Distortions of MX_4 Molecules from T_d Symmetry.
I. Kernel, Co-kernel and Averaged Configurations

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Symmetry coordinates are used to describe nuclear configurations of MX_4 molecules that can be regarded as distorted versions of T_d symmetrical reference structures. This approach provides a basis for assessing approximate symmetries and for testing the validity of averaging over observed molecular parameters. The construction of kernel or co-kernel configurations, allowing for the equation of constraint among the six bond angles, is described.

1. Introduction

Many small molecules possess high symmetry in an isotropic environment but exhibit significant deviations from this symmetry in the crystalline state. For example, although the isolated phosphate ion (PO_4^{3-}) is expected to have T_d symmetry, a study of 211 examples in the solid state (Baur, 1974) showed that only one possessed this symmetry exactly; most had no symmetry whatsoever. Several attempts have been made to describe the kinds of distortion that occur and the forces responsible for them and to search for correlations between observed structural parameters in the distorted species (McDonald & Cruickshank, 1967; Baur, 1970, 1974; Brown & Shannon, 1973; Louisnathan & Gibbs, 1972; Lager & Gibbs, 1973). From these studies one becomes aware of the lack of a general method of describing distortions of molecules from reference configurations with a given symmetry. Jørgensen (1971) has stated that one of the main problems of applied group theory is to investigate the physical significance of the phrase 'The molecule MX_N *almost* has the symmetry G' though it may seem intuitively clear to the chemist.

Symmetry coordinates have been much used for discussing molecular vibrations (Wilson, Decius & Cross, 1955). In this paper we describe the use of symmetry coordinates for analysing static distortions of MX_4 molecules from T_d symmetry. Results for several classes of MX_4 molecules in various crystal environments are discussed in the following paper.

2. Description of distorted molecules

Say we wish to describe the observed structure of a molecule as a distorted version of a more symmetrical reference molecule with the same atomic connectedness or constitution. We may then express the overall distortion in terms of a total displacement vector $\mathbf{D} = d_j \mathbf{p}_j$ where d_j's are components along some set of displacement coordinates, $\mathbf{p}_j$. Insofar as we can ignore the absolute position and orientation of our molecule, it is often convenient to use internal displacement coordinates. For a molecule consisting of N atoms there are $3N - 6$ such coordinates that are linearly independent. Alternatively, we may choose a new coordinate system in which the basis vectors are particular linear combinations of the internal displacement coordinates that transform according to the irreducible representations of the point group $\mathbf{G}$ of the reference molecule. A set of basis vectors with this property is called a set of symmetry displacement coordinates $\mathbf{S}_i$, and methods of deriving such coordinates are described in most books on applied group theory. Since the number of internal coordinates sometimes exceeds the number of degrees of freedom, the choice of independent and redundant symmetry coordinates is not always unique. For some molecules this point is discussed in the literature on normal coordinate analysis.

In terms of symmetry displacement coordinates the total displacement vector can be written $\mathbf{D} = D_i \mathbf{S}_i = D_i T_{ij} \mathbf{p}_j$. Since the transformation is unitary, the matrix

T that transforms the initial basis vectors $\mathbf{p}_j$ into the new basis vectors $\mathbf{S}_i$ also transforms the initial displacements d_j into the new symmetry displacements D_i. For this reason the distinction between the symmetry displacement coordinates $\mathbf{S}_i$ and the symmetry displacements D_i along these coordinates is often ignored.

Given the point group $\mathbf{G}$ and internal parameters $d_j(\text{ref})$ of the reference molecule, we can construct the total displacement vector $\mathbf{D} = d_j\mathbf{p}_j = [d_j(\text{obs}) - d_j(\text{ref})]\mathbf{p}_j$ from the parameters $d_j(\text{obs})$ of the observed molecule. In transforming d_j to symmetry displacements D_i the actual values of $d_j(\text{ref})$ are important only for the totally symmetric symmetry coordinate, since they cancel out for all the others.

The operation of the total displacement vector on the reference structure leads to the observed structure; this could also be reconstructed by distorting the reference structure along each $\mathbf{S}_i$ in turn and summing the corresponding displacements. A displacement along an $\mathbf{S}_i$ transforming as the totally symmetric irreducible representation (IR) produces a configuration with the same symmetry as the reference structure, whereas a displacement along any other $\mathbf{S}_i$ leads to a configuration of lower symmetry.

