$\Delta\varepsilon_L (\Delta\varepsilon_S)$	The larger (the smaller) of $\Delta\varepsilon_0$ and $\Delta\varepsilon_1$.
$\varepsilon_L (\varepsilon_S)$	The angle ε_0 or ε_1 associated with $\Delta\varepsilon_L (\Delta\varepsilon_S)$.
θ_H	Bragg angle corresponding to $\mathbf{b}_H$ and wavenumber k_H.
$\Delta\theta_0 \Delta\theta_1$	Angular opening of primary beam and detecting device in the plane containing $\mathbf{s}_0$ and $\mathbf{s}_1$.
$\Delta\theta_L (\Delta\theta_S)$	The larger (the smaller) of $\Delta\theta_0$ and $\Delta\theta_1$.
$\theta_L (\theta_S)$	The angle θ_0 or θ_1 associated with $\Delta\theta_L (\Delta\theta_S)$.
μ, ν, τ	Angles defining misorientation of crystallite.
σ	Mosaic spread.
φ, ψ	Angles defining direction of the axis of rotation (equation 18).
ω	Angular velocity of rotating crystal.
Ω_0, Ω_1	Solid angular opening of primary beam and detecting device ($\Omega_0 = \Delta\theta_0 \Delta\varepsilon_0$, $\Omega_1 = \Delta\theta_1 \Delta\varepsilon_1$).

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'Polar Flattening': Non-Spherical Effective Shapes of Atoms in Crystals

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Abstract

An examination of the nearest non-bonded interatomic distances found in crystals shows that where the two atoms are each covalently bound to only one other atom they exhibit non-spherical effective shapes. Such atoms behave as if flattened at their poles. Despite the large number of crystal structures now known in detail, various factors can militate against discovering effective atomic shapes. Possible causes of flattening are briefly discussed.

Introduction

In his review of van der Waals radii, Bondi (1964, p. 442) states '... all atoms have been treated as spheres and sphere segments, although it is well known that many are more nearly pear-shaped'. Bondi cites no references to this 'well known' fact and it is not absolutely clear what is implied by 'pear-shaped'. However, we believe there is now sufficient structural evidence, albeit not as extensive as we might hope, indicating that, for singly bound atoms at least, effective atomic shapes in crystals do deviate from spherical. In their more recent reviews of van der Waals radii, Zefirov & Zorkii (1976) have found considerable variabilities for certain atoms and this might in some cases be due to non-sphericity.

Currently, much effort is being devoted to formulating atom–atom potential energies which, it is hoped, will explain the packing and non-bonded interatomic distances found in crystals. Such an approach is clearly more fundamental, based as it is on the potential energy approximation to the free energy, instead of on the geometric concept of hard spheres.

Although the potential energy between two molecules must have a complicated and specific dependence on the six molecule orientation defining variables, the atom–atom approximation has led to sufficient success for it to be regarded as a useful empirical approximation to this energy. In virtually all cases the atom–atom potential is regarded as being spherical about the nucleus, *i.e.* it has the same functional dependence on distance irrespective of the mutual orientation of the molecules. However, the potential energy between two non-bonded atoms in different molecules can be regarded as composed of an attractive (dispersive) and a repulsive term. To regard both as spherical about the nuclei is to ignore the non-spherically disposed electrons. Thus it is not *whether* atoms in molecules behave as spheres in their non-bonding interactions with other atoms but to what *extent* they are non-spherical.*

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* Bondi and others use 'anisometric' which should probably be avoided in view of 'isometric' being commonly used for the cubic system. 'Aspherical' is a possible alternative but is usually restricted to slight deviations from spherical.

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We present evidence here bearing on the marked non-spherical effective shapes of atoms which are covalently bound to only one other atom in the molecule or complex ion. These atoms are necessarily 'exposed' and their effective shapes thus more readily revealed.

Evidence from crystal structures

Clearly the simplest approach is to examine, in as many crystals as possible, the non-bonded interatomic distances d_{XY} between two atoms X,Y in different molecules as a function of the polar angles μ_X and μ_Y (Fig. 1). We assume that atoms X and Y have cylindrical symmetry about their bonds and that their radii r_X and r_Y are additive. We can expect the nature of the atoms W and Z to have some effect on these radii but (in the absence of electron delocalization) for the remaining atoms in the two molecules to have relatively little effect.

