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Lengths of Phosphorus–Oxygen and Sulfur–Oxygen Bonds. An Extended Hückel Molecular Orbital Examination of Cruickshank's d_π–p_π Picture[1]

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The hypothesis that valence shell ("outer") d orbitals are significant in bonding is reviewed in the light of a series of molecular orbital calculations and other evidence. It is found that EHMO overlap populations for PO and SO bonds closely parallel the p_π–d_π bond orders of Cruickshank's simple valence bond model in accounting for observed trends in molecular structure. On the other hand, it is found that the relative roles of the various d orbitals are substantially different in the Cruickshank and MO schemes. Indeed, it turns out that variations in PO and SO bond lengths can be accounted for even when d orbitals are totally neglected in the MO calculations. Nevertheless, the addition of a small amount of d character to the wave functions has a marked effect on the charge distributions, augmenting the bond overlap populations to more plausible magnitudes and improving the correlation between overlap populations and bond lengths. Calculated bond polarities are correlated as expected with bond lengths. One striking result observed is that nonbonded repulsive stresses acting to stretch bonds tend to increase as the π order of the bonds decreases. These repulsive stresses, diagnosed on the basis of geminal (negative) nonbonded overlap populations, seem quite comparable to π-overlap interactions in governing trends in bond length. Even though the results of an empirical EHMO study lack quantitative validity, the qualitative deductions outlined above appear to be significant; they proved to be insensitive to the parameterization adopted.

Introduction

The importance of "outer d orbitals" in higher valence states of such elements as phosphorus, sulfur, and iodine is an unresolved problem. We wish to point out a few correlations which shed light on the matter and to present some new calculations of diagnostic value. Since several authoritative reviews on the subject have appeared recently,[2-4] we shall make no attempt to discuss the evidence exhaustively or to weigh all alternatives.

Until a few years ago it was common to invoke, for example, two entire d orbitals and "sp^3d^2 hybridization" to describe the σ bonds in SF_6 and similar compounds. Experimental evidence has accumulated from such sources as nqr[5] and electronic spectra,[6] however, which has been interpreted as indicating that d orbitals play only a minor role in bonding in electronic ground states of compounds not containing transition metals. Rundle,[7] among others, was led to suggest that the distinction between first-row atoms (which normally bond to no more than four ligands) and second-row atoms (which readily accept six) lies more in the lack of space in the coordination spheres of the former than in the absence of valence shell (outer) d orbitals.

The unsuitability of d orbitals for bonding is ascribable to their high energy and diffuseness.[8] On the other hand, Craig, *et al.*,[8,9] Cruickshank, *et al.*,[10] and Coulson and Gianturco[11] have suggested that for suitable valence state electron configurations, and under the influence of highly electronegative ligands, the d orbitals may drop in energy and contract sufficiently to become effective in bonding.

Even though advocacy for the picture of one d orbital per "hypervalent" σ bond has waned somewhat in recent years,[12] the case for d orbital participation in π bonding seems to have been steadily growing stronger. The shortness of SO and PO bonds in SO_4^{2-} and F_3PO, for example, together with the considerable variability of SO and PO bond lengths as the intramolecular environment is changed, is taken to be symptomatic of strong d_π–p_π interactions. Expanding upon this idea, Cruickshank[13] advanced some very reasonable rules for assigning d_π–p_π bond orders. These were found to account so convincingly for the observed trends in PO and SO bond lengths[13] and force constants[14,15] that even Rundle, one of the principal skeptics regarding d-orbital interactions, conceded their importance.[7] Further ammunition for adherents of this picture has been provided by the *ab initio* molecular orbital calculations of Boyd and Lipscomb[16]

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[1] This research was supported by a grant from the National Science Foundation.

[2] C. A. Coulson, *Nature*, **221**, 1106 (1969); also *ibid.*, **217**, 220 (1968).

[3] K. A. R. Mitchell, *Chem. Rev.*, **69**, 157 (1969).

[4] D. P. Craig, *J. Chem. Phys. Soc.* (*University College*), **1**, 238 (1958); D. P. Craig and E. A. Magnusson, *J. Chem. Soc.*, 4895 (1956).

[5] C. D. Cornwell and R. S. Yamasaki, *J. Chem. Phys.*, **27**, 1060 (1957).

[6] T. M. Dunn in "Physical Chemistry, An Advanced Treatise," Vol. V, H. Eyring, W. Yost, and D. Henderson, Ed., Academic Press, N. Y., 1970, Chapter V.

[7] R. E. Rundle, *Rec. Chem. Progr.*, **23**, 195 (1962); *Surv. Progr. Chem.*, **1**, 81 (1963).

[8] D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 332 (1954).

[9] D. P. Craig and C. Zauli, *J. Chem. Phys.*, **37**, 601, 609 (1962); D. P. Craig and N. L. Paddock, *J. Chem. Soc.*, 4118 (1962); D. P. Craig and T. Thirunamachandran, *J. Chem. Phys.*, **43**, 4183 (1965), **45**, 3355 (1966); G. L. Bendazzoli and C. Zauli, *J. Chem. Soc.*, 6827 (1965).

[10] D. W. J. Cruickshank, B. C. Webster, and D. F. Mayers, *J. Chem. Phys.*, **40**, 3733 (1964); D. W. J. Cruickshank, B. C. Webster, and M. A. Spinnler, *Int. J. Quantum Chem.*, **18**, 225 (1967).

[11] C. A. Coulson and F. A. Gianturco, *J. Chem. Soc. A*, 1618 (1968).

[12] However see F. P. Boer and W. N. Lipscomb, *J. Chem. Phys.*, **50**, 989 (1969), where 3d orbitals are shown to be not insignificant even for SiH_4. See also K. A. R. Mitchell, *J. Chem. Soc. A*, 2676 (1968); 1637 (1969).

[13] D. W. J. Cruickshank, *J. Chem. Soc.*, 5486 (1961).

[14] D. W. J. Cruickshank and E. A. Robinson, *Spectrochim. Acta*, **22**, 555 (1966).

[15] R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **41**, 2074 (1963); **42**, 2496 (1964).

[16] D. B. Boyd and W. N. Lipscomb, *J. Chem. Phys.*, **46**, 910 (1967); **48**, 4968 (1968).

for the PO, PO^-, and PO_2^- systems. In these calculations it was shown that phosphorus d orbitals significantly lowered the computed ground-state energies and increased the overlap populations.

Persuasive though these and other[2-4] arguments are, lingering doubts remain about the true chemical relevance of outer d orbitals. Earlier work in our laboratory showed that Hückel molecular orbital calculations omitting π orbitals and utterly neglecting d orbitals gave, nevertheless, a good account of structural trends in series of compounds of phosphorus, sulfur, and other atoms with various monovalent ligands.[17-19] These trends closely paralleled those predicted by the Gillespie–Nyholm valence shell electron pair repulsion (VSEPR) model[20] even though it was originally supposed that the VSEPR rules imply the agency of d orbitals.[21] Extensive calculations by Wiebenga, *et al.*,[22] revealed that structures, bond lengths, and charge distributions in interhalogen complexes and polyhalide ions are reproduced quite successfully without the need for invoking d orbitals. Subsequently, approximate SCF–LCAO–MO calculations by Manne[23] and CNDO–MO calculations by Santry and Segal[24] on such molecules as ClF_3 and SF_4 confirmed that calculated bond angles in second-row atoms are substantially independent of whether d orbitals are included or not.

Further doubts are raised by a recent structure determination for F_3NO.[25] If the short[26] PO bond length in F_3PO is ascribable to strong d_π–p_π bonding, it is disquieting to note that the NO bond in F_3NO is also short enough (1.15 Å) to qualify it as a double bond. Rightly or wrongly, few chemists would invoke the 3d orbitals of nitrogen to explain the bonding.