An arbitrary displacement along a symmetry coordinate transforming as the irreducible representation $\Gamma_j(\mathbf{G})$ is transformed into itself by those operations of $\mathbf{G}$ whose character in $\Gamma_j(\mathbf{G})$ equals the character of the identity operation.

The point group composed of these operations is called the kernel $\mathbf{K}$ of the representation; it is an invariant subgroup of $\mathbf{G}$ (that is, it contains complete classes of operations of $\mathbf{G}$).

In addition, a displacement transforming as a degenerate representation may also be transformed into itself by other operations not belonging to the kernel. The point group composed of these operations plus the kernel operations is called a co-kernel $\mathbf{CoK}$ of the representation; it is a non-invariant subgroup $\mathbf{G}$ (i.e. it does not consist exclusively of complete classes of operations of $\mathbf{G}$).

Co-kernels for degenerate representations of all common point groups have been derived by McDowell (1965). They are given in Table 1 (together with the kernels) for the irreducible representations of T_d.

Table 1. *Kernel and co-kernel symmetries for irreducible representations of T_d*

Irreducible representation	Kernel K	Co-kernels CoK
A_1	T_d	–
A_2	T	–
E	D_2	D_{2d}
T_1	C_1	S_4, C_3, C_s
T_2	C_1	C_{3v}, C_{2v}, C_s

3. Kernel, co-kernel and averaged configurations

Just as the operation of the total displacement vector on the reference structure leads to the observed structure, so a subset of symmetry displacements can be chosen to produce the structure of an idealized molecule that contains only a part of the overall distortion of the observed molecule. Such a structure can be selected to have particular kernel or co-kernel symmetries, and we shall refer to it as a kernel or co-kernel configuration. A subset of symmetry displacements belonging to a particular representation produces a configuration which necessarily has the kernel symmetry of that representation, and appropriately chosen subsets may lead to configurations with co-kernel symmetries.

If the transformation from internal displacement coordinates $(\mathbf{p}_j)$ to symmetry displacement coordinates $(\mathbf{S}_i)$ is given by $\mathbf{S}_i = T_{ij}\mathbf{p}_j$, then $D_i = T_{ij}d_j$ and $d_j = (T^{-1})_{ij}D_i = T_{ji}D_i$. The parameters of the kernel or co-kernel configuration are then $d_j(\mathbf{K})$ or $d_j(\mathbf{CoK}) = d_j(\text{ref}) + T_{ji}D_i$ summed over the relevant subset of symmetry displacements. The kernel or co-kernel configurations thus correspond to the configurations that the molecule *would have* if certain symmetry displacements were zero.

Any idealized configuration obtained by appropriate averaging over the internal parameters of a molecule is a kernel or co-kernel configuration. On the other hand, not every kernel or co-kernel configuration can be obtained by a simple averaging process (§ 4.3). This is because a configuration of symmetry $\mathbf{L}$ obtained by averaging includes displacements along *all* symmetry coordinates whose kernel or co-kernel symmetry is $\mathbf{L}$ *plus all* coordinates whose kernel or co-kernel symmetries are supergroups of $\mathbf{L}$. Thus kernel or co-kernel configurations pertaining to particular non-totally symmetric IR's cannot be obtained by averaging.

There is a difficulty. It may turn out that a kernel or co-kernel configuration as defined above (as well as an averaged configuration) may actually correspond to a structure that is geometrically unfeasible in three-dimensional space. This will be the case if the number of internal coordinates used to construct the symmetry coordinates exceeds the number of independent coordinates and if the displacement along any redundant coordinate depends on the displacements along the remaining coordinates. Examples are the symmetry coordinates built from the $N(N - 1)/2$ angles subtended at an N-coordinated atom $(N > 3)$. An illustration of this kind of problem is given in § 4.3 where ways of circumventing it are discussed.