Given a set of d_{XY}, μ_X and μ_Y for two atoms, it is not possible to infer their effective shapes without some simplifying assumptions. The shape must be assumed to have some parametric form so that, by least-squares refinement, or otherwise, the parameters can be refined. A further difficulty is that if the atoms are no longer assumed spherical then the point at which they 'touch' does not, in general, lie on the internuclear line so that d_{XY} which is always $\leq (r_X + r_Y)$ will depend on the dihedral angle between planes WXY and XYZ (Fig. 1). However, except where deviations from spherical are very marked, the present limited structural data justify using the approximation $d_{XY} \simeq r_X + r_Y$.

The determination of r_X and r_Y is made quite simple if atoms X and Y are of the same element or if either is an ion of known effective radius. The problem is also greatly simplified if W and Z are the same kind of atom. In accidental cases where $\mu_X = \mu_Y$ we have $r_X = r_Y = \frac{1}{2}d_{XY}$. Some caution however must be exercised in using this approach. When the μ angles are both small the distances between pairs of atoms WY, XZ and WZ are necessarily large compared with d_{XY}. As the μ's approach 90°, however, this may not necessarily be so, depending on the dihedral angle between planes WXY and XYZ. It is thus best to consider, if possible, two extreme cases; that where the dihedral angle is close to zero and where thus the 'shapes' of atoms X and Y automatically includes effects due to the other pairs of non-bonded atoms and that where the dihedral angle is sufficiently large for these other interactions to be negligible. In particular cases there may be an insufficient number of known crystal structures to permit this division into two classes. In such cases it is safer to confine attention to reasonably small values of μ (*i.e.* somewhat less than 90°).

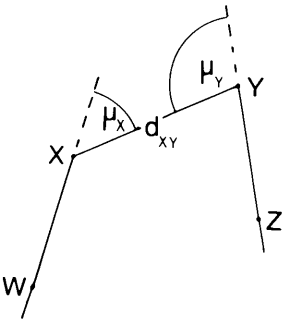

Fig. 1. Definition of μ_X, μ_Y and d_{XY}.

The first application of the above approach seems to have been made by Kitaigorodskii, Khotsyanova & Struchkov (1953) to the crystal structure of I_2. In this case $W = X = Y = Z$ and it is fortunate that for three of the close d_{II} distances $\mu_X = \mu_Y$ (Table 1). Two of these μ angles are close to one of those occurring in the other two short I···I contacts. Consequently, the linear equations can be solved for r at five values of μ. The result is given as a polar diagram in Fig. 2. Of these five orientations, four have the molecules parallel and the fifth has μ small (60°), so that the effective atomic

Table 1. *μ_X, μ_Y (°) and d_{XY} (Å) for nearest* I···I *neighbours in the* I_2 *crystal (after Kitaigorodskii, Khotsyanova & Struchkov,* 1953)

$d_{XY}(\text{calc}) = ab(a^2\cos^2\mu + b^2\sin^2\mu)^{-1/2}$ with $a = 2{\cdot}16$ and $b = 1{\cdot}76$ Å (Table 2).

μ_X	μ_Y	d_{XY}(obs)	d_{XY}(calc)
6	75	3·56	3·84
91·5	91·5	4·04	4·32
72·5	107·5	4·35	4·22
108·5	108·5	4·38	4·21
60	60	4·40	4·07

Table 2. *Least-squares fit of shortest non-bonded interatomic distances*

Same equation as for Table 1.

Atom	System	a (Å)	b (Å)	Reference
F	X–F···F–X (X, halogen)	1·54	1·34	(*a*)
Cl	Cl–Cl···Cl–Cl	1·90	1·67	(*b*)
Cl	C–Cl···Cl–C	1·75	1·69	(*c*)
Br	Br–Br···Br–Br	2·01	1·64	(*d*)
I	I–I···I–I	2·16	1·76	(*e*)
N	RCN$^-$···Y^+	1·69	1·42	(*f*)
H	H–H···H–H	1·53	1·31	(*g*)
H	H–H···H–H	1·78	1·45	(*h*)

