References

CARRELL, H. L. (1972). *Acta Cryst.* **B28**, 1754–1759.

CREECH, H. J., PRESTON, R. K., PECK, R. M., O'CONNELL, A. P. & AMES, B. N. (1972). *J. Med. Chem.* **15**, 739–746.

GANTZEL, P. K., SPARKS, R. A., LONG, R. E. & TRUEBLOOD, K. N. (1969). *UCLALS*4 program in Fortran IV.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 201–207. Birmingham: Kynoch Press.

JOHNSON, C. K. (1963). 1620 Programs from I.C.R. No. 10. *Absorption Factors for a Crystal Ground as an Ellipsoid of Revolution.*

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee,

MAIN, P., WOOLFSON, M. M. & GERMAIN, G. (1971). *MULTAN. A Computer Program for the Automatic Solution of Crystal Structures.*

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The X-RAY System of Crystallographic Programs. Version of July 1970, updated.

ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1141.

Acta Cryst. (1973). B**29**, 2006

Generalization of Baur's Correlations between Bond Length and Bond Strength in Inorganic Structures

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(*Received* 9 *April* 1973; *accepted* 30 *April* 1973)

From results published by Baur it has been possible to show that for a given cation X with a given coordination number, the percentage variation of an X–O bond length from its average value is proportional to the difference between the actual bond strength received by the oxygen and the strength (2 v.u.) which the oxygen should receive according to Pauling's second rule. A correlation between the reduction of X–O length and the increase in X–O–X angle is discussed.

Introduction

Many authors have recently tried to establish empirical relationships between bond lengths and angles in inorganic structures and quantities involved in theoretical models of the chemical bond. Baur (1970), Brown & Shannon (1972, 1973) and Donnay & Allmann (1970) have introduced modifications to Pauling's second rule by correlating bond lengths with bond strengths; Cruickshank (1961), Gibbs, Hamil, Louisnathan, Bartell & Yow (1972) and Louisnathan & Gibbs (1972*a*, *b*, *c*) have related bond lengths and angles directly to the contribution of different electronic orbitals involved in the chemical bond; in addition, Kálmán (1971) has found a linear relationship between X–O average distances and the number n of the non-compensated electrons delocalized on the corresponding XO_4^{n-} tetrahedra. We shall be concerned essentially with the first approach.

Pauling's (1929, 1960) statement that 'in a stable ionic structure the valence of each anion, with changed sign, is exactly or nearly equal to the sum of the strengths of the electrostatic bonds to it from the adjacent cations' is borne out in practice by most ionic structures.* Deviations from this rule are usually interpreted by stating that the electrostatic bond strength p received by anions must depend on anion–cation distances.

Within this context, Donnay & Allmann (1970) and Brown & Shannon (1972, 1973) have defined a new bond strength s_i for a given bond X_i–O with length L, such that the relation $\sum s_i = 2$ v.u. is still valid. Brown & Shannon (1972, 1973) have found the following empirical equation:

$$s_i = s_{i,0}(L/L_0)^{-N} \; ; \qquad (1)$$

L_0 and N are parameters to be fitted and $s_{i,0}$ is an 'arbitrarily' chosen parameter which, however, has been set very close to Pauling's bond strength p_i; L_0, in its turn, approaches closely the mean value L_m of measured bond lengths L. Similar equations have been given by Donnay & Allmann (1970) and by Pyatenko (1973).

Baur (1970, 1971) considered the dependence of the single cation–oxygen distance on the total bond

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* Terms such as 'ionic structure' and 'electrostatic bond strength' will always have a strictly formal meaning, without the claim that a real ionic model is exactly valid.

strength $p=\sum p_i$ which is received by the oxygen atom, O, from all the cations, X_i, surrounding it. He investigated fourteen coordination systems (Table 1) and found that for them the following linear equation (Baur's second rule) is valid:

$$L=a+bp; \qquad (2)$$

a and b are parameters to be fitted for each cation with a given C.N. [for Si–O see also Baur (1971)]. An analogous relationship has been obtained between the length $D\cdots A$ of hydrogen bonds and the corresponding value of (p_D-p_A), where A (acceptor) is always oxygen and D (donor) may be either oxygen (Baur, 1970) or an ammonium group (Khan & Baur, 1972).