4. MX_4 molecules

4.1. Symmetry coordinates of MX_4 molecule with $\mathbf{G} = T_d$

The internal coordinates $r_1, r_2, r_3, r_4, \theta_{12}, \theta_{13}, \theta_{14}, \theta_{23}$,

θ_{24}, θ_{34} transform as $2A_1 + E + 2T_2$; symmetry coordinates may be chosen as:

$$S_1(A_1) = \tfrac{1}{2}(r_1 + r_2 + r_3 + r_4)$$

$$S_{3a}(T_2) = \tfrac{1}{2}(r_1 + r_2 - r_3 - r_4)$$

$$S_{3b}(T_2) = \tfrac{1}{2}(r_1 - r_2 + r_3 - r_4)$$

$$S_{3c}(T_2) = \tfrac{1}{2}(r_1 - r_2 - r_3 + r_4)$$

$$S_{2a}(E) = \frac{1}{\sqrt{12}}(2\theta_{12} - \theta_{13} - \theta_{14} - \theta_{23} - \theta_{24} + 2\theta_{34})$$

$$S_{2b}(E) = \tfrac{1}{2}(\theta_{13} - \theta_{14} - \theta_{23} + \theta_{24})$$

$$S_{4a}(T_2) = \frac{1}{\sqrt{2}}(\theta_{12} - \theta_{34})$$

$$S_{4b}(T_2) = \frac{1}{\sqrt{2}}(\theta_{13} - \theta_{24})$$

$$S_{4c}(T_2) = \frac{1}{\sqrt{2}}(\theta_{14} - \theta_{23})$$

$$S_5(A_1) = \frac{1}{\sqrt{6}}(\theta_{12} + \theta_{13} + \theta_{14} + \theta_{23} + \theta_{24} + \theta_{34}). \quad (1)$$

A displacement along any single coordinate produces a configuration with the kernel or co-kernel symmetry.

The six angles are not independent, being related by the condition

$$\begin{vmatrix} 1 & \cos\theta_{12} & \cos\theta_{13} & \cos\theta_{14} \\ \cos\theta_{12} & 1 & \cos\theta_{23} & \cos\theta_{24} \\ \cos\theta_{13} & \cos\theta_{23} & 1 & \cos\theta_{34} \\ \cos\theta_{14} & \cos\theta_{24} & \cos\theta_{34} & 1 \end{vmatrix} = 0. \quad (2)$$
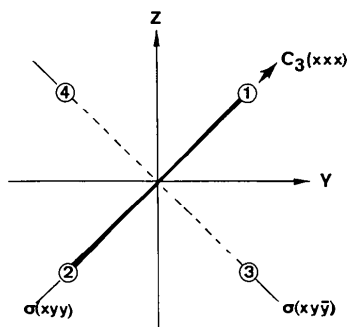

Fig. 1. Projection of MX_4 molecule showing ligands 1 and 2 above the plane of the paper, ligands 3 and 4 below. The X axis of the Cartesian coordinate system runs perpendicular to the plane of the paper.

For infinitesimal angular displacements, the positive and negative deviations from 109° 28′ cancel, so that the totally symmetric angular displacement is redundant $[D_5(A_1) = 0]$. There are thus nine linearly independent symmetry coordinates, four involving r's and five involving θ's.

The above symmetry coordinates have been chosen in a self-consistent way, that is, the particular linear combinations of r's and θ's transforming as T_2 match in pairs. For example, S_{3a} and S_{4a} with C_{2v} co-kernel symmetry are transformed into themselves by the same twofold axis, $C_2(x)$, and mirror planes, $\sigma(xyy)$ and $\sigma(xy\bar{y})$, and similarly for the other two matching pairs (Fig. 1). However, the above choice is in no way unique and several other sets of self-consistent symmetry coordinates can be chosen. One such choice would be:

$$S_{a'} = \frac{1}{\sqrt{3}}(S_a + S_b + S_c)$$

$$S_{b'} = \frac{1}{\sqrt{6}}(2S_a - S_b - S_c)$$

$$S_{c'} = \frac{1}{\sqrt{2}}(S_b - S_c) \quad (3)$$

leading to

$$S_{3a'}(T_2) = \frac{1}{\sqrt{12}}(3r_1 - r_2 - r_3 - r_4)$$

$$S_{3b'}(T_2) = \frac{1}{\sqrt{6}}(2r_2 - r_3 - r_4)$$

$$S_{3c'}(T_2) = \frac{1}{\sqrt{2}}(r_3 - r_4)$$

$$S_{4a'}(T_2) = \frac{1}{\sqrt{6}}(\theta_{12} + \theta_{13} + \theta_{14} - \theta_{23} - \theta_{24} - \theta_{34})$$

$$S_{4b'}(T_2) = \frac{1}{\sqrt{12}}(2\theta_{12} - \theta_{13} - \theta_{14} + \theta_{23} + \theta_{24} - 2\theta_{34})$$

$$S_{4c'}(T_2) = \tfrac{1}{2}(\theta_{13} - \theta_{14} + \theta_{23} - \theta_{24}). \quad (4)$$

The relation between the two coordinate systems is shown in Fig. 2.