(*a*) Nyburg & Szymański (1968). (*b*) Collin (1956). (*c*) Sakurai, Sundaralingam & Jeffrey (1963). (*d*) Vonnegut & Warren (1963). (*e*) Kitaigorodskii, Khotsyanova & Struchkov (1953). (*f*) Andersen, Klewe & Thom (1967). (*g*) Calculated from data given by Etters, Danilowicz & England (1975). (*h*) Calculated from data given by Kochanski (1973).

shape for iodine is that for the case of zero dihedral angle. The pronounced flattening of the iodine atom in the polar region ($\mu \sim 0°$) should be noted. Solid Cl_2 and Br_2 are isostructural with I_2 and, in principle, a similar analysis can be carried out. Unfortunately, because of the different sizes of the atoms, the fortuitous near-equality of certain μ angles in the I_2 structure does not arise in Cl_2 and Br_2. Accordingly, we assume a simple functional form for r and establish the values of the parameters by least-squares calculation. Our experience of non-sphericity is limited but as a first approximation we use the ellipse $(x^2/a^2) + (y^2/b^2) = 1$ with x the equatorial and y the polar axis and for which $r = ab(a^2\cos^2\mu + b^2\sin^2\mu)^{-1/2}$. The results for Cl, Br and I are given in Table 2 and Fig. 3.

Nyburg & Szymański (1968), unaware of Kitaigorodskii, Khotsyanova & Struchkov's (1953) analysis, made a similar investigation of the effective shape of the fluorine atom by pooling the results found in a number of halogen fluoride crystal structures. This revealed a flattening at the pole similar to that in the other halogen atoms. Its shape and equation are given in Table 2 and Fig. 3. Both the steadily increasing width at the equator ($\mu \sim 90°$; increasing a) and the similarity and lack of general trend in r values for halogen atoms at the pole ($\mu \sim 0°$) should be noted. [Bondi, 1964 (footnote to Table IV), refers to their 'probable pear shape'. It is still an open question whether this flattening is due to intermolecular bonding in the solid halogens, but in fluorine at least, this seems highly unlikely.]

Sakurai, Sundaralingam & Jeffrey (1963) note that in the crystal structure of 2,5-dichloroaniline 'the van der Waals radius (of Cl) is not necessarily constant for all directions relative to the C–Cl bond'. A least-squares analysis of the eight distances and angles they record again reveals flattening of the Cl atoms at the pole but less so than in the case of the Cl–Cl$\cdots$Cl–Cl interaction (Table 2).

We have not been able to apply the above procedure to other first row diatomics (see *Discussion*) and H_2 is treated separately below. We did search the available crystal data to see whether the shape of the N atom in organic nitriles, RCN, could be established. It happens, however, that the dipolarity of this group militates against head-to-head contacts which are found extremely rarely, if at all. Thus the effective shape of nitrogen in its polar region cannot be discovered and we have been unable in such cases to confirm positively Bondi's (1964, p. 446) statement that 'triple-bonded nitrogen ... appears to be quite anisometric with r = 1·40 Å parallel to bonds up to 1·7 Å in the direction normal to bonds'.

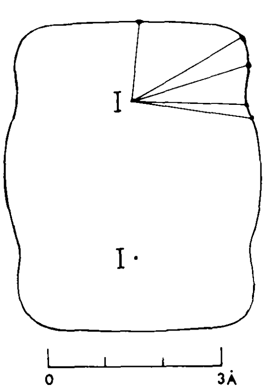

Fig. 2. The effective shape of the I_2 molecule in the crystal (after Kitaigorodskii, Khotsyanova & Struchkov, 1953).

Although there are few crystal structures in which the effective shape of atom X can be inferred from $X\cdots X$ distances, the shape of X can be inferred from $(RX)^{\pm}\cdots Y^{\mp}$ distances where Y is a monatomic ion of known radius. Thus Andersen, Klewe & Thom (1967) examined the dependence of $R\mathrm{CN}^{-}\cdots Y^{+}$ distance on μ angle and their results are plotted in polar form in Fig. 4. There is a good fit with observed r_N values and those calculated with a = 1·69 and b = 1·42 Å. Thus Bondi's remarks about triple bonded nitrogen seem to be well substantiated.

