A COMPARISON OF THEORETICAL AND OBSERVED BRIDGING BOND LENGTHS AND ANGLES IN CONDENSED PHOSPHATES AND SULFATES

by

William Joseph Dytrych

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APPROVED:

G.V. Gibbs, Chairman

J.D. Rimstidt

P.E. Field

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(ABSTRACT)

Ab initio STO-3G* MO calculations for the diphosphoric acid ($H_4P_2O_7$) and disulfuric acid ($H_2S_2O_7$) molecules reproduce the bridging bond length and angle averages observed in solid phosphates and sulfates. Potential energy curves calculated for both molecules relate the observed bridging bond length and angle variations in their solids. Orbital population analyses for both molecules suggest that all five 3d-orbitals play a role in bonding instead of just the two proposed by Cruickshank (1961). The accuracy with which the molecular geometries account for the averages and trends observed in related solids supports the assertion that the local bonding forces in solid phosphates and sulfates behave as though they are short range.

ACKNOWLEDGEMENTS

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Introduction

Computational quantum chemistry is a powerful method for studying the microscopic properties of chemical bonding. In the last decade, it has found use in many areas in chemistry where the calculations have successfully generated geometries, potential energy surfaces spectra and chemical reactions for a variety of small molecules. Recently, these calculations have been used in mineralogy as a tool for obtaining quantitative information about the structures, charge density distributions and bonding in minerals. These calculations reproduced the Brown-Shannon bond strength-bond length curves (Gibbs, 1982), and they have been used to mimic the bond length, angle and bond strength sum variations for a number of silicates (Newton and Gibbs, 1980; Gibbs et al., 1981; Newton, 1981; Downs and Gibbs, 1981; Chakoumakos et al., 1981; Geisinger, 1983). The success of the silicate calculations suggests that the forces that bind the atoms together and govern bond length and angle variations behave as though they are short range. The purpose of this study is to extend similar calculations to phosphate and sulfate molecules.

The molecules chosen for the calculations in this study are diphosphoric acid ($H_4P_2O_7$) and disulfuric acid ($H_2S_2O_7$). Previous work on the PO_4^{3-} and $P_2O_7^{4-}$ ions by Lager and Gibbs (1973) and on the SO_4^{2-} ion by Louisnathan et al. (1977) has been done. Semi-empirical extended Huckel

theory (EHT) was used to rank the tetrahedral bond lengths with Mulliken overlap populations. EHT is only qualitative because electrostatic interactions are not explicitly taken into account. Ab initio self-consistent field (SCF) methods can be used to calculate bond lengths and angles. Two studies on $H_4P_2O_7$ (Hayes et al., 1975; Hayes et al., 1978) have used the ab initio SCF method to calculate hydrolysis energies in biological reactions. The primary focus of this study is to see whether bond lengths and angles calculated for two phosphate and sulfate molecules support the proposal that bonding forces behave as though they are short range. Experimental values will be compiled from the literature.

Orbital populations will be examined to see the role played by the d-orbitals. Pauling (1952) proposed d-orbital participation to account for the contraction of observed P-O bond lengths relative to the hypothetical single-bond P-O bond length. Cruickshank (1961) developed this idea further through group theoretical arguments in which a double system of π-orbitals extended throughout the diphosphate molecule. The system predicted PO(bridging) bonds to be longer than PO(nonbridging) bonds. Cruickshank held however that only two of the five 3d-orbitals, d_{z^2} and $d_{x^2-y^2}$, of phosphorus were responsible for this delocalized π-system. Subsequent EHT overlap calculations for P-O bonds by Bartell et al. (1970) agree with Cruickshank's total 3d population, but apportion usage instead to all five

3d-orbitals. The adaptability of the diphosphate anion and its π-system to a wide range of structures (Mandel, 1975) is due to the strong influence of cationic effects (Calvo, 1965, 1967; Corbridge, 1974). A cation disturbs the π-orbital system of the anion (Calvo and Au, 1967), to give electron delocalization from the anion to the cation (Calvo, 1967). Because the bridging oxygen is so inert (Collin and Willis, 1971; Pletcher and Sax, 1972; Schneider and Collin, 1973), this cationic effect is a result of bonding to nonbridging oxygen atoms. Consequently, the bridging bond length PO(br) is lengthened with respect to the PO(nbr) bonds (Calvo, 1967; Calvo and Au, 1969).

The orbital populations of the sulfates will be studied to examine the role played by the d orbitals. As McDonald and Cruickshank (1967b) noted in their refinement of the structure of S_3O_9 (γ-SO_3), there is a difference in the bridging and nonbridging S-O bond lengths which is more pronounced than is observed for the P-O bond lengths of $Na_3P_3O_9$. Given the analogous bonding of condensed phosphates and sulfates, the findings on phosphates will be extended to S-O bond lengths, providing an explanation of d-p π-bonding in solid polysulfates. In a study of the polyhedral distortions in phosphates, Baur (1974) offers the observation that: "Most phosphate tetrahedra deviate significantly in their dimensions from the values expected for a regular tetrahedral arrangement." With respect to

condensed phosphates, the polymerization of corner sharing PO_4 tetrahedra which generates all such phosphate structures (Corbridge, 1974) also distorts any given tetrahedron from ideal T_d point symmetry (Nord and Kierkegaard, 1980). This tetrahedral distortion receives expression through a given structure's bond lengths and angles, as found by Faggiani and Calvo (1976). In their study of the $CdK_2P_2O_7$ structure, Faggiani and Calvo find that the phosphorus atom is displaced from the center of the tetrahedron toward the nonbridging oxygen atoms. This produces a bridging bond PO(br) = 1.64 A that is much longer than the average of the three nonbridging bonds, PO(avg) = 1.51 A.