Alternatively, the radial and angular T_2 displacements can each be referred to a set of four equivalent, linearly dependent, symmetry coordinates $S_{a''}$, $S_{b''}$, $S_{c''}$, $S_{d''}$ (running along the four C_3 axes of a tetrahedron). Displacements along each of these show C_{3v} co-kernel symmetry.
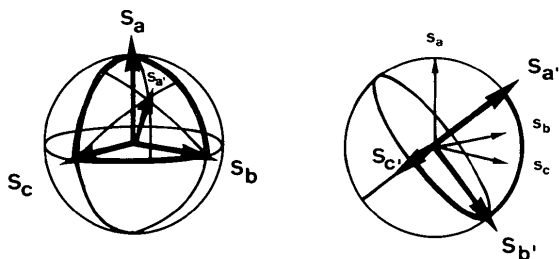
Fig. 2. Symmetry displacement .coordinates. Left: the relation between $S_a(T_2)$, $S_b(T_2)$, $S_c(T_2)$ and $S_{a'}(T_2)$. A displacement along S_a, S_b or S_c corresponds to a C_{2v} co-kernel configuration, one along $S_{a'}$ to a C_{3v} co-kernel configuration. Displacements on any of the three circles intersecting on $S_{a'}$ correspond to C_s co-kernel configurations. Right: relation between unprimed and primed displacement coordinates with S_a, $S_{a'}$ and $S_{b'}$ in the plane of the paper.

Fig. 3. Scheme showing that the sum of two different C_{3v} co-kernel configurations is a C_{2v} co-kernel configuration.

$$S_{3a''}(T_2) = \frac{1}{\sqrt{12}}(3r_1 - r_2 - r_3 - r_4)$$

$$S_{3b''}(T_2) = \frac{1}{\sqrt{12}}(-r_1 + 3r_2 - r_3 - r_4)$$

$$S_{3c''}(T_2) = \frac{1}{\sqrt{12}}(-r_1 - r_2 + 3r_3 - r_4)$$

$$S_{3d''}(T_2) = \frac{1}{\sqrt{12}}(-r_1 - r_2 - r_3 + 3r_4)$$

$$S_{4a''}(T_2) = \frac{1}{\sqrt{6}}(\theta_{12} + \theta_{13} + \theta_{14} - \theta_{23} - \theta_{24} - \theta_{34})$$

$$S_{4b''}(T_2) = \frac{1}{\sqrt{6}}(\theta_{12} - \theta_{13} - \theta_{14} + \theta_{23} + \theta_{24} - \theta_{34})$$

$$S_{4c''}(T_2) = \frac{1}{\sqrt{6}}(-\theta_{12} + \theta_{13} - \theta_{14} + \theta_{23} - \theta_{24} + \theta_{34})$$

$$S_{4d''}(T_2) = \frac{1}{\sqrt{6}}(-\theta_{12} - \theta_{13} + \theta_{14} - \theta_{23} + \theta_{24} + \theta_{34})$$

(5)

The resultant of two equal displacements along different C_{3v} co-kernel directions is a displacement along a C_{2v} co-kernel direction. In other words, a distortion of a tetrahedron conserving C_{2v} symmetry can be regarded as a combination of two equivalent distortions
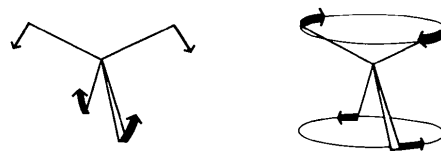
conserving C_{3v} symmetry (Fig. 3), and similarly for other kinds of distortion.

