

A Molecular-Orbital Study of the Bond-Length Variations in Lithium Polysilicate

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Bond-length variations within the SiO_4 and LiO_4 tetrahedra in $(\text{Li}_2\text{SiO}_3)_x$ are examined in terms of valence-electron population analyses obtained from extended Hückel molecular orbital theory. The results indicate that a significant improvement in the correlations between observed bond length and Mulliken overlap population is obtained when the 'first coordination sphere' of tetrahedral groups is included in the calculations.

Introduction

The prediction and rationalization of observed polyhedral distortions in inorganic crystal structures is one of the more challenging problems of crystal chemistry. Indeed, with increasing numbers of precisely refined crystal structures now available for study, it is clear that the deviations from ideal shapes can often be related to particular characteristics of the bonded atoms and their environments. Among the most commonly used methods for systematizing these variations we may include the classic set of rules proposed by Pauling (1929, 1960) and later extended by Baur (1970, 1972) and Brown & Shannon (1973), the well-known electron-pair repulsion model of Gillespie (1963), the crystal-field and ligand-field theories (Orgel, 1960; Burns, 1970) of transition-metal compounds including the so-called Jahn–Teller effect (Jahn & Teller, 1937), and the $d-p$ π -bonding model of Cruickshank (1961).

As one of many examples of the utility of these concepts we may quote a recently published refinement of the crystal structure of lithium polysilicate, $(\text{Li}_2\text{SiO}_3)_x$, containing chains of corner-sharing SiO_4 and LiO_4 tetrahedra (Hesse, 1977). Although both O atoms in the asymmetric unit are coordinated by four cations [the O(2) atom by 2 Li + 2 Si and O(1) by 3 Li + 1 Si], the bonds to O(2) are observed to be significantly longer than those to O(1). Since these atoms are respectively the bridging and terminal atoms in the silicate chain Hesse (1977) was able to rationalize the Si–O bond-length variations in terms of Cruickshank's (1961) $d-p$ π -bonding theory, but offered no explanation for the variation of Li–O distances. Indeed, while the longer bonds from O(2) to Si are consistent with the smaller values observed for $\langle \text{O–Si–O}(2) \rangle_3$, the average of the three angles common to each Si–O(2) bond (Louisnathan & Gibbs, 1972), the same is not true, as might be expected, for the significantly larger LiO_4 group. Moreover, despite the approximate C_{3v} point symmetry of the LiO_4 group, its bond length and angle data also deviate from the general trend evinced by the bond length–bond

angle curves of Bürgi (1975). However, the longer bonds to O(2) from both Si and Li are consistent with Baur's (1970) extended electrostatic valence rule since O(2) receives a significantly larger sum of bond strengths (Pauling, 1960) from its coordinating cations than does O(1).

Despite the remarkable success of these essentially phenomenological approaches to the prediction and rationalization of individual bond lengths in a host of crystalline compounds, it is generally accepted that they contribute little to our understanding of chemical bonding and that they cannot replace a detailed theory based on the electronic structure of the atoms. Fortunately, computational quantum-mechanical chemistry has now advanced to the point where electronic wave functions are in much closer agreement with experiment than was formerly the case. Although exact solutions to the Schrödinger equation are in general not realized for large molecules or solids, approximate semi-empirical molecular-orbital theory has been successfully applied to the study of the geometries and energetics of a number of moderately complex systems (Hoffmann, 1963, 1966; Dewar & Haselbach, 1970; Gibbs, Hamil, Louisnathan, Bartell & Yow, 1972; Tossell, Vaughan & Johnson, 1974; Tossell & Gibbs, 1976).