The same "bond length inequality-tetrahedral distortion" association is observed in condensed sulfates. In their 1960 study of $K_2S_2O_7$, Lynton and Truter have found a nearly trigonal, as opposed to ideally tetrahedral, symmetry about the sulfur atoms. DeVries and Mijlhoff (1969) make a similar observation concerning the terminal sulfur atoms of $K_2S_5O_{16}$. These sulfur atoms are shifted from the centers of their tetrahedra towards the three nonbridging oxygen atoms, resulting in approximately C_{2v} point symmetry and a bridge bond of 1.82 A. DeVries and Mijlhoff conclude that there is a large contribution of the sulfur d_{z^2}-orbital to the S-O σ-bond in these terminal group bridging bonds. This d-orbital participation was proposed by Pauling in 1952 and extended by Cruickshank in 1961. To account for the observed

shortening of S-O bond lengths relative to the ideal σ-bond length, Cruickshank proposed a delocalized π-system extending throughout a condensed sulfate anion. Analogous to condensed phosphates, cation interaction with terminal oxygen atoms in condensed sulfates causes delocalization of the anionic π-system. This results in the disparity between SO(br) and SO(nbr) bond lengths. As in the phosphates Cruickshank (1961) maintained via group theory that only two of the five sulfur d-orbitals were involved in the π-system.

Method

Ab initio SCF closed-shell calculations performed in this study utilized the linear combination of atomic orbitals - molecular orbital (LCAO-MO) approach in GAUSSIAN 80 by Binkley et al. (1980). Previous calculations on a variety of phosphate and sulfate molecules (Hillier and Saunders, 1970; Gelius et al., 1971; Connor et al., 1972; Hayes et al., 1975; Baird and Taylor, 1981) indicate that the addition of 3d polarization functions to a minimal basis results in a simultaneous improvement of both the total electronic energy and the optimum geometry of the molecule (Mezey and Haas, 1982; Zhu and Murrell, 1982). Computations in this study were completed with a STO-3G* basis set (Collins et al., 1976). Optimizations of the bond lengths and angles of the molecules were carried out with a gradient optimization routine of GAUSSIAN 80. In these calculations both molecules were assumed to possess C_{2v} point symmetry and the OPO, POH, OSO and SOH angles were fixed at 109.47^{o}. The O-H bond length was fixed at 0.99 A. Single-point calculations were performed for constructing sections through the potential energy surface by holding one bond parameter at its optimized value (bond length or angle) while varying the other.

A. Phosphates

Introduction

Condensed phosphates are defined as those phosphates with bridging oxygens. A feature of these phosphates is the presence of corner sharing tetrahedra (Corbridge, 1974) which is thought to be due to ionic repulsion between the P^{5+} ions of the PO_4 tetrahedra (Hong, 1974b). Corbridge notes that such corner sharing is limited to a maximum of three corners per tetrahedron thus precluding cross-chain linkages such as those found in framework silicates. Corner sharing also serves as a criterion for classifying condensed phosphates into diphosphates (one corner shared), metaphosphates (two corners shared), and ultraphosphates (three corners shared) (Nord and Kierkegaard, 1980). In addition to corner linking of tetrahedra a suitable molecular model must be computationally tractable.

The experimental phosphate and sulfate bond lengths and angles were compiled from the literature (see Appendix).

The molecule selected to model the bonding in the POP groups was diphosphoric acid ($H_4P_2O_7$). Two PO_4 tetrahedra shared a common corner. Hydrogen atoms were bonded to the non-bridging oxygen atoms to achieve electrostatic neutrality and to maintain connectedness. Optimization of the molecule resulted in the minimum energy configuration shown in Figure 1 and the geometry in Table 1. Table 1 shows the

Figure 1. ORTEP drawing of the diphosphoric acid ($H_4P_2O_7$) molecule in a C_{2v} configuration with OH = 0.99 A. Large spheres represent oxygen; intermediate spheres represent phosphorus; and the small spheres represent hydrogen. No other significance is ascribed to the size of the spheres.

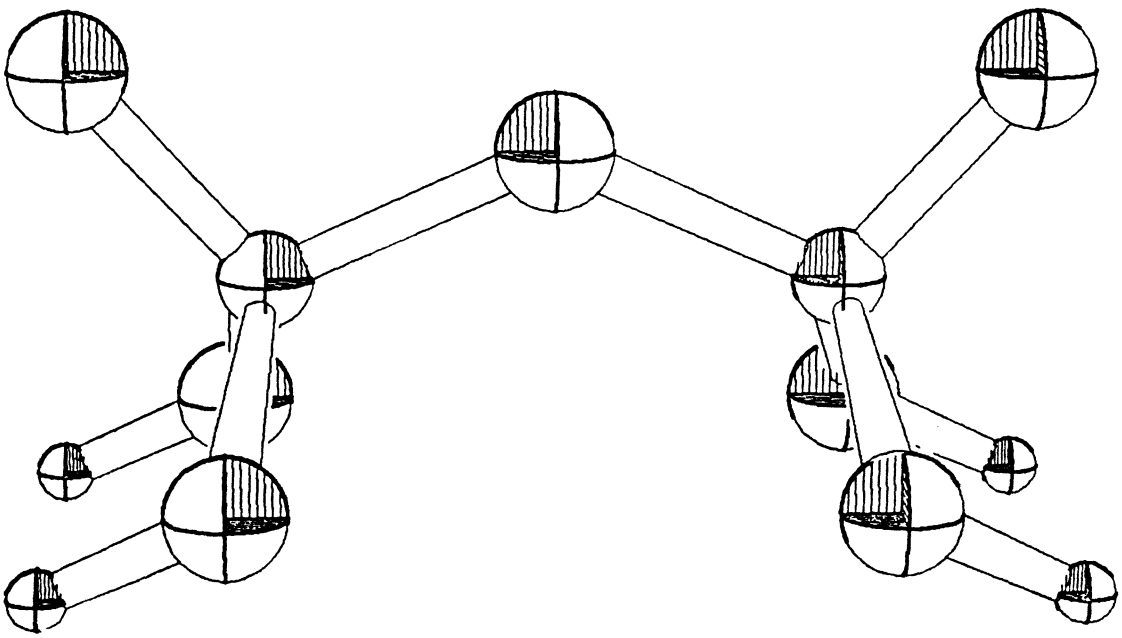


Table 1. Phosphate Bond Lengths and Angles†

R(PO(br))	R(PO(H))	R(PO)	POP	Basis	Reference
(a) Optimized values for $H_4P_2O_7$:					
1.59	1.60	1.44	132.5	STO-3G*	This study
1.69	1.66	1.58	117.0	STO-3G	Hayes et al., 1978
(b) Observed averages in solids:					
1.60	----	----	133.4		

†Bond lengths in angstroms, bond angles in degrees.

bridging bond lengths and bridging bond angle computed by Hayes et al. (1978) in a limited optimization of $H_4P_2O_7$ using a STO-3G basis set.