Similarly, the E displacement (Fig. 4) may be referred to a set of three equivalent, linearly dependent, symmetry coordinates

Fig. 4. The two orthogonal symmetry displacement coordinates S_a (E) (left) and S_b (E) (right).

$$S_{2a'}(E) = \frac{1}{\sqrt{12}}(2\theta_{12} - \theta_{13} - \theta_{14} - \theta_{23} - \theta_{24} + 2\theta_{34})$$

$$S_{2b'}(E) = \frac{1}{\sqrt{12}}(-\theta_{12} + 2\theta_{13} - \theta_{14} - \theta_{23} + 2\theta_{24} - \theta_{34})$$

$$S_{2c'}(E) = \frac{1}{\sqrt{12}}(-\theta_{12} - \theta_{13} + 2\theta_{14} + 2\theta_{23} - \theta_{24} - \theta_{34}).$$

(6)

Displacements along any one of these special directions show co-kernel symmetry D_{2d}. The labels a,b,c are chosen to match the labels of $S_4(T_2)$.

It is immaterial which set of symmetry coordinates is chosen, so the choice should be made according to convenience. If several molecules are to be compared, it is useful to label the atoms according to some specific recipe, for example, in order of decreasing bond length, so that corresponding displacement vectors lie in the same asymmetric unit of the vector space defined by the symmetry coordinates.

4.2. Numerical sample calculations

As a numerical example consider a strongly distorted PO_4 tetrahedron found in $Cd_2P_2O_7$ with no crystallographically imposed symmetry (Calvo, 1969). Values of bond lengths and angles have been recalculated from published coordinates:

r_1	1·645 Å	θ_{12}	102·87°	θ_{13} 104·97°	θ_{14} 104·89°
r_2	1·558			θ_{23} 113·12	θ_{24} 116·81
r_3	1·516				θ_{34} 112·55.
r_4	1·449				

The reference molecule is taken as a regular tetrahedron, $r_0 = 1·534$ Å (Murray-Rust, Bürgi & Dunitz, 1975). We obtain

$D_1(A_1) = 0·016$ Å $D_{2a}(E) = -2·59°$
$D_{3a}(T_2) = 0·119$ $D_{2b}(E) = 1·89$

$D_{3b}(T_2) = 0.077$

$D_{3c}(T_2) = 0.010$

$D_{4a}(T_2) = -6.84$

$D_{4b}(T_2) = -8.37$

$D_{4c}(T_2) = -5.81$

$D_5(A_1) = -0.66$.

The length of the three-dimensional $\mathbf{D}_3(T_2)$ displacement vector is 0.142 Å, that of $\mathbf{D}_4(T_2)$ is $12.28°$. The two vectors are nearly antiparallel with an angle of $150°$ between them. The length of the two-dimensional $\mathbf{D}_2(E)$ vector is $3.20°$.

The angles between the $\mathbf{D}_3(T_2)$ displacement vector and the $\mathbf{S}_a$, $\mathbf{S}_b$, $\mathbf{S}_c$ axes (corresponding to C_{2v} co-kernel symmetries) are 33, 57 and $86°$ respectively. The angle between $\mathbf{D}_3(T_2)$ and the $\mathbf{S}_{3a'}$ axis [corresponding to $C_{3v}(xxx)$ co-kernel symmetry] is also $33°$; so as far as bond lengths are concerned the observed distortion is intermediate between one conserving C_{2v} symmetry and one conserving C_{3v} symmetry. The angle between $\mathbf{D}_4(T_2)$ and the $\mathbf{S}_{4a'}$ axis is only $9°$ so that the bond-angle distortion is very nearly such as to preserve $C_{3v}(xxx)$ symmetry. It may be convenient, therefore, to go over to the primed coordinate system:

$D_{3a'}(T_2) = 0.119$ Å

$D_{3b'}(T_2) = 0.062$

$D_{3c'}(T_2) = 0.047$

$D_{4a'}(T_2) = -12.14°$

$D_{4b'}(T_2) = 0.21$

$D_{4c'}(T_2) = -1.81$

where the C_{3v} co-kernel components are brought into prominence. The ratio $D_{3a'}(T_2)/D_{4a'}(T_2)$ is about -0.010 Å deg^{-1} and similar values are found not only for other PO_4 tetrahedra but also for many other tetrahedral molecules (Murray-Rust, Bürgi & Dunitz, 1975). As discussed in the following paper, such correlations between different kinds of displacement transforming as the same irreducible representation may provide information about features of the potential-energy surface of the molecules.