Table 1. *Values of the parameters of equations* (3) *and* (4) *for atoms* X *with coordination number C. N. and average value* L_m *of the bond lengths* X–O

X	C.N.	L_m	$-a'/k$	k
B	3	1·367 Å	2·01 v.u.	0·082
S	4	1·473	1·94	0·087
B	4	1·479	1·97	0·077
P	4	1·537	1·97	0·071
Si	4	1·625	2·03	0·056
Al	6	1·909	1·91	0·132
Ti	6	1·97	2·05	0·102
Fe^{III}	6	2·011	2·05	0·109
Mg	6	2·085	1·96	0·058
Fe^{II}	6	2·138	1·93	0·140
Na	6	2·44	1·95	0·098
Ca	8	2·50	2·00	0·132
Na	8	2·51	2·00	0·124
K	8	2·85	2·00	0·039
H	hydrogen	0·96	2·00	0·012
H	bond	1·96	2·00	0·484

Although the scatter of experimental points around the fitted straight lines is often appreciable, particularly for cations with a formal charge less than 3, relation (2) is useful, at least qualitatively, in several cases; *e.g.*, it can justify irregular coordination polyhedra† and can provide a test for doubtful features of crystal structures, such as the possible existence of hydrogen bonds [see, *e.g.*, Ferraris & Franchini-Angela (1973)]. Apart from those in Baur's papers, some applications of (2) may be found in the study of geometrical features of hydrogen-bonded water molecules (Ferraris & Franchini-Angela, 1972).

The mathematical difference between (1) and (2) should not be surprising, since the two approaches are quite different and the quantities p and s_i have very different meaning.‡

Generalization of Baur's second rule

Let us write (2) in the following way:

$$\Delta L=k(a'/k+p) \qquad (3)$$

where $\Delta L=(L-L_m)/L_m$, and consequently $a'=(a-L_m)/L_m$ and $k=b/L_m$.

An examination of the a and b values published by Baur has shown (Table 1) that $a'/k\simeq -2$ v.u. in all cases. Further, we have obtained relationships of type (2) by plotting against p O–H and H$\cdots$O bond lengths measured in crystalline hydrates studied by neutron diffraction (Ferraris & Franchini-Angela, 1972); the bond strength of a hydrogen bond has been divided in the ratio 0·83/0·17 between the donor and the acceptor atom [see Baur (1970)]. The value -2 v.u. for a'/k has a definite crystallochemical meaning; in fact it allows one to transform (3) into

$$\Delta L=k(p-2)\,, \qquad (4)$$

which states that *the percentage variation of an* X–O *bond length L from its average value* L_m *is proportional to the difference between the actual bond strength received by the oxygen and the bond strength* (2 v.u.) *which the oxygen should receive according to Pauling's second rule.**

Equation (4), derived from experimental data, substantiates the following two hypotheses: (i) L depends linearly on p; (ii) for $p=2$ v.u., L is equal to L_m. Equation (4) is evidently more general than (2), because it contains only one empirical parameter (k) instead of two (a and b), and expresses quantitatively both hypotheses (i) and (ii). Baur's (1970) third rule, valid within one coordination polyhedron, should be equivalent to (4) in the case that the average value of p for the oxygen atoms of the polyhedron were 2 v.u.

It is now generally accepted (see Cruickshank, 1961) that the average value L_m of the bond lengths X–O in a given type of coordination polyhedron is constant in all structures, and so necessarily equal (or very close) to the value assumed by X–O in structures with regular polyhedra, where deviations from Pauling's second rule are rare. If only this hypothesis, clearly an *a priori* justification of assumption (ii), is accepted, (4) may be replaced by the following relationship:

$$\Delta L=f(p-2) \qquad (5)$$

where f is an increasing function which is zero for $p=2$.

The k parameter

The values of k reported in Table 1 have been calculated from the values of a, b and L_m given by Baur (1970)

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† In this paper 'irregular' or 'distorted polyhedron' means a coordination polyhedron with unequal X–O distances; in fact, geometrically irregular polyhedra could have different edges (O$\cdots$O) but equal X–O distances.

‡ Equation (4) can be derived from (1) if one assumes that over small regions the latter can be treated as linear (Brown, 1973).

* This statement was made in a lecture (Ferraris, Franchini-Angela & Catti, 1972) at the IX International Congress of Crystallography, 26 August–7 September 1972, Kyoto, Japan [see also Ferraris & Franchini-Angela (1973)].

or, for the hydrogen bond, derived from data of Ferraris & Franchini-Angela (1972) (see above); improved k values might be obtained by analysing experimental ΔL values plotted against p and interpolating them directly by the straight line of equation (4).