In the light of these facts, it is pertinent to inquire further into Cruickshank's original d_π–p_π model. Cruickshank reasoned that only two of the five 3d orbitals need to be taken into account in SO and PO bonds (the e orbitals in SO_4^{2-} and PO_4^{3-}) but that these two are used fully, where possible. In addition, Cruickshank totally neglected p_π–p_π overlap, which must be crucial in F_3NO. Furthermore, in Cruickshank's simple approach, the assignment of the relative conjugative properties of CH_3, CH_2, NH_2, OR, F, and other groups is quite arbitrary, and it influences derived bond orders. In a molecular orbital approach including all valence electrons, such interactions as well as steric and electronegativity effects (*à la* VSEPR) are automatically taken into account, even if only roughly, and the relative usage of the 3d orbitals may be assessed. Therefore, a reformulation of Cruickshank's approach in terms of molecular orbital theory should be profitable.

Such a test with the relatively inexpensive extended Hückel molecular orbital (EHMO) recipe of Hoffmann, *et al.*,[27] would seem to be a good starting point because it is feasible to apply it to a fair number of moderately complex molecules, permitting an exploration of trends in series. Even if *individual* calculations are much cruder, say, than those already performed on a few simple molecules by Lipscomb, *et al.*,[12,16] they can be justified on the basis of past experience confirming that EHMO calculations quite successfully account for *trends* in a series of molecules. So far, the more accurate existing calculations, in verifying that an increase in the number of parameters improves a wave function, have not fully demonstrated the effectiveness of d orbitals in a chemical sense—the degree to which they are essential in explaining trends in properties of a series of molecules. It is not altogether clear that the coefficients of the d orbitals found are large enough to guarantee that the wave functions escape belonging to Coulson's recently formulated[2] "second case" in which no "really significant chemical meaning" can be attached to the d-orbital contributions. Therefore, without further apology for the known[28,29] lack of rigor of the EHMO method, we shall show what it implies about π contributions and outer d-orbital involvement in P–O and S–O bonds.

Procedure

All calculations were based on EHMO programs originally written by Hoffmann.[27] Slater orbitals were used as basis functions. The formula

$$H_{ij} = 0.5K(H_{ii} + H_{jj})S_{ij} \qquad (1)$$

with K taken as 2.0 was used to generate Hamiltonian matrix elements. In Table I are shown the orbital exponents and diagonal matrix elements adopted for the sake of computation. Neither type of parameter was optimized but, for the most part, the values selected are similar to those adopted by other workers. Most arbitrary and uncertain were the 3d parameters. The 3d orbital exponents appropriate for the present compounds are generally acknowledged[2,3,8-12,16] to be much larger than the neutral atom Slater value of 0.33,

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[17] L. S. Bartell, *Inorg. Chem.*, **5**, 1635 (1966).

[18] L. S. Bartell, *J. Chem. Educ.*, **45**, 754 (1968).

[19] R. M. Gavin, Jr., *ibid.*, **46**, 413 (1969).

[20] R. J. Gillespie and R. S. Nyholm, *Quart. Rev., Chem. Soc.*, **11**, 339 (1957); R. J. Gillespie, *J. Chem. Educ.*, **40**, 295 (1963).

[21] At the time of formulation of the VSEPR theory, comparatively little attention had been given to localized molecular orbital theory. It was not widely understood, then, and it is insufficiently appreciated even today, that the number of localized bonding molecular orbitals radiating from a central atom can exceed the number of atomic orbitals assigned to that atom without violating any fundamental principle.

[22] E. E. Havinga and E. H. Wiebenga, *Recl. Trav. Chim. Pays-Bas*, **78**, 724 (1959); E. H. Wiebenga, E. E. Havinga, and K. H. Biswock, *Advan. Inorg. Chem. Radiochem.*, **3**, 133 (1961); E. H. Wiebenga and D. Kracht, *Inorg. Chem.*, **8**, 738 (1969). See also J. Hinze and K. S. Pitzer in "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p 340.

[23] R. Manne, *Theor. Chim. Acta*, **6**, 312 (1966).

[24] D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **47**, 158 (1967); D. P. Santry, *J. Amer. Chem. Soc.*, **90**, 3309 (1968).

[25] K. Hedberg, V. Plato, and W. Hartford, private communication, 1969.

[26] L. E. Sutton, "Tables of Internuclear Distances and Configurations in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.

[27] R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179, 3489 (1962); **37**, 2872 (1962); R. Hoffmann, *ibid.*, **39**, 1397 (1963); R. S. Mulliken, *J. Chim. Phys.*, **46**, 497, 675 (1949); M. Wolfsberg and L. Helmholtz, *J. Chem. Phys.*, **20**, 837 (1952).

[28] L. C. Allen and J. D. Russell, *ibid.*, **46**, 1029 (1967); L. C. Allen, to be submitted for publication.

[29] See G. Blyholder and C. A. Coulson, *Theor. Chim. Acta*, **10**, 316 (1968); H. H. Jaffé, *Accounts Chem. Res.*, **2**, 136 (1969); M. D. Newton, F. P. Boer, W. E. Palke, and W. N. Lipscomb, *Proc. Nat. Acad. Sci. U. S.*, **52**, 890 (1964), and references therein; C. W. Kern and M. Karplus, *J. Chem. Phys.*, **40**, 1374 (1964).

TABLE I
ORBITAL PARAMETERS

Atom	Atomic orbital	Orbital exponent	Diagonal matrix element, eV
Hydrogen	1s	1.200	−13.60
Nitrogen	2s	1.950	−28.13
	2p	1.950	−14.54
Carbon	2s	1.625	−21.34
	2p	1.625	−11.27
Oxygen	2s	2.275	−35.13
	2p	2.275	−13.62
Fluorine	2s	2.600	−42.51
	2p	2.600	−17.42
Chlorine	3s	2.033	−26.00
	3p	2.033	−13.01
Sulfur	3s	1.817	−23.06
	3p	1.817	−10.36
	3d	1.200	−2.50 or −7.00
Phosphorus	3s	1.600	−20.30
	3p	1.600	−11.00
	3d	1.100	−2.50 or −7.00

and to be sensitive to the molecular environment. We did not vary them from compound to compound, or from orbital to orbital in a given compound[13] but, rather, fixed them and the $H_{3d,3d}$ elements at plausible intermediate values.

We established by a series of calculations, some of which are outlined in the Appendix, that the results we sought were insensitive to the 3d orbital exponents in the range we considered reasonable. More troublesome were the $H_{3d,3d}$ elements, for the numerical results were strongly dependent upon the values adopted. Therefore, the $H_{3d,3d}$ were adjusted (to a value −7.0 eV) to force the EHMO 3d populations for PO, SO, PO_2, PO_2^-, and SO_4^{2-} to closely simulate, in the mean, the *ab initio* SCF populations[16,30] for the same systems. This adjustment gave π-overlap populations in approximate agreement with the *ab initio* calculations but gave σ and, hence, total overlap populations which were too large. Presumably, the deficiencies of the EHMO model should tend to cancel in the trends we seek to explore. Lending confidence in this cancellation was the finding that the qualitative trends discussed in the following sections proved to be independent of the value of $H_{3d,3d}$ we adopted. Parallel calculations run with $H_{3d,3d} = -2.5$ eV are also reported.

The derived wave functions were subjected to Mulliken population analyses[31] with a view to determining whether MO bond overlap populations resemble Cruickshank bond orders, whether 3d contributions parallel those in Cruickshank's model, and whether resultant d-orbital populations are more suggestive of Coulson's first case (chemically significant) or second case (small polarization). Not only were conventional overlap populations between two bonded atoms k and l considered [*e.g.*, $n(\mathrm{k}, \mathrm{l}) = \Sigma_{\mathrm{r,s}}\Sigma_{\mathrm{i}}2N(\mathrm{i})C_{\mathrm{rki}}S_{\mathrm{rksl}}C_{\mathrm{sli}}$][31] but so also were geminal nonbonded overlap populations which give a measure of the intramolecular repulsive forces tending to stretch bonds.[32-34] The geminal overlap populations about a bond k–l with adjacent atoms j and m, for example, as in j–k–l–m, were taken to be the algebraic sum over all geminal interactions across the bond [*e.g.*, n(j, l) and n(k, m) in our example].