4.3. Calculation of C_{3v} co-kernel and averaged configurations with inclusion of the redundant coordinate

There is no problem about the bond distances since no redundant coordinate is involved here. The bond lengths of the $T_2(C_{3v})$ co-kernel configuration are obtained by adding the $D_{3a'}(T_2)$ displacement to the reference structure $(r_0 = 1.534$ Å$)$

$$r_1' = r_0 + \frac{\sqrt{3}}{2} D_{3a'}$$

$$= r_0 + \frac{1}{4}(3r_1 - r_2 - r_3 - r_4) = 1.637 \text{ Å}$$

$$r_2' = r_3' = r_4' = r_0 - \frac{1}{\sqrt{12}} D_{3a'}$$

$$= r_0 - \frac{1}{12}(3r_1 - r_2 - r_3 - r_4) = 1.500 \text{ Å}.$$

These values are nearly but not quite the same as those obtained by averaging the appropriate quantities in the distorted molecule:

$$r_1^{av} = 1.645 \text{ Å}, \quad r_2^{av} = r_3^{av} = r_4^{av} = 1.508 \text{ Å}.$$

The discrepancy occurs because the C_{3v} co-kernel configuration obtained by averaging is the resultant of summing over all symmetry coordinates that preserve the C_3 axis along r_1, i.e. $\mathbf{S}_{3a'}(T_2)$ and $\mathbf{S}_1(A_1)$.

With no restriction on the angles, the six angular symmetry coordinates would form an orthogonal vector set, but if the angles are to describe a geometrically feasible structure in three-dimensional space then the displacements along these coordinates are not independent. This means that each displacement can be expressed as a function of the other five; in particular, the displacement along the redundant angular symmetry coordinate $\mathbf{S}_5(A_1)$ is a function of the three T_2 and the two E displacements. The analytic function involved is complicated (see determinant in § 4.1). Unless the appropriate displacement along $\mathbf{S}_5(A_1)$ is added to a kernel or co-kernel structure the bond angles will not satisfy the determinantal equation of § 4.1 and the structure would be geometrically feasible only in a space of four or more dimensions (Mackay, 1974). The corrections to be applied to the bond angles to make the structure feasible in three dimensions can be evaluated numerically or estimated from an approximation formula (see Appendix).

The bond angles obtained by adding the $D_{4a'}(T_2)$ displacement to the reference structure $(\theta_o = 109.47°)$ are

$$\theta_{12}' = \theta_{13}' = \theta_{14}' = \theta_0 + \frac{1}{\sqrt{6}} D_{4a'}$$

$$= \theta_0 + \frac{1}{6}(\theta_{12} + \theta_{13} + \theta_{14} - \theta_{23} - \theta_{24} - \theta_{34}) = 104.51°,$$

$$\theta_{23}' = \theta_{24}' = \theta_{34}' = \theta_0 - \frac{1}{\sqrt{6}} D_{4a'}$$

$$= \theta_0 - \frac{1}{6}(\theta_{12} + \theta_{13} + \theta_{14} - \theta_{23} - \theta_{24} - \theta_{34}) = 114.43°.$$

In deriving these angles, the displacement along the redundant angular coordinate $\mathbf{S}_5(A_1)$ has been ignored, and as a consequence, the angles do not satisfy the determinantal equation, which, for C_{3v} symmetry, takes the simple form

$$\cos \theta_{23} = (3 \cos^2 \theta_{12} - 1)/2.$$

For example, the value of θ_{23} that corresponds to $\theta_{12} = 104.51°$ should be 113.94 rather than $114.43°$. Since the contribution from $\mathbf{S}_5(A_1)$ affects all angles equally, corrected values for the angles can be calculated from

$$\cos(\theta_{23} + \varepsilon) = [3 \cos^2(\theta_{12} + \varepsilon) - 1]/2.$$

The correction ε is $-0.27°$ and the corrected angles of the C_{3v} co-kernel configuration are $\theta'_{12} = 104.24$, $\theta'_{23} = 114.16°$, equal to the values obtained by averaging. This comes about because, for our example, the value of $D_5(A_1)$ is more sensitive to $D_{4a'}(T_2)$ than to the other angular displacements and because the latter are small. The above angles are self-consistent within $0.01°$, *i.e.* in this case the averaged structure corresponds very closely to a feasible configuration. In general, for non-infinitesimal distortions from T_d symmetry, angles obtained by averaging will not satisfy the feasibility condition exactly. Analogous considerations have to be applied for other types of averaging and for other types of kernel or co-kernel configuration.