Of these methods, extended Hückel theory (Hoffmann, 1963; Allen, 1970) has proven to be an objective algorithm for the rationalization and correlation (although not prediction *a priori*) of bond length and angle data in a variety of non-transition metal tetrahedral oxyanions, TO_4^{n-} (Bartell, Su & Yow, 1970; Tossell & Gibbs, 1978). In these calculations, Mulliken electronic-population analyses (Mulliken, 1955) have been undertaken on various insular and polymerized oxyanions isolated from their nontetrahedral cation neighbors in the respective crystal structures. Since shorter bonds necessarily tend to produce larger overlap populations, this induced correlation is removed from consideration by stretching all T–O bond lengths to an average value for the particular TO_4^{n-} group. However, the O–T–O and T–O–T

angles are maintained at their observed values, thereby allowing the energy and shape of the molecular-orbital wave functions to respond to the angular distortions by establishing different overlap populations for the individual bonds. With this model it is therefore asserted that the bond-length variations are primarily a function of the valence angles imposed upon the oxyanion by packing and bonding requirements of the cations external to the group. Despite the neglect of the nontetrahedral cations and the assumption of constant bond lengths, the resultant bond-overlap population parameters, $n(T-O)$, correlate linearly with the observed $T-O$ bond lengths, shorter bonds tending to involve larger $n(T-O)$ values.

Although extended Hückel theory is based on a strictly covalent model and would therefore be expected to work best for oxyanions in which the electronegativity difference between the bonded atoms is small (Allen, 1970, 1972), previous experience suggests (Hill, Gibbs, Craig, Ross & Williams, 1978) that changes in

overlap population are essentially independent of the exact orbital parameterization and are instead a simple geometric function of orbital overlap. With no nontetrahedral cations, significant differences in electronegativity, and large ranges in both length and valence angle, the structure of lithium polysilicate is an ideal candidate for further testing of these concepts.

Results and discussion

In an attempt to account for the influence of the surrounding framework on the individual bond lengths within the SiO_4 and LiO_4 tetrahedra in lithium polysilicate we have included the 'first coordination sphere' of tetrahedral groups in both instances with the result that the calculations were undertaken for clusters containing a total of 42 atoms (Fig. 1). The theoretical basis for the neglect of even more distant atoms has been discussed by Kier (1968). For the reason outlined in the *Introduction*, the $Si-O$ and $Li-O$ bond lengths within each oxyanion cluster were fixed at values of 1.63 and 2.00 Å, respectively, while the valence angles within and between the tetrahedra were maintained at their observed values. All calculations were performed with the extended Hückel theory program originally written by Hoffmann (1963) assuming a minimum-valence sp -basis for Si, Li and O, and using the valence-orbital ionization energies and Slater-orbital exponents listed in Table 1.

Values of calculated bond-overlap population, $n(T-O)$, and observed bond length, $d(T-O)$, for the four bonds in the central TO_4 tetrahedron of each cluster are given in Table 2. It should be noted that although the value of $n(T-O)$ cannot be regarded as the actual number of electrons in the internuclear region the obvious correlation between $n(T-O)$ and $d(T-O)$ for each tetrahedron is certainly in agreement with the general belief (Coulson, 1970) that they are closely related. Moreover, the average value of $n(T-O)$ for the SiO_4 group is considerably larger than that of LiO_4 , consistent with the relative ionic character of the $Si-O$ and $Li-O$ bonds (Pauling, 1960), and with previously obtained trends for other second, third and