In calculations of the present type, the question arises as to what assignment of molecular structure parameters should be made. The prime significance of results is in the *trends* that are yielded and not in the absolute results for any one molecule. A complication is that, if observed bond lengths are fed into the calculations, short bonds with large overlap integrals will necessarily tend to have larger overlap populations than long bonds. It is desirable to distinguish this induced correlation from the intrinsic differentiation between bond types dictated by the intramolecular environment. Therefore, as is commonly done in the case of π-electron calculations on polynuclear aromatic systems,[35] a set of calculations was performed with preset, fixed bond lengths and observed bond angles. Values of 1.50 and 1.45 Å were chosen for PO and SO, respectively. Another, smaller, set was performed for comparison using observed[36] bond lengths. In each case computations were carried out both including and excluding 3d orbitals.

Results

Molecules and ions selected for study included those in Cruickshank's original paper[13] insofar as was economically practical. The systems are depicted in Figure 1 where individual bonds are labeled for identification in the subsequent figures. In Figures 2 and 3 are plotted the observed lengths[36] of individual PO and SO bonds as a function of the associated bonded overlap populations calculated by the fixed bond length method. Results including and excluding 3d orbitals are presented. In Figures 4 and 5 are shown the corresponding quantities calculated by the observed bond length method. That the nonbonded interactions as well as the bonded interactions are significant is illustrated in Figures 6 and 7. Similar plots of P–O and S–O calculated bond polarities [*i.e.*, net atomic charge differences $Q(\mathrm{P}) - Q(\mathrm{O})$ and $Q(\mathrm{S}) - Q(\mathrm{O})$] are given in Figure 8.

Suggestive though the above results are, they are not easy to assess quantitatively unless they are compared with similar results for more familiar systems (first-row atoms) subject to smaller theoretical uncertainty. Therefore, calculations for nitrogen and phosphorus analogs are listed together in Table II and variations in bond length with overlap population are compared for

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(30) I. M. Hillier and V. R. Saunders, unpublished results for SO_4^{2-} ions.

(31) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).

(32) G. Dallinga and P. Ros, *Recl. Trav. Chim. Pays-Bas*, **87**, 906 (1968).

(33) L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960).

(34) E. J. Jacob, H. B. Thompson, and L. S. Bartell, *ibid.*, **47**, 3736 (1967).

(35) C. A. Coulson, "Valence," Oxford University Press, London, 1952.

(36) Experimental bond lengths were taken from the following sources: SO, SO_2, SO_3, SO_2F_2: L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publications No. 11, The Chemical Society, London, 1958, and No. 18, 1965; SO_3NH_3, $O_3SCH_2SO_3^{2-}$, PO_4^{3-}: ref 13; SO_4^{2-}: ref 13; M. Atoji and R. E. Rundle, *J. Chem. Phys.*, **29**, 1306 (1968); $SO_4C_2H_5^-$: ref 13; J. A. J. Javis, *Acta Crystallogr.*, **6**, 327 (1953); M. R. Truter, *ibid.*, **11**, 680 (1958); $O_3SOSO_3^{2-}$: ref 13; M. Lynton and M. R. Truter, *J. Chem. Soc.*, 5112 (1960); $S_3O_{10}^{2-}$: ref 13; D. W. J. Cruickshank, *Acta Crystallogr.*, **17**, 674 (1964); F_2HPO: L. F. Centofanti and R. L. Kuczkowski, *Inorg. Chem.*, **7**, 2582 (1968); $PO_3NH_3^-$: ref 13; W. S. McDonald and D. W. J. Cruickshank, *Acta Crystallogr.*, **22**, 43 (1967); $P_3O_{10}^{5-}$: ref 13; D. W. J. Cruickshank, *Acta Crystallogr.*, **17**, 674 (1964).

TABLE II

OVERLAP POPULATIONS OF VARIOUS BONDS CALCULATED FOR MOLECULES USING REFERENCE BOND LENGTHS[a]

		$\sigma + \pi$	π			$\sigma + \pi$	π	$\Delta(\sigma + \pi)^b$	$\Delta\pi^b$
$F_3C—F$	CF	0.405	0.043	$(CH_3)_3C—F$	CF	0.338	−0.020	0.067	0.063
(1.32 Å)$_{obsd}$[c]		. . .	. . .	(1.43 Å)$_{obsd}$[d]	CC	0.775	−0.015	. . .	. . .
$F_3N{=}O$	NO	0.753	0.141	$(CH_3)_3N^+—O^-$	NO	0.576	−0.048	0.177	0.189
(1.15 Å)$_{obsd}$[e]	NF	0.413	0.034	(1.44 Å)$_{obsd}$[f]	NC	0.664	−0.016	. . .	. . .
$F_3P{=}O$	PO	0.695	0.111	$(CH_3)_3P{=}O$	PO	0.652	0.058	0.043	0.053
excl 3d	PF	0.453	0.049	excl 3d	PC	0.745	−0.002	. . .	. . .
$F_3P{=}O$	PO	1.387	. . .	$(CH_3)_3P{=}O$	PO	1.359	. . .	0.028	. . .
incl 3d	PF	0.829	. . .	incl 3d	PC	0.936	. . .	. . .	. . .

[a] Reference bond lengths adopted: CF = 1.35 Å, CC = 1.52 Å, CH = 1.11 Å, NO = 1.30 Å, NF = 1.37 Å, NC = 1.47 Å, PO = 1.50 Å, PF = 1.54 Å, PC = 1.80 Å; all angles assumed to be tetrahedral; *K* assumed to be 2.0; $H_{3d,3d}$ = −7.0 eV for phosphorus. [b] Difference between methyl derivative and fluoride. [c] C. G. Thornton, *Diss. Abstr.*, **14,** 604 (1954). [d] D. H. Lide and M. Jen, *J. Chem. Phys.*, **38,** 1504 (1963). [e] Reference 25. [f] R. E. Rundle as quoted by P. W. Allen and L. E. Sutton, *Acta Crystallogr.*, **3,** 46 (1950).

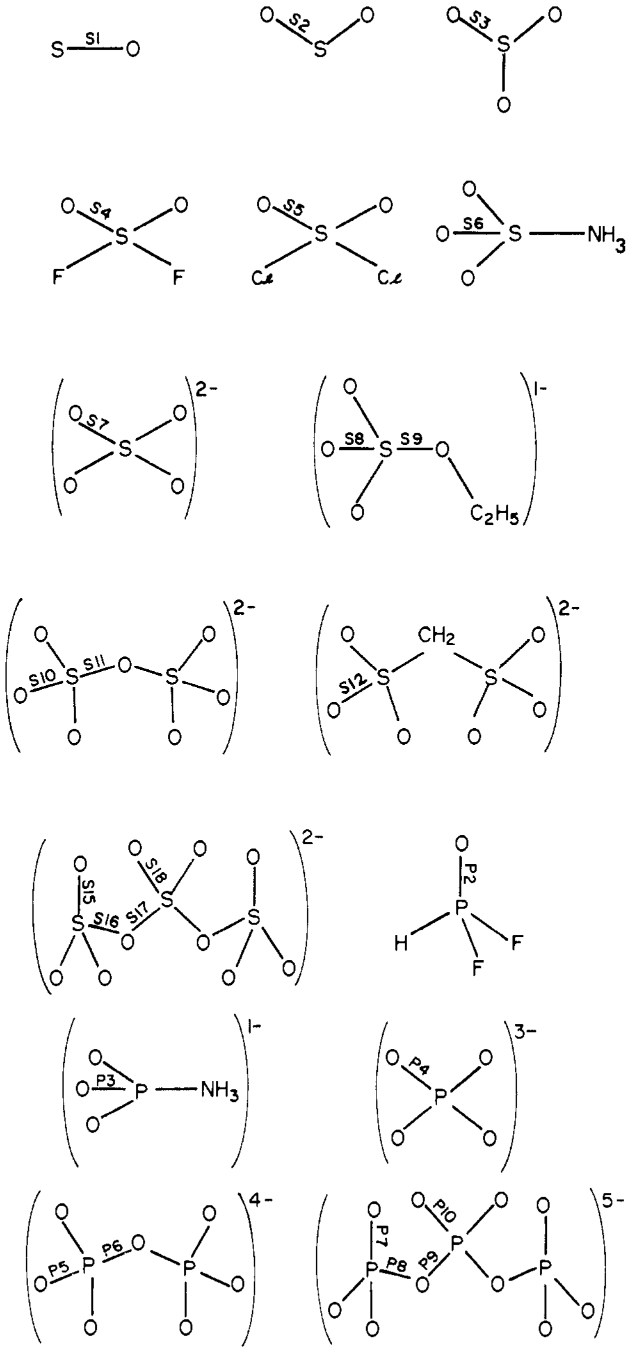

Figure 1.—Molecules and ions investigated.