Qualitative relationships can be found between the k parameter and features of the corresponding cations. If Baur's fourteen cases are divided into three groups (with C.N. 4, 6, and 8), a tendency for k to decrease with increasing ionic radius of the cation is evident. In the case of S, P, and Si, the increase of k from Si to S has a clear meaning: for a given $(p-2)$ value, the deviation of L from L_m increases with the covalent character of the bond X–O. Such behaviour is justifiable intuitively: the larger the departure from the ionic model, the larger will be the deviation from Pauling's second rule, which is based on that model. A similar interpretation could also be accepted for C.N. 8 (Ca, Na, and K); for C.N. 6, on the other hand, the situation is less clear, partly because the variations in the ionic radii of transition metal cations cannot be directly related to the covalency of the X–O bond.

For O···O hydrogen bonds, k is much larger for the H···O bond than for the O–H, even though H···O is more ionic than O–H; on the other hand, the two bonds differ too greatly in strength and other features to be truly comparable as in the above cases.

Correlations between X–O distances and X–O–X angles in XO$_4$ groups

On the assumption that the variations of the X–O bond lengths in XO$_4$ groups can be explained by a model in which the central atom X moves within a rigid tetrahedron of oxygen atoms, Baur (1970) derived the following relationship (Fig. 1):

$$L=L_1 \sin(\beta/2)\cdot\frac{1}{\sin(\alpha/2)} \qquad (6)$$

where L_1 represents the X–O distance when X lies at the geometrical centre of the tetrahedron.

From the dependence of the bond length Si–O on the angle Si–O–Si (ε) in SiO$_4$ groups sharing oxygen atoms, Louisnathan & Gibbs (1972*a*) and Gibbs *et al.* (1972) found a linear decreasing relation between L and $-1/\cos\varepsilon$, which means that L decreases as $\varepsilon(>90°)$ increases [for Al, P, S, and Cl see Louisnathan & Gibbs (1972*b*)]. The variation of ε (and thus of L) is correlated with the relative contribution of σ and π electrons in the Si–O bonds. Nevertheless, independently of the 'correct' theoretical explanation, it is easy to show that such a result is qualitatively consistent with Baur's equation (6). In fact, (6) may be written

$$L \propto 1/\cos\gamma; \qquad (7)$$

thus, following Baur's hypothesis of rigid tetrahedra, γ $(<90°)$ and L decrease together. Under the additional plausible assumption that the two tetrahedra do not change their relative positions, a narrowing of γ causes a widening of ε, and the result is that L decreases as ε increases.

Conclusions

The proposed generalization of Baur's second rule evidently has the same limits of validity and the same fields of application as the original rule. One limitation is that it does not account for small deviations of bond lengths when $p=2$ v.u., which sometimes occur; this drawback may be attributed to the exclusion from equations (2) and (4) of such causes of deviations as interactions with second neighbours and possible correlations between ionic radius and C.N. of the oxygen (Shannon & Prewitt, 1969).

Furthermore, we can point out that, strictly speaking, Pauling's second rule simply establishes a relation between the coordination numbers, charges, and numbers of cations which surround an oxygen anion; it does not state anything directly about the distances of the cations from the oxygen. Therefore, in this context, the fact that a coordination polyhedron is geometrically regular or distorted is completely independent of the existence of deviations from Pauling's second rule. Equation (4), which directly relates the deviations from Pauling's second rule to distortions of the polyhedra, adds further information to the said rule and makes possible the calculation of effective bond distances in the coordination polyhedra of crystalline substances. It is this last point that makes Baur's approach advantageous in comparison with equation (1), since the latter requires the bond lengths to be independent variables.

The interesting development of Baur's approach does not mean that an ionic model alone is sufficient to explain the crystal-chemical behaviour of distances and angles in inorganic structures. The contributions from molecular orbitals must be taken into account for a deeper understanding of the problem, but any future theory will have to account for the empirical relationships derived by the simple ionic model.

Research was supported by the Consiglio Nazionale delle Ricerche, Roma. We would like to thank Pro-

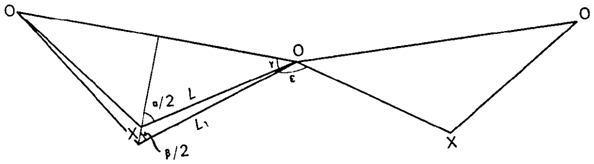

Fig. 1. Sketch of two XO$_4$ tetrahedra sharing a corner, assuming that X shifts within a rigid oxygen framework. L_1 and L, $\beta/2$ and $\alpha/2$ are bond lengths and angles for an ideal and a real tetrahedron, respectively; $\gamma=\angle$OOX and $\varepsilon=\angle$XOX.

fessors I. D. Brown and G. V. Gibbs for sending us pre-prints of their papers.