5. Approximate symmetry

As an example of the utility of symmetry coordinates for describing approximate symmetries we discuss some results obtained in a recent gas-phase electron diffraction study of 1-methyl-1-silabicyclo[2.2.1]-heptane (Hildebrandt, Horner & Boudjouk 1976, hereinafter HHB). In this molecule the bond angles at Si were found to be: $\alpha_{12} = 119$, $\alpha_{13} = \alpha_{14} = 122$, $\alpha_{23} = \alpha_{24} = 95$, $\alpha_{34} = 98°$ [for numbering see (1); the angles given correspond to model III of HHB, other models tested yielding only slightly different values]. The observed angles were interpreted by HHB in terms of a geometry 'quite close to that of a trigonal bipyramid' (2) with C(2) at the apex and C(1), C(3), C(4) as equatorial groups. An attacking nucleophile 'could occupy the other apex of a nearly perfect trigonal bipyramidal transition state'.

(1)   (2)   (3)
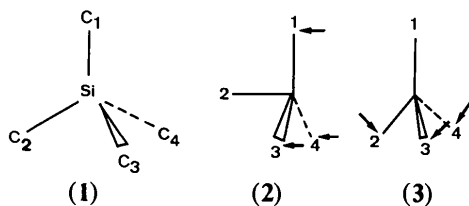
Inspection of the above angles suggests that a more accurate description would be in terms of a distorted tetrahedral coordination that still retains an approximate threefold axis, but passing through C(1) rather than C(2) and with C(2), C(3), C(4) squeezed together (3) rather than with C(1), C(3), C(4) spread apart (2). The actual angles do not show exact threefold symmetry but are somewhere between situations (2) and (3). Qualitatively, (3) seems a better description than (2) because α_{23} is closer to α_{34} than to α_{12}, and this impression is confirmed by transforming to symmetry coordinates.

For a deformation maintaining exact trigonal symmetry with C(1) as apex, the angular deformation components $D_{4b'}(T_2)$, $D_{4c'}(T_2)$, $D_{2a}(E)$ and $D_{2b}(E)$ are zero, *i.e.* the displacement vector D points exactly

along $\pm S_{4a'}(T_2)$. With C(2) as apex, D would point along $\pm S_{4b''}(T_2)$ for exact trigonal symmetry. Evaluation of the actual displacement vector D yields $D_{4a'} = 30.6°$, $D_{4b'} = -3.5°$, $D_{4c'} = 0$. Thus, the largest component is along $+S_{4a'}$ and the angle between D and $+S_{4a'}$ is only $6°$; the angle between D and $-S_{4b''}$ is $64°$. It is therefore clear that the observed angle deformation at the Si atom is much closer to (3) than to (2).

The literature abounds with loose descriptions of structures as corresponding to 'approximately symmetrical' arrangements of one kind or another. Since the ideas outlined in this paper may be generalized to $(3N - 6)$-dimensional spaces of any symmetry, they can be applied to provide a measure of deviations from symmetric reference structures and, thereby, a general basis for defining approximate symmetry.

APPENDIX

Formulae for producing feasible from unfeasible tetrahedral angles obtained from averaged or co-kernel configurations

The six bond angles in an MX_4 molecule must satisfy the determinantal equation

$$R = \begin{vmatrix} 1 & \cos\theta_{12} & \cos\theta_{13} & \cos\theta_{14} \\ \cos\theta_{12} & 1 & \cos\theta_{23} & \cos\theta_{24} \\ \cos\theta_{13} & \cos\theta_{23} & 1 & \cos\theta_{34} \\ \cos\theta_{14} & \cos\theta_{24} & \cos\theta_{34} & 1 \end{vmatrix} = 0.$$

The influence of rounding-off errors on the value of R can be seen from the following tabulation (all θ_{ij} equal):

$\theta_{ij} =$ 109·47122	$R = 7.1 \times 10^{-8}$
109·471	2.6×10^{-5}
109·5	3.4×10^{-3}
109	5.4×10^{-2}.