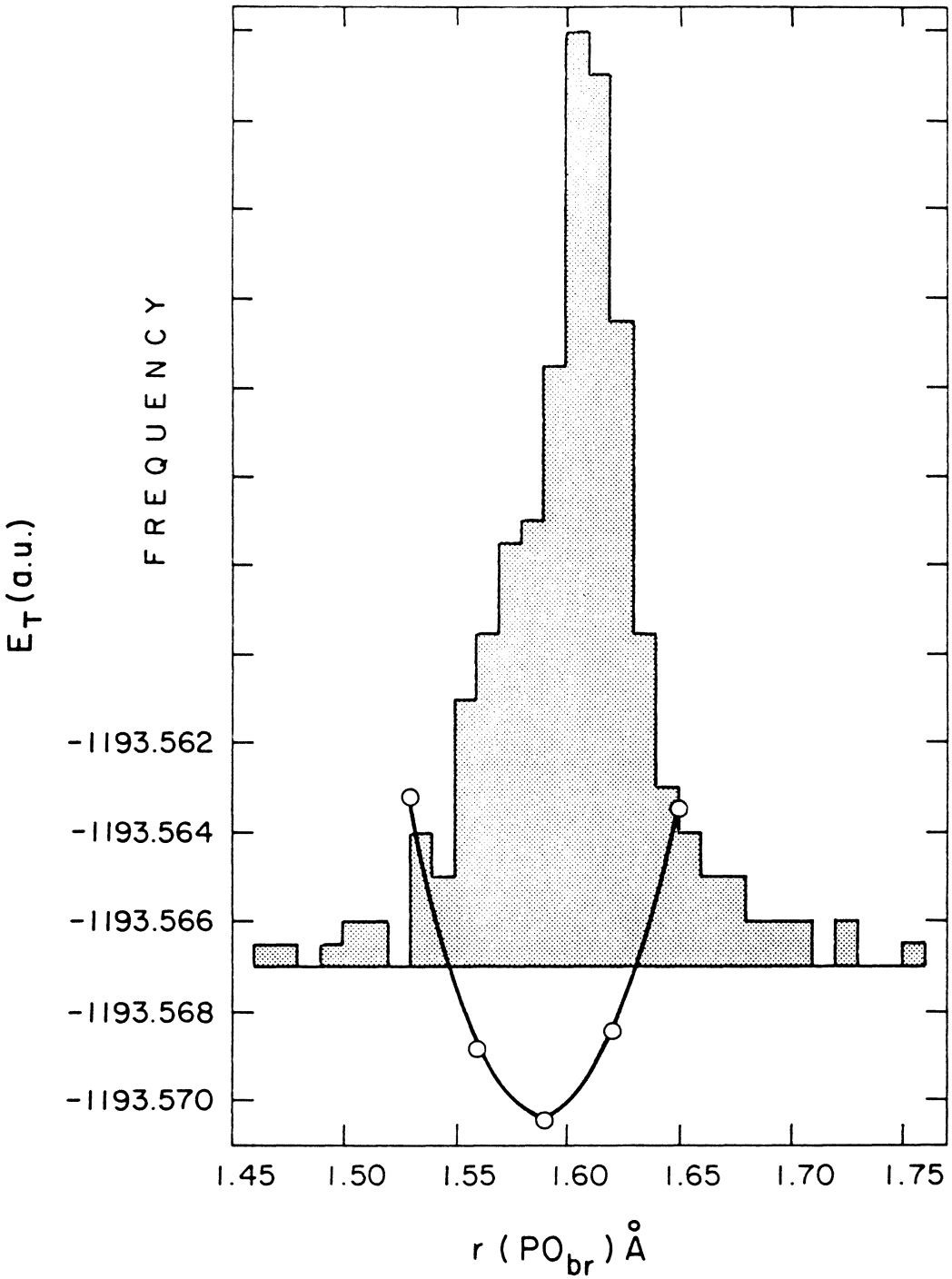
Calculated and Observed Bridging PO Bonds

The following analysis was undertaken to determine whether STO-3G* MO calculations yield reasonable bond lengths and angles. Graphs of single-point calculations through the potential surface minimum were prepared to study the variation of the potential energy as a function of either bond length or angle. A histogram from data in the Appendix was superimposed on the graphs to show the coincidence obtained. Figures 2 and 3 demonstrate that STO-3G* calculations agree with observed bond length and angle variations. Figure 2 displays the potential energy versus bridging bond length curve generated by fixing the POP angle at 132.2°. The overall shape conforms with the observed frequency distribution of PO(br) bond lengths. In Table 1 the calculated bridging bond length value of 1.59 A for PO(br) in this study (STO-3G*) is closer to the observed 1.60 A than the Hayes et al. calculated value of 1.69 A (1978) (STO-3G).

Calculated and Observed Bridging POP Angles

Figure 3 shows that STO-3G* calculations mimic the observed bridging bond angles in solid phosphates. The potential energy variation of the diphosphoric acid molecule was plotted as a function of the bridging bond angle. In

Figure 2. Total potential energy curve calculated as a function of the bridging PO bond in $H_4P_2O_7$. A histogram (insert) of observed bridging bond lengths in condensed phosphates is superimposed upon this curve. The bond angle is held at 132.5°.