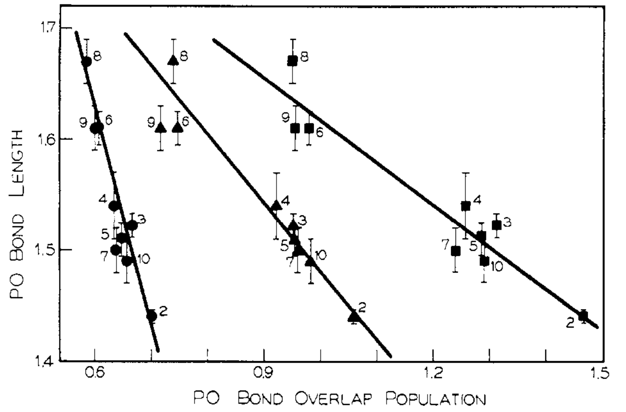

Figure 2.—Experimental PO bond length *vs.* bond overlap population calculated assuming all PO bonds are 1.50 Å long: circles, calculations excluding 3d orbitals; triangles and squares, calculations including 3d orbitals with $H_{3d,3d}$ = −2.5 and −7.0 eV, respectively.

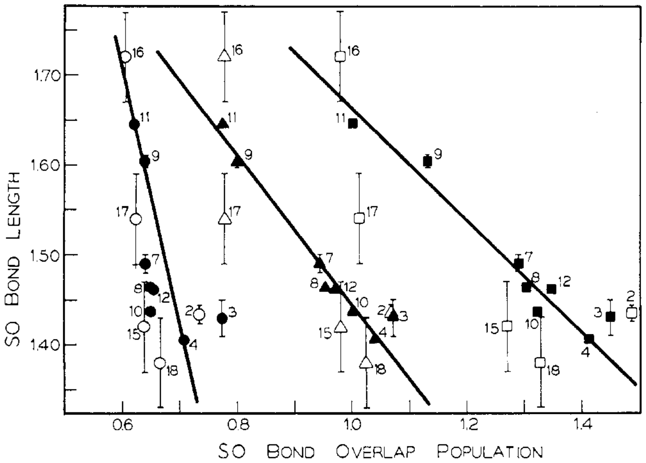

Figure 3.—Experimental SO bond length *vs.* bond overlap population calculated assuming all SO bonds are 1.45 Å long: circles, calculations excluding 3d orbitals; triangles and squares, calculations including 3d orbitals with $H_{3d,3d}$ = −2.5 and −7.0 eV, respectively. Open symbols for S15, S16, S17, and S18 represent the $S_3O_{10}^{2-}$ ion excluded from Cruickshank's plots because of the uncertain bond lengths; S2 contains sulfur in a lower oxidation state than +6.

the well-studied C–C system as well as the present systems in Table III. Out of curiosity, parallel calculations for the nitrogen compounds were run including 3d orbitals in nitrogen with $H_{3d,3d}$ elements of −2.5

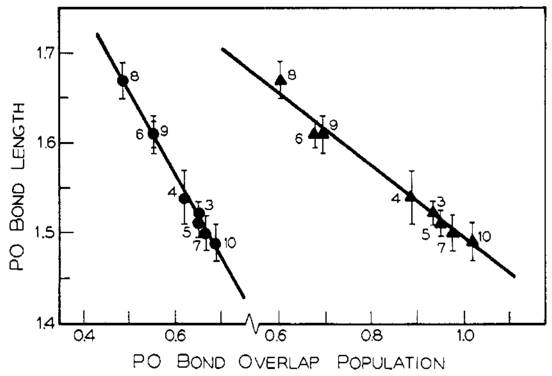

Figure 4.—Experimental PO bond length *vs.* bond overlap population calculated using the observed bond lengths: circles, calculations excluding 3d orbitals; triangles, calculations including 3d orbitals with $H_{3d,3d} = -2.5$ eV.

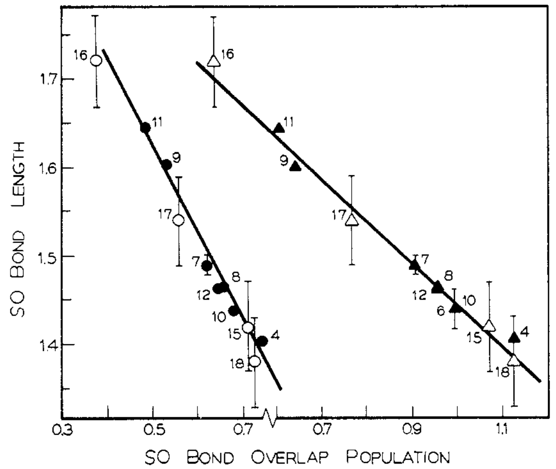

Figure 5.—Experimental SO bond length *vs.* bond overlap population calculated using the observed bond lengths: circles, calculations excluding 3d orbitals; triangles, calculations including 3d orbitals with $H_{3d,3d} = -2.5$ eV; open sysbols, see caption to Figure 3.

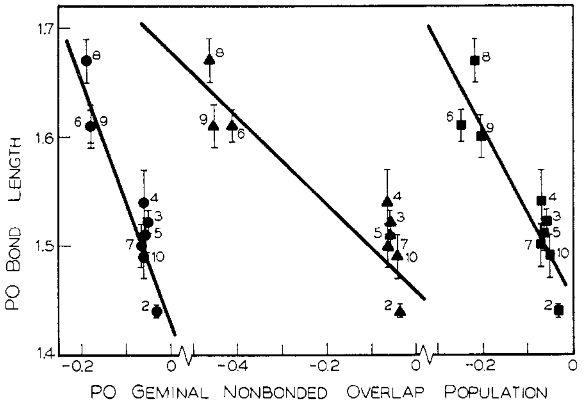

Figure 6.—Experimental PO bond length *vs.* the net geminal nonbonded (repulsive) overlap population calculated assuming all PO bonds are 1.50 Å long: circles, calculations excluding 3d orbitals; triangles and squares, calculations including 3d orbitals with $H_{3d,3d} = -2.5$ and -7.0 eV, respectively.

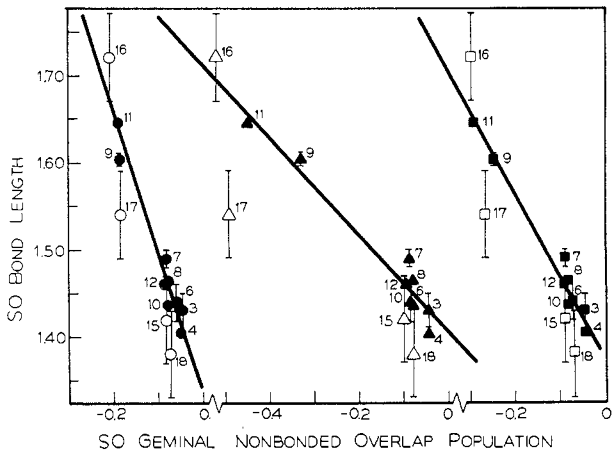

Figure 7.—Experimental SO bond length *vs.* the net geminal nonbonded (repulsive) overlap population calculated assuming all SO bonds are 1.45 Å long: circles, calculations excluding 3d orbitals; triangles and squares, calculations including 3d orbitals with $H_{3d,3d} = 2.5$ and -7.0 eV, respectively; open symbols, see caption to Figure 3.