Once a set of shape parameters has been derived, calculated closest $X\cdots Y$ distances can be compared with those observed. Of particular interest is the $XR\mathrm{CN}\cdots XR\mathrm{CN}$ series where X is a halogen. It has been known for some time that such molecules (which, if linear, tend to crystallize in end-to-end arrays) often show 'short' –N$\cdots X$– distances. For these, special interactions, such as molecular charge-transfer have often been held responsible. However, if we accept that

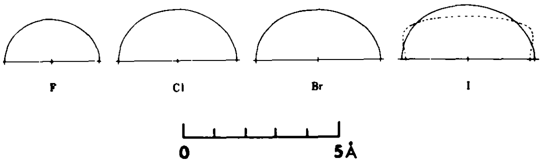

Fig. 3. Best fitting ellipses of atoms X in their $Y–X\cdots X–Y$ interactions in crystals. For fluorine, Y are other halogen atoms (after Nyburg & Szymański, 1968). For Cl, Br and I, $Y = X$. (I has Fig. 2 superimposed.) Coefficients of ellipses from Table 2.

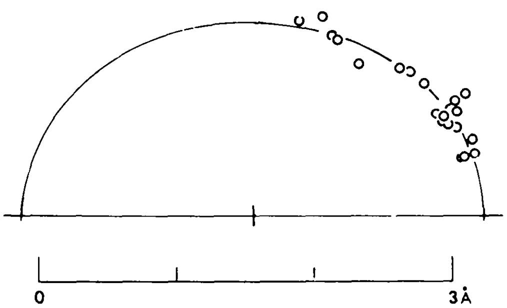

Fig. 4. Effective shape of nitrogen in $R\mathrm{CN}^{-}\cdots Y^{+}$ interactions (after Andersen, Klewe & Thom, 1967).

Table 3. *Calculated shortest and observed distances in* $-C{=}N\cdots X{-}C-$ (X = *halogen*) *with parameters from Table* 2

Angles are in degrees, distances in Å. For further examples see Prout & Kamenar (1973).

	X	μ_N	μ_X	r_N	r_X	d_{NX} calc	d_{NX} obs	Reference
2,4,6-trichlorobenzonitrile	Cl	57·6	2·5	1·60	1·67	3·27	3·22	(*a*)
cyanogen chloride	Cl	0·0	0·0	1·42	1·67	3·09	3·01	(*b*)
chlorocyanoacetylene	Cl	1·7	0·0	1·42	1·67	3·09	2·97	(*c*)
2,4,6-tribromobenzonitrile	Br	49·9	11·1	1·56	1·65	3·21	3·07	(*a*)
cyanogen bromide	Br	0·0	0·0	1·42	1·64	3·06	2·87	(*d*)
bromocyanoacetylene	Br	0·4	0·0	1·42	1·64	3·06	2·96	(*c*)
iodocyanoacetylene	I	1·3	2·6	1·42	1·76	3·18	3·02	(*e*)

(*a*) Carter & Britton (1972). (*b*) Heiart & Carpenter (1956). (*c*) Bjorvatten (1968). (*d*) Geller & Schawlow (1955). (*e*) Borgen, Hassel & Rømming (1962).

these distances are simply a consequence of the intrinsic shapes of the atoms concerned then, using the data from Table 2, we can calculate the shortest $-N\cdots X-$ distances to be expected in each case. The agreement is good (Table 3). This in itself does not prove the absence of 'special' interactions but polar flattening does seem a simpler and more consistent explanation.

Theoretical results

The interaction between hydrogen and other atoms is especially soft and hence, because of thermal vibration, we can expect wide variations in the shortest $H\cdots H$ contacts as a function of μ angle. However, we can appeal to the theoretical results of Etters, Danilowicz & England (1975) who give the $H_2\cdots H_2$ interaction energy for a number of mutual orientations and intermolecular distances.

We have selected those cases where the two molecules are co-planar with the μ angles equal and plotted half the equilibrium distance between closest hydrogen atoms in Fig. 5. There is slight, but significant, polar flattening (Table 2). Kochanski (1973) has also given several calculated interactions for the $H_2\cdots H_2$ system based on various theoretical models. Typically, from the published results, a is *ca* 1·78 and b *ca* 1·45 Å. This represents a significant difference (*i.e.* both 'fatter' and 'flatter') from the results given by Etters, Danilowicz & England (1975). [On The other hand, according to the potential energy calculations on pairs of X_2 molecules given by Koide & Kihara (1974) based on second virial coefficients, each of X = D, N, O and F has a slightly longer radius in the polar direction than at the equator.]