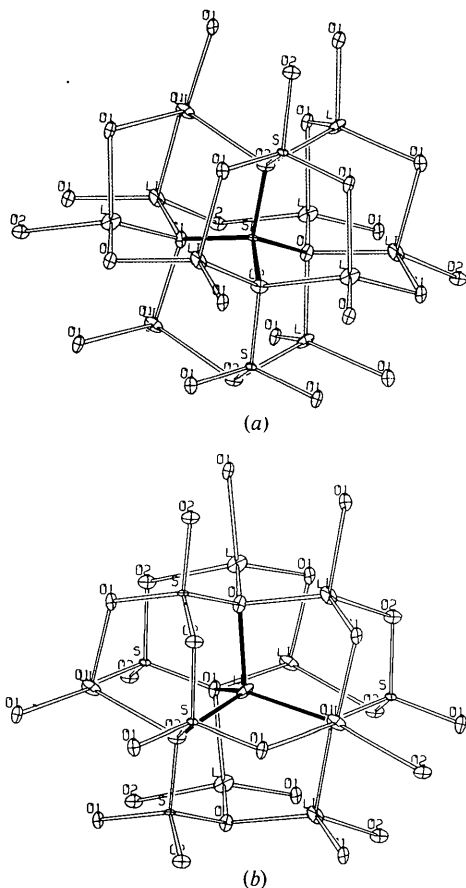


Fig. 1. Coordination diagrams of (a) the $[Si_3Li_{10}O_{29}]^{36-}$ cluster and (b) the $[Si_2Li_8O_{29}]^{30-}$ cluster in lithium polysilicate. Both diagrams were drawn with the program *ORTEP* (Johnson, 1965) using crystal structure data from Hesse (1977). The central SiO_4 and LiO_4 groups have been indicated by filled conical bonds in each cluster.

Table 1. *Valence-orbital ionization potentials and Slater exponents (ζ)*

Atom	Orbital	Potential (eV)*	ζ^\dagger
Si	3s	14.83	1.634
	3p	7.75	1.428
Li	2s	5.38	0.640
	2p	3.63	0.515
O	2s	32.33	2.246
	2p	15.79	2.227

* Ionization potentials from Basch, Viste & Gray (1965).

† Exponents from Clementi & Raimondi (1963).

Table 2. Observed tetrahedral bond lengths, $d(T-O)$, and corresponding bond-overlap populations, $n(T-O)$, calculated assuming constant Si-O and Li-O bond lengths of 1.63 and 2.00 Å respectively, along with their deviations from the mean, $\Delta d(T-O)$ and $\Delta n(T-O)$, for the TO_4 groups in lithium polysilicate

T-O	$d(T-O)$	$n(T-O)$	$\Delta d(T-O)$	$\Delta n(T-O)$
Si-O(1) × 2	1.592 Å	0.619	-0.044 Å	0.019
Si-O(2)	1.678	0.578	0.042	-0.022
Si-O(2)'	1.681	0.583	0.045	-0.017
Li-O(1)	1.937	0.049	-0.063	0.033
Li-O(1)'	1.938	0.042	-0.062	0.026
Li-O(1)''	1.955	0.027	-0.045	0.011
Li-O(2)	2.170	-0.054	0.170	-0.070

fourth-row tetrahedral oxyanions (Tossell & Gibbs, 1978). In fact, when the difference in mean size and overlap population for each tetrahedron in lithium polysilicate is removed from consideration by calculating the deviation of individual $d(T-O)$ and $n(T-O)$ values from their respective averages (Table 2), it is clear that the relation between $\Delta d(T-O)$ and $\Delta n(T-O)$ is the same for both the SiO_4 and LiO_4 groups (Fig. 2).

In contrast, previous studies of the dependence of calculated overlap population (and observed bond length) on valence-angle distortions in a large number of *isolated* tetrahedral oxyanions of the second, third and fourth-row elements indicate that this dependence decreases with increasing ionic character of the bonds and/or mean T-O bond length (Tossell & Gibbs, 1978; Hill *et al.*, 1978). Indeed, whereas the correlation between $d(T-O)$ and $n(T-O)$ for the small, highly covalent SO_4 and SeO_4 groups is very well defined (Louisnathan, Hill & Gibbs, 1977; Gibbs, Chiari, Louisnathan & Cruickshank, 1976), in the case of the