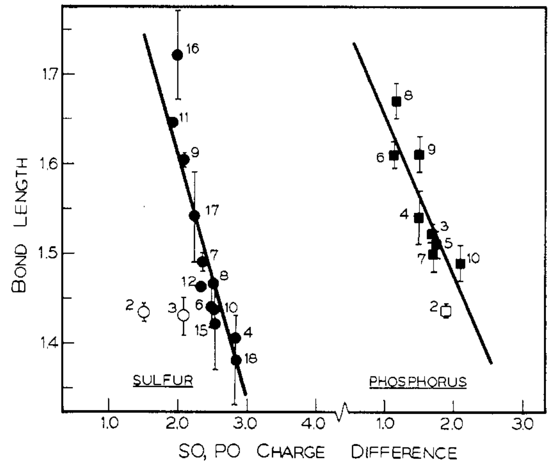

Figure 8.—Experimental SO and PO bond lengths *vs.* the difference in charge between the central atom and the oxygen. Open circles represent lower valence states of sulfur than +6 or lower coordination numbers than 4 and, consequently, less polar bonds for a given bond length. The molecule SO is off scale to the left. The open square represents a nominally lower oxidation state of phosphorus than the solid squares. Calculations were performed at the fixed reference SO and PO bond lengths including 3d orbitals, $H_{3d,3d} = -7.0$ eV. If 3d orbitals are neglected, the calculated points are shifted to the right by about two electronic charges but follow a very similar pattern.

eV. Inclusion of the 3d orbitals had no appreciable effect unless the orbital exponents were made much larger than 0.33.

A direct comparison of Cruickshank d_π–p_π bond orders and EHMO overlap populations is shown in Figure 9. A strong correlation is evident. Overlap populations from calculations excluding d orbitals are contrasted with those including d orbitals in Figure 10.

Another question considered was the relative roles of the 3d orbitals of t_2 symmetry (neglected by Cruickshank as of secondary importance[13]) and of e symmetry (emphasized by Cruickshank) in tetrahedrally ligated P and S complexes. In the prototype system, SO_4^{2-}, it was found that the net t_2 contribution to overlap population and to energy stabilization was *greater* than the net e contribution. Results are illustrated in the Appendix. On the face of it, this result contradicts

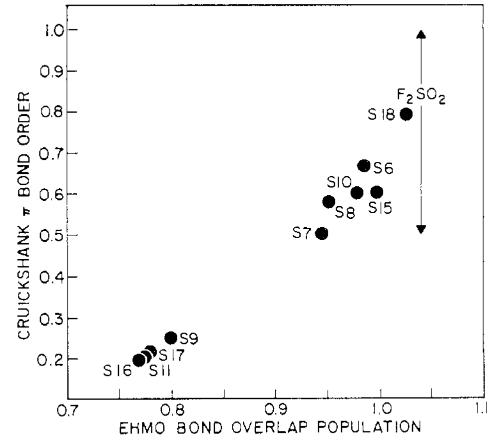

Figure 9.—Cruickshank d_π–p_π bond order for SO bonds *vs.* EHMO overlap population calculated with the inclusion of 3d orbitals, $H_{3d,3d} = -2.5$ eV, and fixed reference SO bond lengths. In the case of F_2SO_2, for which the Cruickshank scheme does not give an unambiguous bond order, the arrow illustrates the possible range of orders corresponding to different assumptions about fluorine π participation. If $-H_{3d,3d}$ is increased to 7.0 eV, the linear correlation between the Cruickshank and EHMO points deteriorates somewhat.

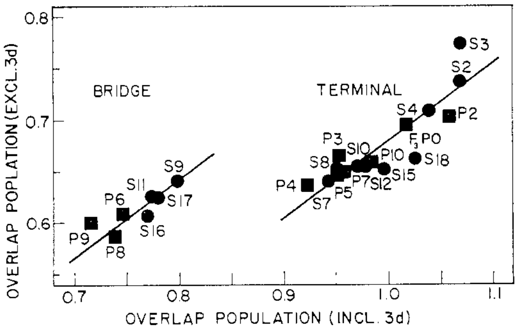

Figure 10.—Comparison of EHMO overlap populations calculated excluding 3d orbitals with those calculated including 3d orbitals, $H_{3d,3d} = -2.5$ eV: circles, SO bonds; squares, PO bonds.

Table III

Mean Slope, $-\Delta n(\mathrm{i,\,j})/\Delta r_{\mathrm{ij}}$, of Calculated Overlap Population *Vs.* Experimental Bond Length

Bond	Calculations based on fixed bond length[a]		Calculations based on observed bond length		Bond length range, Å
	Bonded	Non-bonded	Bonded	Non-bonded	
C–C, aromatic	1.3[b]	. . .	3.2[c]	. . .	1.36–1.44
C–F in X_3CF	0.7[d]	. . .	. . .	. . .	1.32–1.43
N–O in X_3NO	0.6[d]	. . .	2.0[d]	. . .	1.15–1.44
P–O					
Excl d	0.5	1.0	1.1	0.7	1.43–1.67
Incl d (−2.5 eV)	1.7	2.5	2.5	1.4	1.43–1.67
(−7.0 eV)	2.7	1.3	. . .	. . .	1.43–1.67
S–O					
Excl d	0.2–0.4	0.7	1.1	0.4	1.38–1.72
Incl d (−2.5 eV)	1.1	1.9	2.0	1.2	1.38–1.72
(−7.0 eV)	1.6	1.1	. . .	. . .	1.38–1.72

[a] Reference bond lengths adopted: CC = 1.40 Å; all others as in Table II. [b] Calculated from results of R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963), based on $K = 1.75$. [c] Calculated from eq 1 of R. Hoffmann, *Tetrahedron*, **22**, 521 (1966), based on $K = 1.75$. [d] From difference between molecules with X = CH_3 and X = F.

the Cruickshank assumption[13] and stems, at least in part, from the fact that the t_2 but not the e 3d orbitals can mix with ligand σ orbitals. It must be noted, however, that our calculations represented the t_2 and e type 3d orbitals by Slater orbitals with identical orbital exponents and degree of diffuseness. It is conceivable, as hinted by Cruickshank, that SCF calculations would make the t_2 orbitals more diffuse and less effective. Our plots in the Appendix indicate that our results are quite insensitive to the relative diffuseness, however, and the relative populations were independent of the coulomb integrals adopted.

Finally, a comparison of our results for SO_4^{2-} with those of Manne[37] and of Bishop, Randic, and Morton[38] is germane. Manne's calculation was a nonempirical SCF–LCAO–MO calculation excluding d orbitals but neglecting no important integrals involving s and p orbitals. Manne expressed the opinion that the inclusion of d orbitals would not change the results essentially. Bishop, *et al.*, used valence shell orbitals only with approximately SCF atomic basis functions except for sulfur 3d orbitals where STO's identical with ours were adopted. The calculational scheme was potentially superior to ours, also, in its correction of diagonal matrix elements H_{ii} for atomic charges and for its discrimination between H_{ij} elements for σ and for π interactions. Otherwise, the empirical calculation followed the EHMO scheme. Unfortunately, the Manne and Bishop calculations are in sharp disagreement in atomic charges and the ordering of the MO orbital energies. It is of some interest to note that our own calculations, which are the crudest of the lot in basic method, closely parallel those of Manne and disagree with those of Bishop, *et al.*, as may be checked from our tabulations in the Appendix. Manne suggested that the charge dependency of the Bishop H_{ii} is the source of the trouble.[37]

Discussion

Correlations with Gillespie–Nyholm Theory.—Brief note should be made of the parallels between the present calculations and the implications of the Gillespie–Nyholm VSEPR model.[20] Of the molecules studied, three series qualify for comparison. These are each listed in order of decreasing ligand electronegativity: $F_2SO_2 > Cl_2SO_2 \gtrsim (O_2SO_2)^{2-}$; $F_3NO > (CH_3)_3NO$; $F_3PO > F_2HPO \approx F_2CH_3PO > (CH_3)_3PO$. Almost all of the calculated results are as would be expected according to VSEPR theory. In every case except F_2HPO the bonded overlap population to oxygen is increased the the oxygen charge is decreased by increasing ligand electronegativity, irrespective of whether or not d orbitals are included. Other cases in which H atoms depart from VSEPR behavior have been noted elsewhere.[18] Several years ago it was noted that simple Hückel MO calculations on inorganic compounds with monovalent ligands strikingly reproduced VSEPR stereochemical implications and electronegativity effects even though only σ interactions were in-

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(37) R. Manne, *J. Chem. Phys.*, **46**, 4645 (1967).