FREQUENCY
E_T (a.u.)
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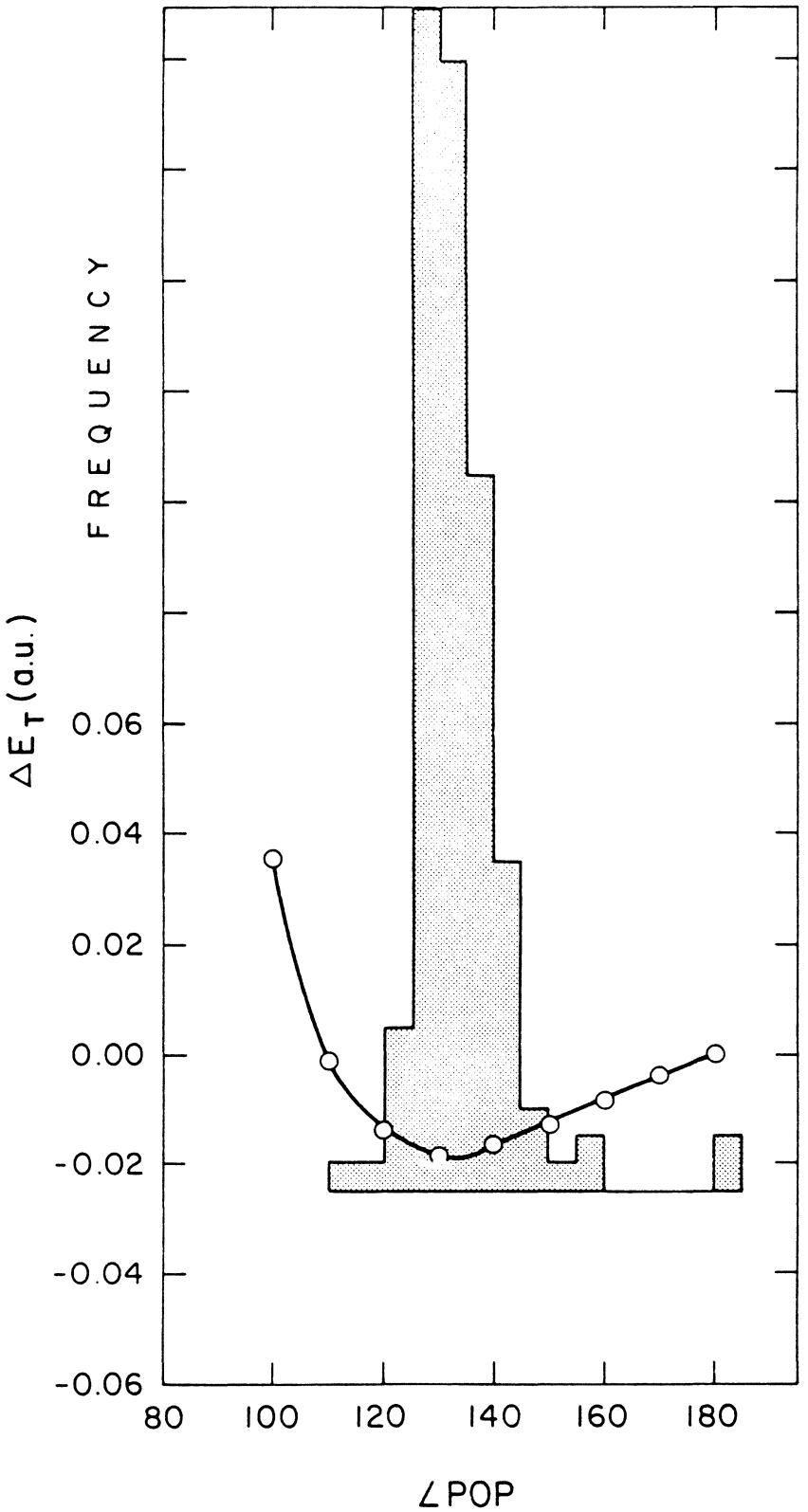
-1193.564
-1193.566
-1193.568
-1193.570
1.45
1.50
1.55
1.60
1.65
1.70
1.75
r (PO_{br}) Å

Figure 3. Potential energy curve $\Delta E_T = E(180^o) - E(<POP)$ as a function of the bridging POP angle in $H_4P_2O_7$. A histogram (insert) of bridging bond angles observed in condensed phosphates is superimposed. The bond length is held at 1.59 A.


FREQUENCY
ΔE_T (a.u.)
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0.04
0.02
0.00
-0.02
-0.04
-0.06
80
100
120
140
160
180
∠POP

Figure 3, a comparison of the frequency distribution of observed values with the potential energy curve demonstrates the agreement between bridging bond angles in solid phosphates and those calculated for the diphosphoric acid molecule. The equilibrium bridging angle of 132.5^{o} in the STO-3G* calculations is closer to the observed average of 133.4^{o} compiled from the Appendix. The STO-3G study computes the bridging angle to be 117.0^{o} (Hayes et al., 1978). The observed average angle was obtained by averaging 138 values of the <POP compiled from 60 separate solid phosphates.

An apparent inconsistency in Figure 3 results from the reported linear bridging angles of diphosphates (Calvo, 1965a,b; Robertson and Calvo, 1968; Tillmanns et al., 1973). All single crystal x-ray analyses which report linear bridging angles also mention large thermal vibration parameter values for the bridging oxygen atoms. This implies a high degree of thermal motion and, as Corbridge notes, "...suggests thermal averaging to give an effectively linear anion." Nord and Kierkegaard (1980) interpret this large thermal motion as a statistical distortion of the bridging oxygen atom. The POP angle appears linear while each individual linkage is actually bent. To support this interpretation, Nord and Kierkegaard undertook a hypothetical calculation for divalent metal diphosphates. The grand mean linear bridging bond length (PO(br) = 1.54 A) was

increased to 1.60 A which is the grand mean bridging bond length in the bent configuration. This entailed decreasing the POP angle from 180° to 148°, a value they found agreed with their own observed values in bent diphosphates. This value of 148° agrees with the 144°-149° range proposed by Tillmanns et al. (1973) to explain the reported linear linkages in SiP_2O_7. These bridging angle values, given by Nord and Kierkegaard (1980) and Tillmanns et al. (1973), provide better agreement with the single-point curve in Figure 3. Since the single-point curve was derived by *ab initio* methods, the above agreement further demonstrates the ability of STO-3G* MO calculations to reproduce the observed range of bridging angles.