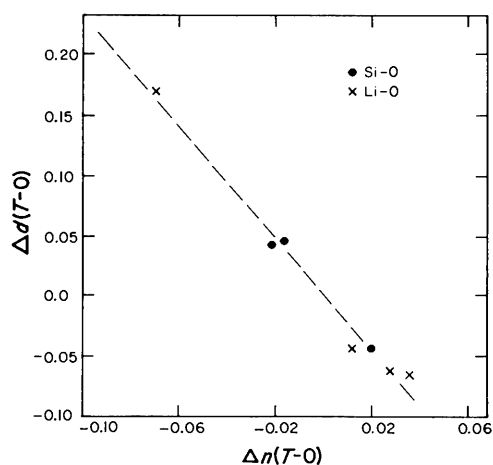


Fig. 2. Scatter diagram of $\Delta n(T-O)$, the deviation of an individual bond-overlap population parameter from the mean value for each tetrahedral group, vs $\Delta d(T-O)$, the corresponding deviation (in Å) of observed bond length from the mean. The broken line represents the least-squares regression trend relating the two parameters.

larger, more ionic GeO_4 , AlO_4 and BeO_4 groups the relation, although still present, is more poorly developed (Hill, Louisnathan & Gibbs, 1977; Louisnathan & Gibbs, 1972; Schlenker, Griffen, Phillips & Gibbs, 1977). Consistent with this trend, it is found that when the molecular-orbital calculations are repeated for the tetrahedral oxyanions in lithium polysilicate without the incorporation of their surrounding shells of tetrahedra the correlation between $\Delta d(T-O)$ and $\Delta n(T-O)$ is markedly reduced, especially for the LiO_4 group.

It is therefore clear that although extended Hückel theory is capable of rationalizing bond-length variations (given the observed valence angles) in small, highly covalent oxyanions without the inclusion of the first coordination sphere of cations and anions, for larger, more ionic tetrahedral groups it becomes necessary to incorporate the effect of the surrounding framework in order to ensure the success of the model. As one might expect, this is particularly true when the group under consideration is not the most strongly bonded unit in the structure.

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Generalized Temperature-Factor Formulation with Application to Cadmium Selenide and Other Wurtzites

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The generalized temperature factor is formulated within the framework of the one-particle potential in terms of functions derived from the harmonic functions of Stewart. This formulation is then applied to the wurtzite structure and projection analysis is used to eliminate one component of the potential. Inclusion of the generalized temperature factor in the structure-factor expression for wurtzite leads to the appearance of harmonically forbidden reflections and the loss of equivalence of non-symmetry-related reflections which occur at the same Bragg angle. The results of a room-temperature X-ray experiment with cadmium selenide are interpreted within the above model to yield cubic anharmonic parameters $|\beta_{332}| = |\beta_{337}| = |\beta_{313}| \approx (0.13 \pm 0.01) \times 10^{-12}$ erg \AA^{-3} . These are used to estimate the anharmonic effect on the position parameter u . Some general conclusions are drawn regarding the possibility of observing similar effects in other wurtzite structures.

Introduction

The effects of anharmonic thermal vibrations on the intensities of Bragg reflections have been investigated in a number of cubic structures with both neutrons and X-rays (for a summary see Willis & Pryor, 1975). The interpretation of these effects has been successfully based on the effective one-particle potential (OPP) within the framework of Dawson's (1967) generalized structure-factor formulation. Recently, Mair & Barnea (1975) have extended this treatment to materials having the wurtzite structure. However, while the importance

of the first-order component in the anharmonic temperature factor was recognized, it was neglected in the potential expansion. Anharmonic contributions to the atomic vibrations in hexagonal zinc have also been considered by several authors and their presence has been established by both neutron and Mössbauer techniques (Nizzoli, 1976; Merisalo & Larsen, 1977; Albanese, Deriu & Ghezzi, 1976).

The present paper details a general formulation of anharmonicity within the OPP approximation in terms of functions derived from the harmonic functions listed by Stewart (1972, 1973). This formulation is then applied to the case of wurtzite. In § 2 the resulting temperature-factor expressions for wurtzite are shown to predict X-ray intensity differences between some

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