

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.

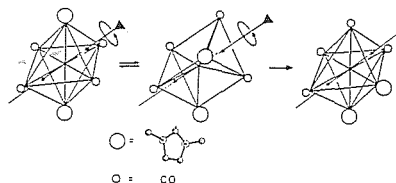
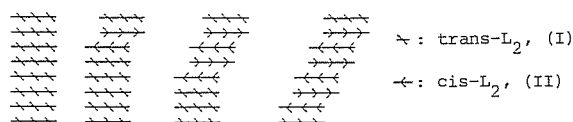
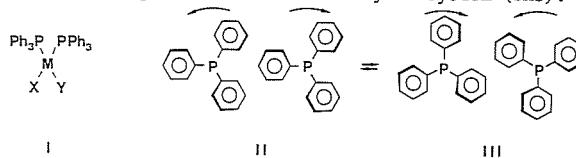


Fig. 2: Stepwise dislocation of close packed double layers in the crystal during the martensitic type phase transition (I) \rightarrow (II).



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

group rotations and PPh_3 gearing motion was inferred: $(+C) \rightleftharpoons (+A) \rightleftharpoons \{(+B) \text{ or } (+B)\} \rightleftharpoons (-A) \rightleftharpoons (-C) \rightleftharpoons \text{etc.}$

The above analysis of a molecule with many (>3) torsional degrees of freedom is based on specially developed concepts and methods. First, the conformation of each PPh_3 -group and of each phenyl group is described by a single torsion angle, thus disregarding deviations from local C_{3v} - or C_{2v} -symmetry, respectively. Second, the symmetry of the resulting 8-dimensional conformational space is taken into account. Symmetry implies - among other things - a periodic structure of this space due to the cyclic nature of torsional coordinates. (Murray-Rust, Bürgi and Dunitz, Acta Cryst. A35 (1979) 703). This structure may be utilized by analyzing several, adjacent asymmetric units together (i.e. a data set containing an integer multiple of the original 62 data points) and by transforming torsion angles into appropriate sine and cosine values. Regions in conformational space which are densely populated with data points, were located using Ward's method of cluster analysis (Ward, J. Am. Stat. Ass. 58 (1963) 236) as implemented in SAS-procedure CLUSTER (SAS User's Guide: Statistics, SAS Institute Inc. (1982) Cary NC, USA). The clustering process treats every data point as a cluster, then joins neighboring clusters into new ones until all data points form a single cluster. For present purposes the process is intercepted, however: the final set of clusters is obtained with the following two criteria: (1) the set must conform to the symmetry of conformational space, and (2) a statistical clustering criterion must be a maximum.

04.3-7 INTERACTIONS BETWEEN DIAZONIUM GROUPS AND NUCLEOPHILIC CENTRES ATTACHED TO THE PERI POSITIONS OF NAPHTHALENOID RING SYSTEMS. IMPLICATIONS FOR THE PREFERRED DIRECTION OF NUCLEOPHILIC ATTACK ON N,N TRIPLE BONDS. By John D. Wallis and Jack D. Dunitz Organic Chemistry Laboratory, Swiss Federal Institute of Technology, ETH-Zürich, CH-8092 Zürich, Switzerland.

The crystal structures of the BF_4^- salts of the 8-quinolinediazonium-1-oxide (1), 8-dimethylamino-naphthalene-1-diazonium (2) and 8-nitronaphthalene-1-diazonium (3) cations have been measured at low temperatures (95 - 150 K, $R \leq 0.04$). All three structures show an interaction between the α -N of the diazonium group and a nucleophilic centre (O for 1 and 3, N for 2). Distances between these interacting atoms lie in the range 2.44 - 2.54 Å, i.e. they are less than the sum of the appropriate van der Waals radii. The diazonium groups are bent ($C-N_\alpha \equiv N_\beta$ angles of $167^\circ - 171^\circ$) so that N_α deviates from the $C \cdots N_\beta$ vector towards the nucleophilic centre.

In 1 and 2 the substituents are not splayed apart; instead the bond to the diazonium group bends outwards and the one to the nucleophilic centre bends inwards by a similar amount (1 by 2° , 2 by $3-4^\circ$). This helps to increase the $O \cdots N_\alpha \equiv N_\beta$ and $N \cdots N_\alpha = N_\beta$ angles to 104° and 106° from near 90° in the undistorted molecule. Since in 1 there is no steric hindrance to distortion in the opposite direction the preferred direction of nucleophilic attack on the $-N \equiv N$ bond makes an angle of at least 104° to the bond axis.

04.3-8 UNEXPECTED REACTIONS WITH 1,3-DIAZABUTA-1,3-DIENES. By A. Gieren, T. Hubner, C.-P. Kaerlein, G. Weber, H. Betz and K. Burger*, Max-Planck-Institut für Biochemie, Abt.f.Strukturforschung I, Martinsried, BRD; *Institut für Organische Chemie der TU, München, BRD.

In the case of reactions of very polar dienes with dienophiles in contrast to conventional [4+2] cycloadditions following the concerted Diels-Alder scheme, more step processes are favoured as we could demonstrate with 2-phenyl-4,4-bis(trifluoromethyl)-1-(aryl)-1,3-diazabuta-1,3-dienes (1) as a model. The adducts 6-10 of the reactions of 1 (1a, 1b) with the nitriles 2-4 and the α,β -unsaturated ketone (5) have been characterized by X-ray structure analyses and new reaction patterns could be deduced.

The reactions of 1 with the nitriles 2-4 and the α,β -unsaturated ketone (5) follow different more step mechanisms. In the case of reaction with 2 a reorganisation of the diene skeleton occurs during the reaction. In the reaction with 3 a five membered ring system (7) is formed, which formally can be described as an isonitrile adduct. In the case of the reaction with 4, the [4+2] adduct formed reacts further in a very complex manner with a second molecule of the heterodiene under elimination of HF, yielding 8. With respect to the formation of the isomers 9 and 10 a reaction sequence diene metathesis/intramolecular ene reaction and diene metathesis/electrocyclic ring closure is proposed, respectively.

