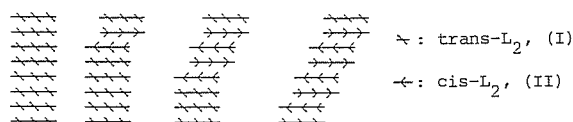
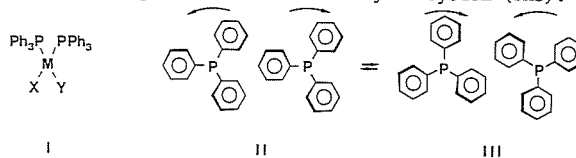


Fig. 2: Stepwise dislocation of close packed double layers in the crystal during the martensitic type phase transition (I) \rightarrow (II).



04.3-6 CONFORMATIONAL INTERCONVERSIONS OF CIS-SQUARE PLANAR BIS-TRIPHENYLPHOSPHINE COMPLEXES, cis-(Ph_3P) $_2$ MX $_2$. By L. Nørskov-Lauritsen and H.B. Bürgi, Laboratorium für Kristallographie, Universität Bern, CH-3012 Bern, Switzerland.

Conformations of 62 metal complexes of type I were retrieved from the Cambridge Structural Database and analysed using the Statistical Analysis System (SAS).



The observed torsion angles about the M-P bonds show a distribution suggesting that the two PPh_3 -groups behave like inter-locked gears. This is shown schematically as II and III above (cylindrical projections of I). In a more complete analysis the 8 degrees of torsional freedom of two coupled PPh_3 -groups were studied. Using a cluster analysis technique 61 of the 62 observed conformations could be assigned to one of the three quite compact groups, A, B, and C (the sum of the volumes of the three enclosing hyperspheres is 0.2 % of the total volume of conformational space). A typical molecule in group A shows the (somewhat idealized) conformation II with equal helicity of the two PPh_3 -propellers, abbreviated as (++A) or (--A). In group B the conformations about the M-P bonds are similar to those of II but the PPh_3 -propellers have opposite helicity, (+-B) or (-+B). The conformations in group C resemble III with C_2 symmetry, (++C) or (--C). From the distances between clusters A, B, C and the symmetry of conformational space the following coupling between individual phenyl