(38) D. M. Bishop, M. Randic, and J. R. Morton, *ibid.*, **45**, 1880 (1966).

cluded.[17-19,22] It is significant that, in the present calculations with bivalent ligands, the VSEPR electronegativity effect on bonds to oxygen turns out to be almost purely π in character, even when the central atom is denied its complement of d orbitals.

It is to be recalled that the EHMO model used in these calculations altogether neglects explicit electrostatic repulsions and that the VSEPR model considers only electron pair repulsions. It has become clear that occupied, *localized* molecular orbitals do indeed experience strong, mutually repulsive, interactions.[18,39,40] Although purely electrostatic forces between electrons are strong, the repulsive interaction between *localized orbitals* stems from orthogonality-exclusion principle requirements, as was intimated in the original VSEPR paper.[20]

Comparison with Cruickshank Theory.—Figures 2–5 and, even more directly, Figure 9 reveal that the MO overlap populations are, *in trend*, closely similar to Cruickshank bond orders.[13] There is little to choose between the two approaches, as far as can be seen in faithfulness of correlation with experiment, in those cases where Cruickshank π-bond order can be assigned unambiguously. The MO approach has the advantage that it may be applied as easily to other cases, such as F_2SO_2 and F_3PO, with satisfactory results. The aforementioned examples are isoelectronic with SO_4^{2-} (π order $^1/_2$) with d_π–p_π valence bond orders somewhere between the extremes of $^1/_2$ and 1 (F_2SO_2) or 2 (F_3PO) depending upon one's viewpoint.

Cruickshank attributed some of the irregularities in trends of bond length with bond order to deformations of bond angles from idealized values.[13] In this regard, it is worth noting that, as shown in the Appendix, EHMO bond overlap populations for F_2SO_2 and Cl_2SO_2 varied scarcely at all when the OSO angles were varied from 110 to 132°.

Even though the numerical results of applying the Cruickshank and MO theories are similar, there is a substantial difference in detail. As mentioned in the previous section, Cruickshank considers that only two of the central atom d orbitals are effective (the e orbitals in T_d systems). Our calculations apportion a greater effectiveness to Cruickshank's neglected d orbitals than to the two orbitals he retains. As shown in the Appendix, our calculations suggest a usage of e type d orbitals about half that implied by Cruickshank's model (a 3d(e) population in SO_4^{2-} of about one electron instead of two electrons) but a total 3d population entirely comparable to Cruickshank's.

Effects over and above Bond Overlap Populations.—Table III and Figures 6–8 furnish evidence that bonded overlap populations are far from the whole story in bond length variations. Cruickshank[13,41] had noted that nonbonded interactions are formally in a direction to augment the π-bond order variations, but he expressed an opinion that the nonbonded forces are probably of secondary import. The numbers in Table III, however, by no means lay to rest the suspicion that nonbonded interactions may be competitive with π orders in inducing shifts in bond lengths. Mean slopes of nonbonded overlap population *vs.* bond length are very large in the fixed bond length calculations. They are rather smaller in the observed bond length calculations, just as one would expect. Nonbonded repulsions are believed to fall off steeply with increasing internuclear distance[33] and would be relieved, rapidly, as a molecule relaxed from a highly stressed reference structure (fixed r_{ij}) to an equilibrium structure.[34] It might be asked whether the nonbonded results are excessive because of oversimplifications in the EHMO scheme. A firm answer cannot be given but a preliminary indication is provided by Ne···Ne results. For neon, which is isoelectronic with the oxide ion, STO EHMO repulsions are found to be not strong enough![42]

Also correlated in the mean with equilibrium bond length is bond polarity, as is apparent in Figure 8. The trend is in a direction to enhance the influence of π overlap, according to an idea expressed many years ago by Pitzer in a discussion of PO and SO bonds.[43] Pitzer recognized that nonbridging oxygen atoms tend to be more negative than bridging oxygens. He inferred that atoms linked by the more polar bonds would experience a greater mutual electrostatic attraction than those in less polar bonds and demonstrated that the expected magnitude of electrostatic shortening was far from trivial. The point for SO_2 in Figure 8 falls far to the left of the main grouping. This is undoubtedly associated with the fact that the oxidation state of sulfur in SO_2 is lower than that in the other compounds. Correspondingly, the SO_2 bond length is longer for its bond order than the other bond lengths, partly, no doubt, because its electrostatic shortening is less. A better correlation between theory and existing experiments would result if some index based on all three quantities—bond overlap population, nonbonded overlap population, and charge difference—were plotted against bond length. For the present purposes, however, it hardly seems warranted to indulge in such manipulations of parameters.

That the EHMO scheme falls far short of giving a complete characterization of the situation is compellingly revealed in a comparison of PO overlap populations *vs.* SO overlap populations for exact analogs (*e.g.*, a comparison of corresponding bonds in $O_3POPO_3^{4-}$ with those in $O_3SOSO_3^{2-}$, etc.). The EHMO n(PO) *vs.* n(SO) points deviate very little from a straight line with unit slope. By contrast, an analogous plot of experimental bond lengths has a substantially shallower slope as is also reflected in the numbers in Table III. Two glaring deficiencies of the EHMO calculations may be to blame. First, the calculations completely neglected any effects of neighboring ions in the

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[39] O. J. Sovers, C. W. Kern, R. M. Pitzer, and M. Karplus, *J. Chem. Phys.*, **49**, 2592 (1968).

[40] R. S. Berry, M. Tamres, C. J. Ballhausen, and H. Johansen, *Acta Chem. Scand.*, **22**, 231 (1968).

[41] W. S. McDonald and D. W. J. Cruickshank, *Acta Crystallogr.*, **22**, 37 (1967).

[42] Unpublished calculations by R. M. Gavin, Jr.

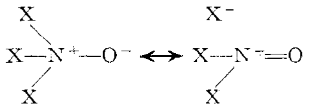
[43] K. S. Pitzer, *J. Amer. Chem. Soc.*, **70**, 2140 (1948).

crystalline solids involved. Second, the EHMO method itself is utterly devoid of a proper accounting of coulomb interactions,[28-30] and each phosphorus ion possesses one unit charge per P atom more than its sulfur counterpart.

Correlations Not Depending Critically on d Orbitals.—Figures 2–7 and Tables II and III demonstrate that trends in bond length for a given type of bond are correctly accounted for by MO calculations even if d orbitals are not invoked. The question is not, then, whether d orbitals are needed to explain the *direction* of the shifts in bond length but, rather, whether they are essential to make understandable the large magnitudes of the shifts. It might be hoped that the shift in π-bonding overlap population required to induce a bond shortening of, say, 0.1 Å could be calibrated by referring to the exhaustively studied C–C bond system.[44] The plausibility of such a calibration is reinforced by the relative success of Pauling's relation between bond order and bond length.[45] On the basis of this simple criterion the numbers in Table III make the MO results look more convincing if d orbitals are included than if they are neglected.