References

BAUR, W. H. (1970). *Trans. Amer. Cryst. Assoc.* **6**, 129–155.
BAUR, W. H. (1971). *Amer. Min.* **56**, 1573–1599.
BROWN, I. D. (1973). Private communication.
BROWN, I. D. & SHANNON, R. D. (1972). *Acta Cryst.* A**28**, S107.
BROWN, I. D. & SHANNON, R. D. (1973). *Acta Cryst.* A**29**, 266–282.
CRUICKSHANK, D. W. J. (1961). *J. Chem. Soc.* pp. 5486–5504.
DONNAY, G. & ALLMANN, R. (1970). *Amer. Min.* **55**, 1003–1015.
FERRARIS, G. & FRANCHINI-ANGELA, M. (1972). *Acta Cryst.* B**28**, 3572–3583.
FERRARIS, G. & FRANCHINI-ANGELA, M. (1973). *Acta Cryst.* B**29**, 859–863.
FERRARIS, G., FRANCHINI-ANGELA, M. & CATTI, M. (1972). *Acta Cryst.* A**28**, S65.
GIBBS, G. V., HAMIL, M. M., LOUISNATHAN, S. J., BARTELL, L. S. & YOW, H. (1972). *Amer. Min.* **57**, 1578–1613.
KÁLMÁN, A. (1971). *J. Chem. Soc.* (*A*), pp. 1857–1859.
KHAN, A. A. & BAUR, W. H. (1972). *Acta Cryst.* B**28**, 683–693.
LOUISNATHAN, S. J. & GIBBS, G. V. (1972*a*). *Amer. Min.* **57**, 1089–1108.
LOUISNATHAN, S. J. & GIBBS, G. V. (1972*b*). *Mater. Res. Bull.* **7**, 1281–1292.
LOUISNATHAN, S. J. & GIBBS, G. V. (1972*c*). *Amer. Min.* **57**, 1614–1642.
PAULING, L. (1929). *J. Amer. Chem. Soc.* **51**, 1010–1026.
PAULING, L. (1969). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.
PYATENKO, YU. A. (1973). *Sov. Phys. Crystallogr.* **17**, 677–682.
SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* B**25**, 925–946.

Acta Cryst. (1973). B**29**, 2009

The Crystal Structure of β-Barium Orthotitanate, β-Ba_2TiO_4, and the Bond Strength–Bond Length Curve of Ti–O

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(*Received* 29 *January* 1973; *accepted* 10 *April* 1973)

The crystal structure of β-barium orthotitanate, β-Ba_2TiO_4, has been refined using 1693 non-equivalent reflexions measured from a twinned synthetic crystal with an automatic X-ray single-crystal diffractometer. It is monoclinic with cell dimensions $a=6{\cdot}096$ (4), $b=7{\cdot}681$ (6), $c=10{\cdot}545$ (9) Å, $\beta=92{\cdot}99$ (6)°, $Z=4$, space group $P2_1/n$. The final weighted agreement index is 0·051. The asymmetric unit contains one almost regular TiO_4 tetrahedron (mean Ti–O = 1·808 Å) and two crystallographically distinct barium atoms. A revised bond strength (s)–bond length (R) relationship of the form $s=0{\cdot}666\,(R/1{\cdot}953)^{-5\cdot25}$ is proposed for Ti–O bonds.

Introduction

The crystal structure of β-barium orthotitanate, β-Ba_2TiO_4, was first determined by Bland (1961). Because this compound is one of the few examples of Ti coordinated by four oxygen atoms, it is of particular importance in determining the bond strength (s)–bond length (R) curve for Ti–O (Brown & Shannon, 1973). Unfortunately, because of the twinning, Bland was only able to measure the Ti–O bond length to an accuracy of 0·2 Å. We have therefore redetermined the crystal structure in order to obtain a more accurate Ti–O distance.

Structure determination

Crystals of β-Ba_2TiO_4 were prepared by the method described by Bland (1961). The white crystals (Ba_2iT_4O) were separated from the dark crystals ($BaTiO_3$) by hand. Weissenberg and precession photographs showed that most crystals contained not only twinned β-Ba_2TiO_4 but also at least one related orthorhombic phase with a tripled b axis. Such polymorphism is expected from Todd & Lorenson's (1952) observation that the heat capacity and entropy of Ba_2TiO_4 are anomalously large at room temperature. Ca_2SiO_4 has a similar series of polymorphs including a monoclinic