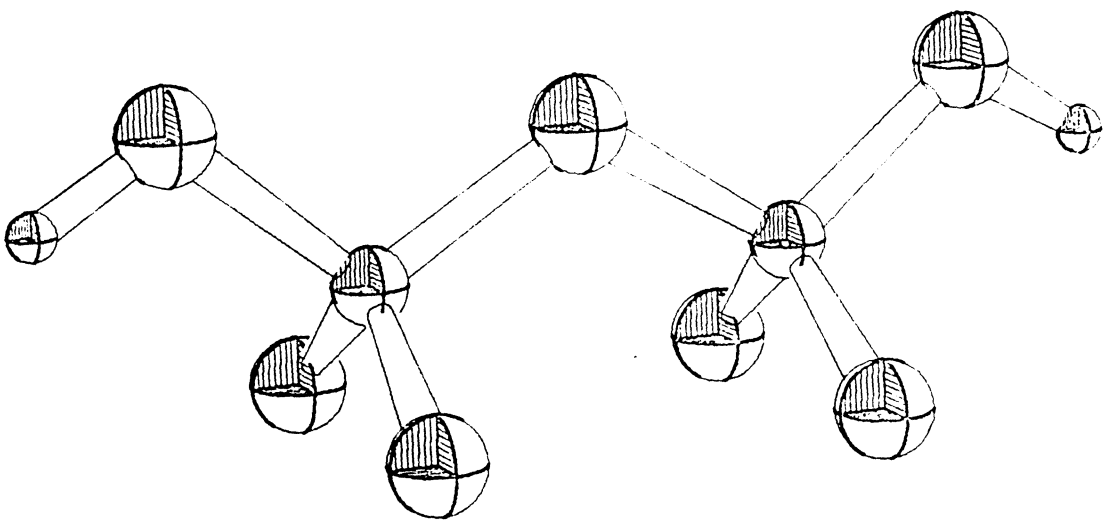
B. Sulfates

Introduction

The stereochemistry of solid sulfates is similar to that of solid phosphates. Polysulfur oxides which contain a bridging oxygen atom shared by two tetracoordinate sulfur atoms are, in general, "...not multiples of a uniform monomeric sulfur oxide..." (Schenk and Steudel, 1968); however, those considered in this study can be regarded as the result of a polymerization of SO_4 tetrahedra. Laur (1972) proposes an alternative interpretation of linear condensed sulfates. He suggests that their structures are derived from the successive addition of SO_3 groups to a SO_4 tetrahedron. In either case, ligation gives rise to polysulfates in which each sulfate tetrahedron shares at most two corners. A representative molecule incorporates this sharing of a bridging oxygen atom by two four-coordinate sulfur atoms.

Disulfuric acid ($H_2S_2O_7$) was chosen because it models the bonding in SOS linkages in solids. As in the case of the phosphate this acid consists of two corner sharing sulfate tetrahedra. A hydrogen atom is bonded to one terminal oxygen atom on each of the tetrahedra to preserve both the electrostatic neutrality and the connectedness of the structure (Fig. 4).

Figure 4. ORTEP drawing of the disulfuric acid ($H_2S_2O_7$) molecule in a C_{2v} configuration with OH = 0.99 A. Large spheres represent oxygen; intermediate spheres represent sulfur; and the small spheres represent hydrogen. No other significance is ascribed to the size of the spheres.



Calculated and Observed Bridging SO Bonds and SOS Angles

The sulfate study was carried out in a manner similar to the phosphate study. The calculated value of 1.64 A for the bridging SO bond compares favorably with the observed average of 1.63 A in the sulfate solids (see Table 2, Figure 5 and Appendix).

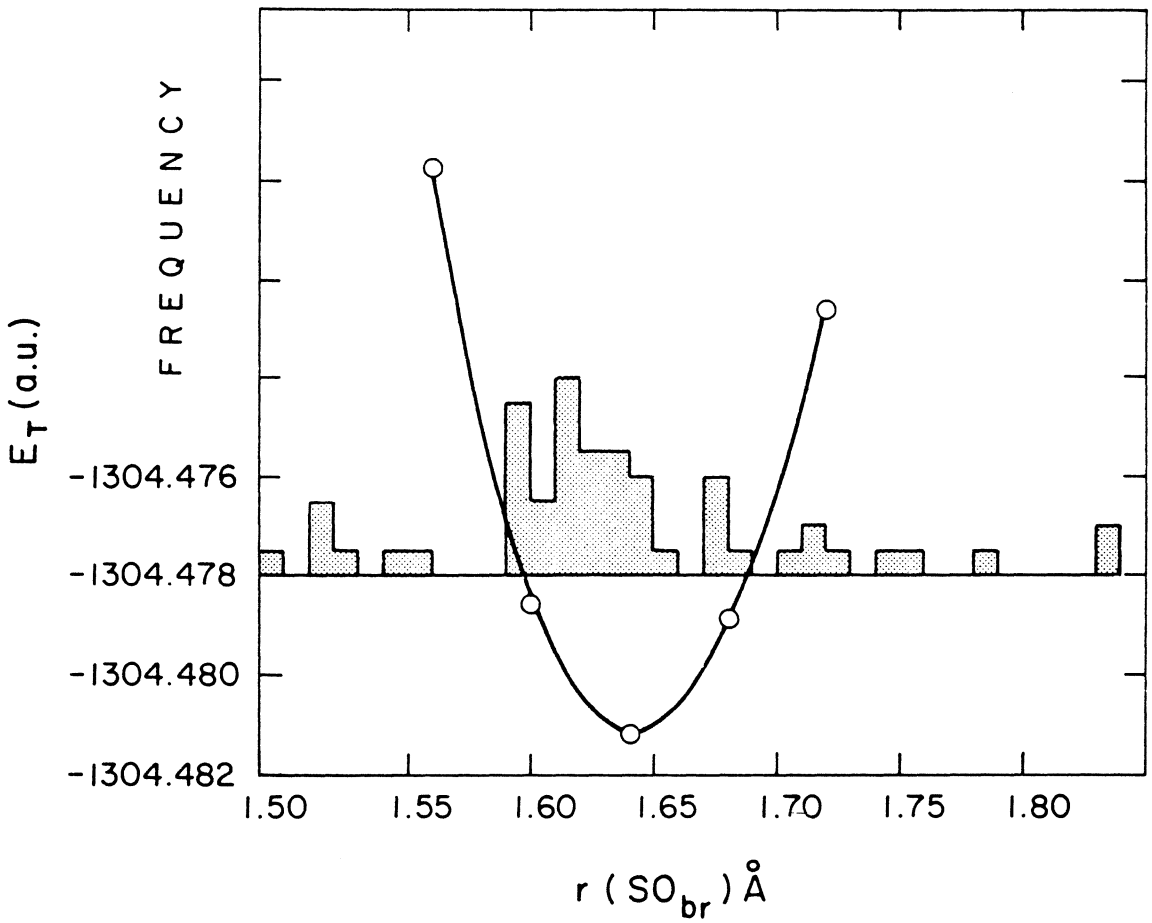
The calculated SOS angle is 117.4^{o} and the observed angle is 121.8 (Fig. 6). Table 2 reports the agreement between the minimum energy bridging value and the average of the 26 observed angles in the frequency plot. The contour of this single-point curve is shown with the frequency distribution. The SOS angles in polymerized sulfates have a smaller range than the TOT angles observed for polymerized AlO_4, SiO_4 and PO_4 tetrahedral oxyanions (Louisnathan et al., 1977). Louisnathan et al. did not account for the narrow range. In Figure 6 the potential energy goes through a minimum at 117.4^{o} and then rises at angles greater than 140°, indicating a barrier to wide bridging angles.