A warning that we must not jump hastily to conclusions in this subtle problem is provided, in addition to the aforementioned charge and nonbonded effects, by the example of F_3NO. In some ways the X_3NO and closely similar, isoelectronic X_3CF systems are more logical models for the present compounds (X_3PO, etc.) than are the polynuclear aromatic molecules. On this basis, the fixed bond method PO results most closely resembling the NO and CF results are those calculated *neglecting* d orbitals.

Obviously, a full resolution of the PO and SO systems will not come before a quantitative understanding of the simpler NO and CF systems has been achieved—and this has yet to come. In focusing attention on the variability of NO bonds in X_3NO compounds (or, for that matter, in the similar XNO series[46]), it must not be overlooked that a shortening of the NO bond is attended by a relative lengthening of the XN bonds and a substantial shift in charge. This latter response is suggested at once by the "double bond–no bond (dbnb) theory of resonance" widely believed to account for NO and CF trends.[46,47] In the case of



for example, the shortness of the NO bond in F_3NO in comparison with that in $(CH_3)_3NO$ and the length of the NF bond (about 0.09 Å longer than in NF_3[25]) are facts easily rationalized in terms of the suitability of the right-hand resonance form if X is fluorine. This dbnb π-bond theory may be considered the valence bond counterpart of the present MO theory (in the variant neglecting d orbitals).[48]

The above argument weighs against adopting the X_3NO results as a calibration basis for the P_xO_y and S_xO_y molecules and ions. For F_3NO in comparison with $(CH_3)_3NO$, a driving force to shorten NO by an amount exceeding that expected from the "reference structure" π-bond order is supplied by the large electronegativity of fluorine, as suggested by the dbnb diagram above. A similar electronegativity imbalance does not exist in the P and S compounds containing only oxygen ligands.

What Is Gained by the Use of d Orbitals?—Many of the foregoing paragraphs emphasize negative aspects of the d-orbital picture. It is only fair to point to some very suggestive positive evidence provided by the present calculations. For one thing, the SO and PO overlap populations themselves are of a more appealing magnitude when d orbitals are included than when they are neglected, it being quite necessary to include them to attain population analyses comparable with the few *ab initio* analyses available. For another, perhaps more conspicuously for SO than for PO, the correlation between bond length and overlap population is better and of more convincing slope when d orbitals are included. Perhaps the most striking benefit gained by including d orbitals is that portrayed in Figure 10. Curiously, while calculations ignoring d orbitals seem to show the right trends for bridge bonds or for terminal bonds taken separately, they do not sharply distinguish bridge bonds from terminal bonds. Surely the difference in length between bridge and terminal bonds is partly steric and partly due to electrostatic forces not reflected in overlap populations,[44] but it is doubtful that all of the difference can be explained away in this fashion.

If d orbitals are important, it must be emphasized that a little contribution goes a long way in lowering energy[12,16] or in augmenting overlap population. This augmentation is clearly illustrated in Figures 2 and 3. Even in calculations with $H_{3d,3d}$ assigned the unfavorable value of -2.5 eV, where d coefficients in the MO's rarely approach 0.1, the overlap populations are, nevertheless, strongly enhanced over those calculated with the exclusion of d orbitals.

Little significance can be attached to the actual numbers arrived at by the EHMO recipe both because of the crudeness of the approach and because population parameters do not represent real physical observables, anyway. Nevertheless, it appears that the d char-

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[44] See N. S. Ham and K. Ruedenberg, *J. Chem. Phys.*, **29**, 1199, 1215 (1958); D. W. J. Cruickshank and R. A. Sparks, *Proc. Roy. Soc., Ser. A*, **258**, 270 (1960); R. Hoffmann, *Tetrahedron*, **22**, 521 (1966), and references therein.

[45] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 239, 400.

[46] R. D. Spratley and G. C. Pimentel, *J. Amer. Chem. Soc.*, **88**, 2394 (1966); M. I. Davis, J. E. Boggs, D. Coffey, Jr., and H. P. Hanson, *J. Phys. Chem.*, **69**, 3727 (1965).

[47] L. O. Brockway, *ibid.*, **41**, 185 (1937); J. Hine, *J. Amer. Chem. Soc.*, **85**, 3239 (1963).

[48] The VSEPR description, while very different in wording, cannot be considered to be fundamentally distinct from the dbnb or the MO descriptions. On the other hand, the alternative pictures of such systems by C. E. Mellish and J. W. Linnett, *Trans. Faraday Soc.*, **50**, 657 (1954), and H. Bent, *Can. J. Chem.*, **38**, 1235 (1960), *are* essentially different even though they lead to similar structural implications. These pictures emphasize the s and p character of σ bonds, attributing an intrinsic shortness to bonds with high s character. Although the reasonably successful EHMO model automatically apportions s and p character to bonds, our adopted prescription for overlap population weights s overlap and p overlap equally. Consequently, it neglects the special effectiveness (if any) of s character.

acter associated with the MO picture may be roughly comparable to the d character implicit in the Cruickshank valence bond picture. Hence, it is likely that the d contribution is high enough to correspond to Coulson's first case (chemically significant) rather than the second case (polarization). In any event, it is certain that the d contribution molds the charge distribution in a significant way. Although it is questionable that d orbitals are leading determinants of molecular structure, they are quite necessary, according to Santry and Segal,[24] in successful calculations of dipole moments.

Conclusion

We have shown that the EHMO picture of bonding in PO and SO bonds closely parallels the simple Cruickshank d_π–p_π valence bond scheme in accounting for observed trends in molecular structure. The MO results imply a different apportionment of d-orbital contributions than Cruickshank's picture, however, and the MO method can be applied, nonarbitrarily, to a wider variety of compounds. It emerged that PO and SO bond lengths could be accounted for, better than popularly believed, even when d orbitals were completely neglected, thereby supporting Rundle's contention that the structural role of outer d orbitals is modest. It is probably often true that the old picture of including an entire d orbital for every extra "bond" in hypervalent cases is as poor as a picture completely excluding d orbitals. Nevertheless, it is increasingly clear that outer d orbitals cannot be dismissed as trivial. Even if they are of little import in establishing bond angles[17-19,24] and even if they are not the *sine qua non* of trends in bond lengths, they play an important role in shaping the electron distributions of molecules.

Acknowledgment.—We are pleased to acknowledge a generous allowance of computing time from the University of Michigan Computing Center.

Appendix

Sensitivity of Computations to Input Parameters.—In empirical calculations of the present type, there is no built-in guarantee that results will accurately correspond to physical reality, although past experience justifies optimism about the trends afforded. Therefore, it seemed prudent to investigate whether output parameters depended critically on the more arbitrary

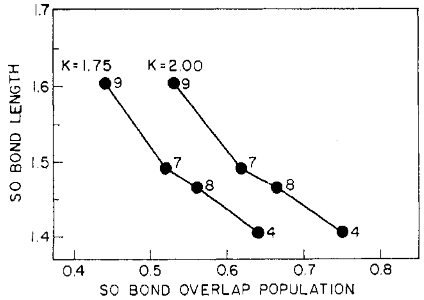

Figure 11.—Effect of choice of K on SO overlap population trend. $H_{3d,3d} = -2.5$ eV.

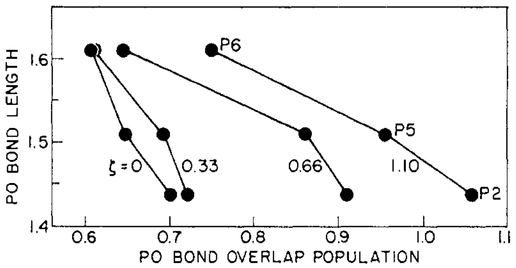

Figure 12.—Effect of variation of 3d orbital exponent (ζ) on PO overlap population trend. $H_{3d,3d} = -2.5$ eV.