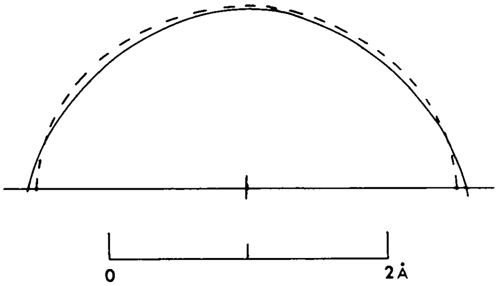

Fig. 5. Effective shape of H in $H_2\cdots H_2$ interactions calculated at $\mu_X = \mu_Y$ from the theoretical results of Etters, Danilowicz & England, 1975 (full line). Broken line: ellipse with a = 1·53 and b = 1·31 Å.

Discussion

Despite the large volume of crystal structure data now available it is surprisingly difficult to establish the effective atomic shape for the type of case we are interested in here. We have already seen how bond polarity can militate against head-to-head (μ = 0) orientation which would yield the effective shape at the poles of the outermost atoms. Another factor militating against establishing the atomic profile is high crystal symmetry which lessens the number of different r and μ values present in any one structure. Furthermore, many series of crystals containing, say, the same complex anion but differing cations are isostructural; thus no new r or μ values are generated. Disorder, of course, also prevents the establishment of effective atomic shapes. Thus we cannot establish with any certainty the atomic profiles of N in N_2 or of O in O_2 because of the high symmetry or disorder present in these crystalline elements.

Normally a substantial number of r *vs* μ values is required to establish effective atomic shapes with any confidence. There has to be a 'bunching' of comparably short interatomic distances. If one has relatively few observations this bunching is not possible. In particular, if r values are very sparse over a particular μ range an adventitiously large value of r in this range (caused by the inability of the atoms or ions in question to come into close contact) can give an erroneous shape correlation. This is the case with the thiocyanates Na, K and CsSCN. These crystal structures yield a satisfactory number of r values in the range $60° < \mu < 90°$ but for S there are no other values and for N only one other value in the range $0 < \mu < 60°$. Although for N this is sufficient to establish polar flattening, no confidence can be placed on the exact form of the parameters obtained from such sparse information. Similarly, Pringle & Noakes (1968) pooled the results from a number of azide (N_3^-) crystal structures and they also noted polar flattening of the terminal nitrogen atoms. However, to establish a smooth curve (they assumed an ellipse) some rather large $-N^- \cdots Na^+$ distances had to be excluded.

Because of one or other of the reasons given above we have been unable at present to determine polar flattening parameters for the outer atoms in any of the following complex ions: CN^-, $(N-C-N)^{2-}$, $(C-N-O)^-$, $(N-C-O)^-$ or $(C-C)^{2-}$. What evidence there is, however, does suggest polar flattening.

As stated at the outset, in the normal application of the atom–atom potential method, spherical atomic shapes are assumed. The introduction of additional factors or modifications may however be equivalent to assuming non-spherical atomic shapes. Thus the addition of bond polarization terms (Caillet & Claverie, 1974) will be equivalent to polar flattening of the atoms involved. Alternatively, shifting the center of attraction–repulsion away from the nucleus in the direction of the bond as Williams (1965) has suggested for hydrogen, is also equivalent to polar flattening (see Fig. 5).

The cause of polar flattening cannot be given adequately in simple terms. It is probably due, however, to two dominant factors. First to the shape of the electron density profile of the bound atom, as suggested by Kitaigorodskii (1961) for I_2. This density profile will govern the shape of the repulsive part of the interaction potential. There is, for example, a striking resemblance between the outer electron density contours found by Hartree–Fock SCF calculations for F_2 (Wahl, 1964) and the shape of the F atom given in Fig. 3. In the former $a/b = 1{\cdot}11$, in the latter $a/b = 1{\cdot}15$. The second cause of flattening is almost certainly bond polarizability. This adds a significant non-spherical term in the direction of the bond vector.

In conclusion, we believe there is sufficient evidence to show that polar flattening as described here is a common, if not universal, feature of atoms covalently bound to only one other. As more crystal structure data accumulate and retrieval of data from compilations such as the Cambridge Data File becomes easier, so the effective shapes of atoms in crystals can be put on a sounder empirical basis.

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