Table 2. Sulfate Bond Lengths and Angles[†]

R(SO(br))	R(SO(H))	R(SO)	SOS
(a) Optimized values for $H_2S_2O_7$:			
1.64	1.61	1.46	117.4
(b) Observed averages in solids:			
1.63	----	----	121.8

[†] Units as given in Table 2.

Figure 5. Total potential energy curve calculated as a function of the bridging SO bond in $H_2S_2O_7$. A histogram (insert) of observed bridging bond lengths in condensed sulfates is superimposed upon this curve. The bond angle is held at 117.4°.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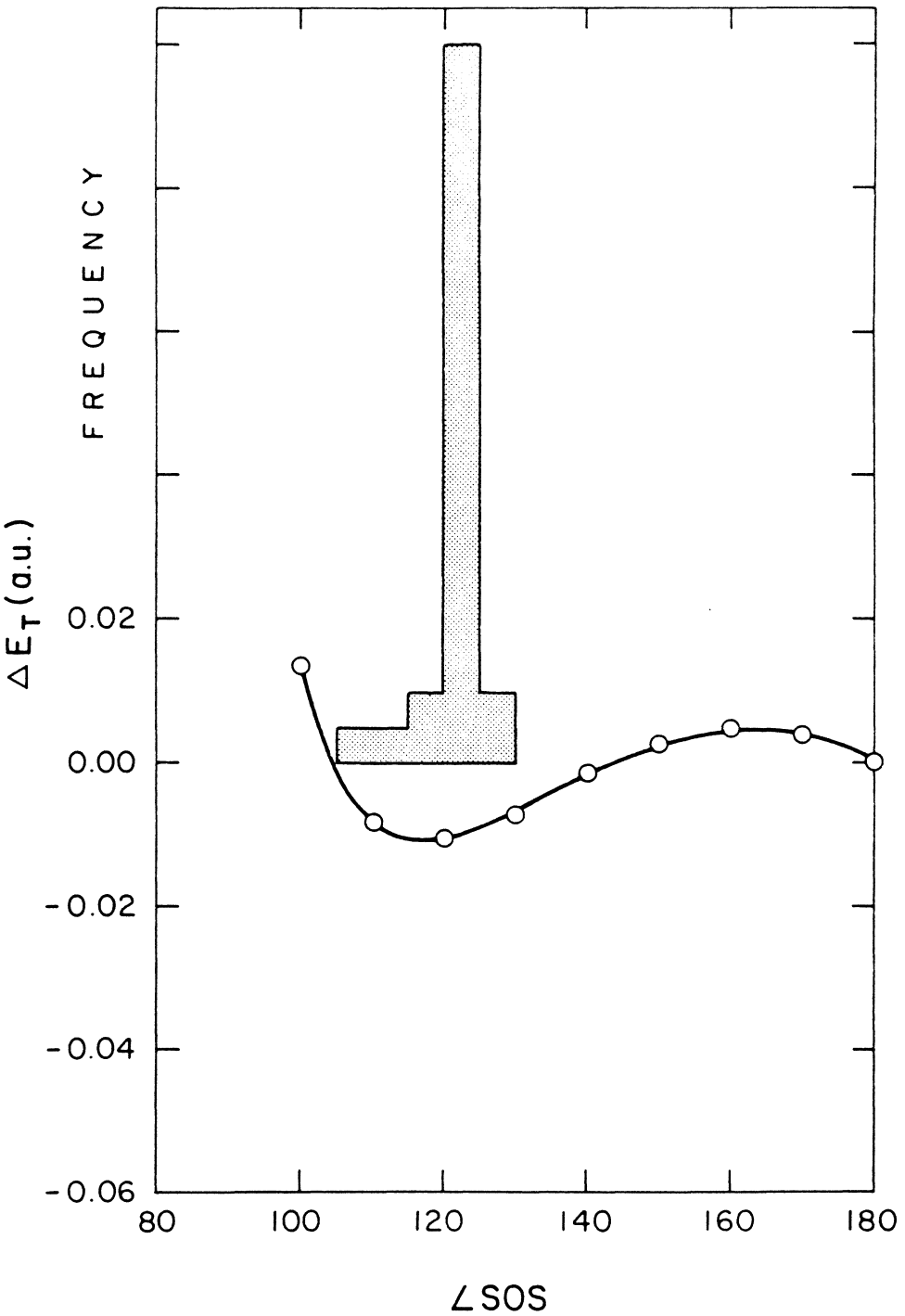
-1304.478
-1304.480
-1304.482
1.50
1.55
1.60
1.65
1.70
1.75
1.80
r (SO_{br}) Å

Figure 6. Potential energy curve $\Delta E_T = E(180^\circ) - E(<SOS)$ as a function of the bridging POP angle in $H_2S_2O_7$. A histogram (insert) of bridging bond angles observed in condensed sulfates is superimposed. The bond length is held constant at 1.64 A.


FREQUENCY
ΔE_T (a.u.)
0.02
0.00
-0.02
-0.04
-0.06
80
100
120
140
160
180
∠SOS

C. 3d Orbital Calculations for Phosphates and Sulfates

Results given in Table 3 support the participation of all five 3d-orbitals, as suggested by Bartell et al. (1970). These STO-3G* calculations probably exaggerate the role of the d-orbital; however split valence calculations (Gibbs, personal communication) still support populations associated with 3d's. The GAUSSIAN 80 calculations for the phosphate show that in the 3d orbital the largest population is 0.30 electrons with m = +1, and the smallest population is 0.15 electrons with m = -1. For the sulfate the situation changes with the largest population, 0.32 electrons, associated with m = -2 and the smallest charge, 0.24, with m = 0. The total population associated with the d orbital of phosphorus is 1.2 electrons and the total population associated with the d orbital of sulfur is 1.4 electrons. The percentage contribution of the d orbitals to the total phosphorus atom is eight percent, while the corresponding value for sulfur is nine percent corresponding to sulfur's greater electronegativity.