For any arbitrary set of six angles θ_{ij} we can obtain a more self-consistent set of angles $\theta'_{ij} = \theta_{ij} + \varepsilon$ by expanding R around the θ_{ij}'s to first order and by recycling to the desired degree of self-consistency;

$$\cos\theta'_{ij} = \cos\theta_{ij} - \varepsilon\sin\theta_{ij} = C_{ij} - \varepsilon S_{ij},$$

$$R = 1 - \sum_{i \neq j} (C_{ij}^2 - 2\varepsilon S_{ij}C_{ij})$$

$$+ \sum_{i \neq j \neq l \neq k} (C_{il}^2 C_{jk}^2 - \varepsilon S_{il}C_{il}C_{jk}^2 - \varepsilon C_{il}^2 S_{jk}C_{jk})$$

$$+ 2\sum_{i \neq j \neq k} (C_{ij}C_{jk}C_{ik} - \varepsilon S_{ij}C_{jk}C_{ik} - \varepsilon C_{ij}S_{jk}C_{ik}$$

$$- \varepsilon C_{ij}C_{jk}S_{ik})$$

$$- 2\sum_{i \neq j \neq k \neq l} (C_{ij}C_{kl}C_{il}C_{kj} - \varepsilon S_{ij}C_{kl}C_{il}C_{kj}$$

$$- \varepsilon C_{ij}S_{kl}C_{il}C_{kj} - \varepsilon C_{ij}C_{kl}S_{il}C_{kj}$$

$$- \varepsilon C_{ij}C_{kl}C_{il}S_{kj}).$$

If the angles θ_{ij} are related by symmetry, *e.g.* as in a kernel, co-kernel or averaged configuration, it may be simpler to use the explicit relations between the angles:

$C_{3v}(xxx)$: $2 \cos (\theta_{23} + \varepsilon) = 3 \cos^2(\theta_{12} + \varepsilon) - 1$

$D_{2d}(x)$: $\cos(\theta_{12} + \varepsilon) + 2 \cos(\theta_{13} + \varepsilon) = -1$

D_2: $\cos(\theta_{12} + \varepsilon) + \cos(\theta_{13} + \varepsilon) + \cos(\theta_{14} + \varepsilon) = -1$

$C_{2v}(x)$: $4 \cos^2(\theta_{13} + \varepsilon) = [1 + \cos(\theta_{12} + \varepsilon)]$
$$\times [1 + \cos(\theta_{34} + \varepsilon)]$$

$C_2(x)$: $[\cos(\theta_{13} + \varepsilon) + \cos(\theta_{14} + \varepsilon)]^2$
$$= [1 + \cos(\theta_{12} + \varepsilon)][1 + \cos(\theta_{34} + \varepsilon)]$$

$C_2(xyy)$: $2[\cos^2(\theta_{13} + \varepsilon) + \cos^2(\theta_{23} + \varepsilon) - 2 \cos (\theta_{12} + \varepsilon)$
$$\times \cos (\theta_{13} + \varepsilon) \cos (\theta_{23} + \varepsilon)]$$
$$= \sin^2(\theta_{12} + \varepsilon)[1 + \cos (\theta_{34} + \varepsilon)].$$

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Distortions of MX_4 Molecules from T_d Symmetry. II. Analysis of PO_4, SO_4 and $AlCl_4$ Species

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Deformations of PO_4, SO_4 and $AlCl_4$ fragments observed in crystals are analysed in terms of symmetry coordinates and internal coordinates. Various correlations among individual components of the total deformation are described and used to derive features of the potential-energy hypersurface of tetrahedral MX_4 fragments. Some of the observed correlations for all three systems can be described by a common numerical function based on the Pauling bond-number concept.

1. General background

Many MX_4 molecules that are known or expected to show T_d symmetry as isolated particles deviate from this symmetry in crystal environments. The observed distortions have been related to models of intramolecular bonding (McDonald & Cruickshank, 1967; Bartell, Su & Yow, 1970; Lager & Gibbs, 1973) as well as to the influence of the crystal environment

(McGinnety, 1972). The interdependence of bond-length and bond-angle variations has been studied empirically by Baur (1970, 1974) and by Brown & Shannon (1973).

In this paper we adopt a different point of view. Our premise is that any correlation found among independent parameters defining the structure of a given fragment, *e.g.* MX_4, in a variety of environments maps a region of low potential energy on the corresponding