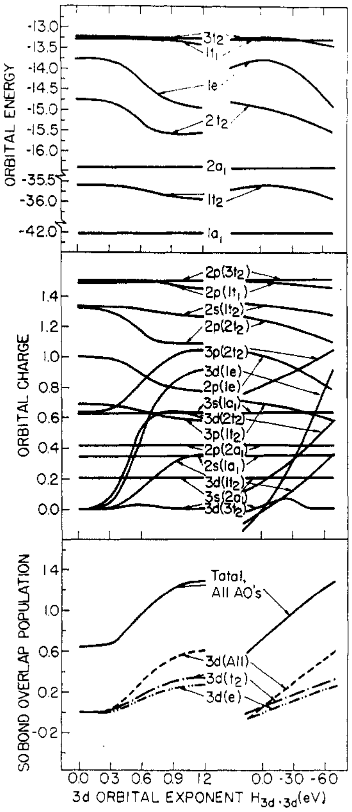

Figure 13.—Sensitivity of EHMO results for the SO_4^{2-} ion upon the sulfur 3d orbital parameters: left side, variation of orbital exponent holding $H_{3d,3d}$ at -7.0 eV; right side, variation of $H_{3d,3d}$ holding ζ at 1.20. Notation as in ref 38.

Table IV

EHMO Calculations for F_2SO_2 and Cl_2SO_2: Effect on MO Energy and Bond Overlap Population of Varying the OSO Angle[a]

	OSO angle, deg			
	110.0	117.5	125.0	132.5
		F_2SO_2		
Overlap population				
SO	1.030	1.037	1.039	1.038
SF	0.549	0.544	0.539	0.533
Total energy, eV	−708.49	−708.63	−708.68	−708.66
		Cl_2SO_2		
Overlap population				
SO	0.966	0.974	0.977	0.976
SCl	0.923	0.917	0.910	0.901
Total energy, eV	−595.52	−595.43	−595.24	−594.96

[a] Calculations include sulfur 3d orbitals and adopt the following values: SO = 1.45 Å, SF = 1.56 Å, ∠FSF = 95°, SCl = 1.99 Å, ∠ClSCl = 111°, $H_{3d,3d} = -2.5$ eV.

of the input parameters. With this in mind, series of calculations were run in which K of eq 1, the degree of contraction of the 3d orbitals, and the matrix elements $H_{3d,3d}$ were varied. Representative results are shown in Figures 11–13. It was found that trends in overlap populations were insensitive to K, as expected, and depended far less on the 3d-orbital exponent than initially feared. Figure 13 displays the detailed response of the individual molecular orbitals of the sulfate ion to variations in the sulfur 3d-orbital exponent and $H_{3d,3d}$ element. It is apparent that, for the adopted value of $H_{3d,3d}$, the quantities of interest change little with orbital exponent in the neighborhood of the exponent assumed in Figures 2–10. Unfortunately, less leeway for error exists for the poorly known $H_{3d,3d}$.

According to Table IV, overlap populations calculated with the inclusion of 3d orbitals exhibit only a modest dependency on the assumed bond angle, consistent with the known small energy required to bend bonds.

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The Copper(I)-Catalyzed Reduction of Nitric Oxide by Tin(II) Chloride

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The reduction of NO by aqueous $SnCl_2$ is strongly catalyzed by Cu(I). The kinetics and stoichiometry are consistent with the sequence of reactions: dissolved NO ⇄ hydrolyzed NO → one-nitrogen intermediate resulting from reaction with the Cu(I)–Sn(II) combination → two-nitrogen intermediate, which competitively forms N_2O or hydroxylamine as a result of further reaction with the Cu(I)–Sn(II) combination.

Introduction

Prior attempts[1] to investigate the kinetics of the reduction of gaseous NO by aqueous tin(II) salts have not succeeded in agitating the aqueous phase vigorously enough to eliminate the effect of gas–liquid mass transfer on the observed rates.[2] We find that the reaction can be followed in a reaction vessel equipped with a vibratory mixer, rather like that used by Schmid and Bähr,[3] to give kinetics demonstrably unaffected by mass transfer, down to a half-life for aqueous NO of 5 sec or less.

Experimental Section

Apparatus.—The reaction vessel (Figure 1) was a Virtis 250-ml freeze-drying flask, only modified by addition of a side arm leading to the manometer and gas-handling system. It was equipped with a Vibro-Mixer (A. G. für Chemie-Apparatebau, Zurich; Chemapec, Inc., Hoboken, N. J.). Although the Vibro-Mixer became a much less efficient stirrer whenever the gas pressure was less than the vapor pressure of water, full efficiency could easily be recovered by adding a few Torr of an inert gas such as nitrogen.

Three lines of evidence indicate that the stirring was vigorous enough to keep the aqueous phase saturated with gas. (1) Reaction rates were, within experimental scattter, independent of stirrer amplitude. (2) The rate measured for reaction of CO_2 with a buffer solution of pH 9.15 ± 0.05 was $(16.0 \pm 0.15) \times 10^{-2}$ sec^{-1}, in good agreement with the literature value obtained from a fast-flow study,[4] $(16.0 \pm 1.2) \times 10^{-2}$ sec^{-1}. (3) At high concentrations of copper(I) or tin(II), the rate of reaction appears to approach a ceiling determined by a hydrolytic reaction of NO (*vide infra*) whose rate at 0° is 0.13 sec^{-1}. We have also measured the kinetics of the reaction of NO with aqueous sulfite[5] and observed a two-term rate law, with one term proportional to sulfite concentration and the other independent of it. The term independent of sulfite, which presumably corresponds to a sequence whose rate-determining step is the hydrolytic reaction of NO, has at 0° the same value, 0.13 ± 0.01 sec^{-1}.

Reagents.—Tank nitric oxide was condensed at liquid nitrogen temperature, pumped on, and distilled at the temperature of *n*-pentane slush, after which it had no contaminants detectable by gas chromatographic or mass spectrometric analysis. All other chemicals were reagent grade, used without further purification. Stannous chloride dihydrate was assayed iodometrically at 99 ± 0.5% purity. All reaction mixtures were degassed before use by freezing and thawing five times under vacuum.

Analyses.—Gases were analyzed on an Aerograph gas chromatograph with a 6-ft column of 30–60 mesh 5A molecular sieve, at 25 or 100°. Tin(II) was titrated under carbon dioxide with triiodide solution standardized against arsenic trioxide. Free acid was determined by titration with standard sodium hydroxide, using a glass electrode pH meter, 2 equiv of base being subtracted for each mole of tin(II) present.

Soluble nitrogenous products were analyzed as follows. One aliquot was boiled for 1 hr to allow the tin(II) to reduce any hydroxylamine to ammonia,[6] which upon Kjeldahl analysis gave the total of ammonia and hydroxylamine originally present. A second aliquot was neutralized with base, the tin(II) hydroxide was centrifuged down, and the supernatant solution was acidified and treated with copper(II) chloride and boiled for 1 hr to drive off nitrous oxide resulting from any hydroxylamine present. Kjeldahl analysis of the remaining solution then gave the amount of ammonia originally present.

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(1) (a) M. L. Nichols and C. W. Morse, *J. Phys. Chem.*, **35**, 1239 (1931); (b) J. E. Chilton, Dissertation, University of California, Berkeley, Calif., 1960; (c) J. N. Cooper, Dissertation, University of California, Berkeley, Calif., 1964.

(2) There is a large chemical engineering literature on the rates of diffusion-affected gas–liquid reactions. *Cf.* H. L. Toor and S. H. Chiang, *A.I.Ch.E. J.*, **5**, 339 (1959); P. V. Dankwerts, *ibid.*, **1**, 456 (1955); F. J. W. Roughton, *J. Biol. Chem.*, **141**, 129 (1941).

(3) G. Schmid and G. Bähr, *Z. Phys. Chem.* (Frankfurt am Main), **41**, 8 (1964).

(4) C. Ho and J. M. Sturtevant, *J. Biol. Chem.*, **238**, 3499 (1963).

(5) T. L. Nunes and R. E. Powell, *Inorg. Chem.*, **9**, 1916 (1970).

(6) L. H. Milligan and G. R. Gillette, *J. Phys. Chem.*, **28**, 747 (1924).