Table 3. 3d Orbital and Total Atomic Populations

Species	$(H_4P_2O_7)$ X=P (in electrons)	$(H_2S_2O_7)$ X=S (in electrons)
A. Orbital:		
X_{3d}: m= 0	0.28	0.24
+1	0.30	0.26
-1	0.16	0.31
+2	0.26	0.28
-2	0.19	0.32
Σ of d orbitals	1.18	1.41
B. Total atomic population:		
X	14.32	15.47
Bridging oxygen	8.28	8.21
O (without H)	8.37	8.23
O (with H)	8.32	8.24
H	0.77	0.71
C. $(\Sigma X_{3d}/\text{Total X})$ %	8	9

Conclusions

Ab initio geometry optimizations of the diphosphoric acid ($H_4P_2O_7$) and disulfuric acid ($H_2S_2O_7$) molecules were carried out under C_{2v} point symmetry at the STO-3G* level. The resulting bridging bond lengths and angles were compared to those observed in solid phosphates and sulfates. The ability of each molecule's geometry to reproduce observed averages and trends supports the supposition that the local bonding forces in condensed phosphates and sulfates behave as though they are short range. Orbital population analyses suggest that all five 3d-orbitals of phosphorus and sulfur participate in bonding.

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APPENDIX A

Table of Solid Phosphate Data

R(PO(br))	R(PO(br))	POP	Compound & Reference
1.575	1.543	136.5	$(NH_4)_4P_4O_{12}.2Te(OH)_6.2H_2O$
1.613	1.588	124.1	Durif et al. (1982)
1.610	1.604	123.2	$KAlP_2O_7$, Ng & Calvo (1973)
1.631	1.642	127.5	$Na_4P_2O_7$, Leung & Calvo (1972)
1.602	1.583	133.6	$C_{12}H_{19}ClN_4O_7P_2S$, Pletcher & Sax (1972)
1.623	1.623	123.1	$Ca_2P_2O_7.2H_2O$, Mandel (1975)
1.566	1.600	143.1	α-$Ca_2P_2O_7$, Krishnamacari & Calvo (1972)
1.603	1.603	138.7	α-$Zn_2P_2O_7$, Robertson &
1.599	1.566	148.4	Calvo (1970)
1.72	1.62	114.4	$Pb_2P_4O_{12}.2H_2O$, Worzala (1978)
1.72	1.62	118.9	
1.70	1.65	126.6	
1.68	1.55	138.9	
1.615	1.611	127.5	$Mn_2P_2O_7.2H_2O$, Schneider & Collin (1973)
1.617	1.622	129.3	$K_2H_2P_2O_7.\frac{1}{2}H_2O$, Dumas et al. (1973b)
1.623	1.649	130.3	$K_4P_2O_7.3H_2O$, Dumas & Galigne (1974)
1.610	1.629	132.8	$K_3HP_2O_7.3H_2O$, Dumas et al. (1973a)
1.612	1.612	130.2	$Na_4P_2O_7.10H_2O$, McDonald & Cruickshank (1967)
1.617	1.637	130.5	β-$Ca_2P_2O_7$, Webb (1966)
1.616	1.590	137.8	
1.598	1.598	136.1	$Na_2H_2P_2O_7.6H_2O$, Collin & Willis (1971)
1.645	1.605	132.3	$Cd_2P_2O_7$, Calvo & Au (1969)
1.576	1.576	157	α-$Cu_2P_2O_7$, Robertson & Calvo (1967)

Table of Solid Phosphate Data: Continued

R(PO(br))	R(PO(br))	POP	Compound & Reference
1.612	1.569	144	α-$Mg_2P_2O_7$, Calvo (1967)
1.640	1.640	128.9	$CdK_2P_2O_7$, Faggiani & Calvo (1976)
1.591	1.631	126.9	α,β-bidentate $Cr(H_2O)_4HP_2O_7.3H_2O$, Merritt et al. (1981)
1.607	1.609	125.7	$Mg_2P_2O_7.2H_2O$, Oka & Kawahara (1982
1.621	1.607	127.0	$Te(OH)_6.Rb_3P_3O_9.H_2O$, Boudjada
1.625	1.622	126.7	& Durif (1982)
1.605	1.618	129.8	
1.621	1.575	153.0	$Fe_2P_2O_7$, Stefandis & Nord (1982)
1.621	1.641	128.7	α-$CaNa_2P_2O_7.4H_2O$, Cheng et al. (1980)
1.601	1.604	129.1	$Te(OH)_6.K_3P_3O_9.2H_2O$,
1.609	1.604	128.6	Boudjada et al. (1981b)
1.622	1.629	128.9	$Ca_3(NH_4)_2(P_2O_7)_2.6H_2O$, Takagi et al. (1980)
1.596	1.555	142.6	ErP_5O_{14}, Jezowska-Trzebiatowska &
1.638	1.535	137.7	Mazurak (1980)
1.602	1.570	134.0	
1.568	1.630	128.6	
1.549	1.601	132.4	
1.638	1.564	125.7	
1.607	1.612	135.9	$K_3Na(H_2P_2O_7)_2$, Dumas et al. (1980)
1.605	1.619	131.3	unidentate $[CoHP_2O_7(NH_3)_5].H_2O$
1.627	1.601	127.1	bidentate $[CoHP_2O_7(NH_3)_4].2H_2O$ Merritt & Sundaralingam (1980)
1.623	1.610	125.2	$CaNH_4HP_2O_7$, Mathew & Schroeder
1.609	1.604	138.7	(1977)
1.605	1.588	130.2	α,β,γ-tridentate
1.605	1.588	130.2	$[Ca(NH_3)_3(H_2P_3O_{10})]$, Merritt & Sundaralingam (1981)
1.5976	1.5943	129.53	$Be(PO_3)_2$ (II), Averbuch-Pouchet
1.5814	1.5763	138.97	et al. (1977)
1.588	1.594	133.6	$Na_7Mg_{4.5}(P_2O_7)_4$, Hanic &
1.639	1.615	126.6	Zak (1974)

Table of Solid Phosphate Data: Continued

R(PO(br))	R(PO(br))	POP	Compound & Reference
1.621	1.591	130.0	$Zn_2NaP_3O_{10}.9H_2O$, Averbuch-
1.596	1.626	128.9	Pouchet & Guitel (1977a)
1.621	1.626	128.2	$[C(NH_2)_3]_3HP_2O_7$, Adams & Ramdas (1976)
1.626	1.594	131.6	$[C(NH_2)_3]_4P_2O_7.1\frac{1}{2}H_2O$,
1.664	1.571	130.3	Adams & Ramdas (1978)
1.592	1.613	133.0	α,γ-$Co(NH_3)_4H_2P_3O_{10}$, Merritt
1.609	1.603	129.7	et al. (1981)
1.579	1.616	130.0	α-$Ca_2P_2O_7$, Calvo (1968)
1.614	1.585	130.7	α-$Sr_2P_2O_7$, Hagman et al. (1968)
1.611	1.580	130.5	$FeH_2P_3O_{10}.H_2O$, Averbuch &
1.611	1.580	130.5	Guitel (1977)
1.6309	1.5842	122.64	$NH_4P_3Be_2O_{10}$, Averbuch-
1.6309	1.5842	122.64	Pouchet et al. (1977)
1.613	1.579	132.4	$AlNH_4HP_3O_{10}.9H_2O$, Averbuch-
1.613	1.579	132.4	Pouchet et al. (1977)
1.628	1.599	129.4	$Zn_2Ag_{0,62}H_{0,38}P_3O_{10}.9H_2O$,
1.596	1.632	128.8	Averbuch-Pouchet & Guitel (1976b)
1.629	1.595	131.2	$Zn_5(P_3O_{10})_2.17H_2O$, Averbuch-
1.592	1.630	128.4	Pouchet et al. (1975b)
1.604	1.584	136.9	$CdBa(PO_3)_4$, Averbuch-Pouchet
1.601	1.584	135.4	et al. (1975a)
1.588	1.585	141.0	
1.592	1.583	132.0	
1.617	1.617	125.6	$Te(OH)_6.2Na_3P_3O_9.6H_2O$,
1.617	1.617	125.6	Boudjada et al. (1981a)
1.617	1.617	125.6	
1.596	1.581	139.2	SiP_2OA_7 III, Bissert & Liebau (1970)
1.622	1.604	129.0	$Zn_2HP_3O_{10}.6H_2O$, Averbuch-
1.592	1.622	130.2	Pouchet & Guitel (1976a)
1.579	1.59	139	NdP_3O_{10}
1.58	1.58	139	
1.62	1.57	140	NdP_5O_{14}
1.64	1.56	138	
1.62	1.56	133	Hong (1974a)
1.62	1.53	135	
1.55	1.67	129	
1.70	1.56	128	

Table of Solid Phosphate Data: Continued

R(PO(br))	R(PO(br))	POP	Compound & Reference
1.57	1.67	129	YbP_3O_9, Hong (1974b)
1.68	1.49	140	
1.65	1.41	157	
1.64	1.65	128	
1.53	1.69	132	
1.75	1.46	136	
1.47	1.66	139	
1.69	1.51	135	
1.67	1.51	138	
1.604	1.552	141.3	HoP_5O_{14}, Bagieu et al. (1973)
1.614	1.574	136.6	
1.551	1.662	125.6	
1.569	1.628	130.8	
1.615	1.571	133.5	
1.581	1.624	128.2	
1.60	1.55	131	YbP_5O_{14}, Hong & Pierce (1974)
1.65	1.53	129	
1.50	1.66	142	
1.51	1.65	127	
1.63	1.54	135	
1.67	1.53	137	
1.600	1.578	144.8	SiP_2O_7, Tillmans et al. (1973)
1.564	1.579	143.5	
1.576	1.578	148.7	
1.569	1.580	146.5	
1.596	1.538	180.0	
1.544	1.544	180.0	
1.609	1.626	131.3	$KADP.2H_2O$, Swaminathan & Sundaralingam (1980)
1.617	1.566	129.6	K_2UDP, Viswamitra et al. (1979)
1.597	1.572	133.7	
1.599	1.607	134.2	Thiamine pyrophosphate hydrochloride, Pletcher et al. (1977)
1.605	1.614	131.8	
1.618	1.550	140.2	NdP_5O_{14}, Albrand et al. (1974)
1.613	1.552	140.1	
1.558	1.617	131.6	
1.551	1.606	135.2	
1.615	1.559	132.5	
1.560	1.606	133.8	

Table of Phosphate Data: Continued

R(PO(br))	R(PO(br))	POP	Compound & Reference
1.608	1.608	135.3	$CdCsP_3O_9$, Averbuch-Pouchet
1.601	1.612	126.1	& Durif (1977)
1.601	1.612	126.1	
1.616	1.578	132.5	$PbK_2(PO_3)_4$, Brunel-Laugt &
1.619	1.601	128.8	Guitel (1977)
1.593	1.609	130.7	
1.605	1.638	129.7	

APPENDIX B

Table of Solid Sulfate Data

R(So(Br))	R(So(Br))	SOS	Compound & Reference
1.72	1.49	124	$(NO_2^+)_2.S_3O_{10}^{2-}$, Cruickshank
1.59	1.71	121	(1964)
1.68	1.52	113.7	$HNO_3.2SO_3$, Steeman & MacGillavry (1954)
1.59	1.63	121	β-SO_3, Westrik & MacGillavry (1954
1.599	1.627	122.4	γ-SO_3, McDonald &
1.619	1.635	121.2	Cruickshank (1967b)
1.629	1.645	120.9	
1.645	1.645	124	$K_2S_2O_7$, Lynton & Truter (1960)
1.611	1.611	123.6	$S_2O_5F_2$
1.613	1.613	123.6	$S_3O_8F_2$
1.613	1.613	123.6	Hencher & Bauer (1973)
1.83	1.51	123	$K_2S_5O_{16}$, DeVries &
1.67	1.59	124	Mijlhoff (1969)
1.59	1.67	124	
1.51	1.83	123	
1.51	1.62	127	$Te(S_2O_7)_2$,Einstein &
1.67	1.63	121	Willis (1981)
1.59	1.70	123	$NO_2(HS_2O_7)$
1.59	1.67	123	$Se_4(HS_2O_7)_2$, Brown et al. (1971)
1.624	1.611	126.5	$Sb_2(S_2O_7)_3$, Douglade &
1.604	1.647	117.7	Mercier (1979)
1.651	1.602	120.1	
1.635	1.626	123.4	$S_3N_2O_5$, Bartl & Rodek (1979)
1.54	1.76	122	$N_2O_5.3SO_3$, Eriks &
1.55	1.78	122	MacGillavry (1954)

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