the other isomers may be kinetically labile as well.

For symmetric, cyclic ethers the method of equivalent cores agrees well with ab initio calculations for three- and four-member rings. Since the O_{1s} ionization energies of tetrahydrofuran and tetrahydropyran are the same (within experimental uncertainty) as that of oxetane, we feel justified in inferring that the strain energies for four-, five-, and six-member cyclic fluoronium ions are the same as for the isoelectronic ethers.

18 **19** (14)

Will cyclic fluoronium ions be stable with respect to the ring opening shown in eq 14? For large n, where the effects of ring strain and fluorine substitution of the ring-opened cation can be neglected, eq 14 should be endothermic by approximately 65 kJ mol^{-1}. Estimated heats of formation for fluorolanium (**18**, $n = 2$) and fluoranium (**18**, $n = 3$) are given in Table VIII. If there is no effect from fluorine substitution of the linear isomers **19**, then eq 14 is endothermic by 35 kJ mol^{-1} for $n = 2$ and by 55 kJ mol^{-1} for $n = 3$.

The combined heats of formation of 1-methylallyl cation and hydrogen fluoride are 560 kJ mol^{-1}.[27] Therefore ions **13** and **19** ($n = 2$) are thermodynamically unstable with respect to elimination. But unless there is a lower energy decomposition pathway than via eq 14, fluorolanium (**18**, $n = 2$) should be kinetically stable, with a barrier that is at least as high as the endothermicity of eq 14.

What experimental evidence supports the existence of kinetic barriers? Elimination of hydrogen fluoride is often a facile process, and it seems reasonable to ask whether thermodynamically unstable fluorine-containing cations can nevertheless be kinetically stable. The answer is affirmative. We estimate the heat of formation of the higher homologue of ion **1**, $(CH_3CH_2)_2CF^+$, to be $\Delta H_f° > 510$ kJ mol^{-1} (by analogy to the relative heats of formation of *sec*-butyl and isopropyl cations[27]), while the heat of formation of 1,3-dimethylallyl cation plus that of hydrogen fluoride is 500 kJ mol^{-1}.[27] The $(CH_3CH_2)_2CF^+$ ion is therefore thermodynamically unstable with regard to elimination, but (as we have elsewhere shown[34]) it is stable in the gas phase. We conclude from this example that thermodynamic instability does not necessarily dictate kinetic lability.

Conclusion

Empirical and ab initio estimates for $\Delta H_f°$ of a variety of monofluorinated cations are, for the most part, in agreement. With the exception of **1** all of the $C_3H_6F^+$ structures are estimated to be thermodynamically unstable with respect to **15**, the ion–molecule complex of allyl cation with hydrogen fluoride. Nevertheless, the possibility that kinetic barriers may exist provides a warrant for continued experimental efforts to observe isomers of **1**.

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Supplementary Material Available: Listing of Cartesian coordinates of optimized geometries (49 pages). Ordering information is given on any current masthead page.

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Chemical Bonding in Hypervalent Molecules. The Dominance of Ionic Bonding and Negative Hyperconjugation over d-Orbital Participation

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Abstract: Does sulfur form six covalent bonds in CH_3SO_2Cl, $F_3S{\equiv}N$ or carbon or phosphorus five bonds in $F_3C{=}O^-$, $F_3P{=}O$? After a brief history of the viewpoints on hypervalent bonding and a comparison of analysis methods (with CH_3SO_2Cl as example), natural population and natural bond orbital analysis is applied to a series of 32-valence-electron species of X_3AY type (CF_4, F_3NO, O_3ClF, O_3PS^{3-}, F_3SN, etc.). The σ-bonding in these systems is found to be significantly ionic, and the strongly polar σ^*_{AX} orbitals are found to be more effective electron acceptors than the extra-valence $d_\pi(A)$ orbitals. Negative $\pi_Y \rightarrow \sigma^*_{AX}$ type hyperconjugation, which results in π_{AY} bonding, is thus the primary contributor to π_{AY} bonding in X_3AY species, with $\pi_Y \rightarrow d_\pi(A)$ overlap secondary. However, the d orbitals serve to polarize the σ^*_{AX} orbitals. This enhances π_{AY} bonding and diminishes σ^*_{AX} antibonding interactions and must be included to obtain a qualitatively correct description. The strength of π_{AY} bonding increases along the series F_3SiF, F_3PO, F_3SN, F_3ClC, but the latter species, as well as F_3IC and F_3TeC^-, are found computationally to be incapable of existence. By generalizing our discussion to n-coordinate $8n$-valence-electron species (HF_2^-, BF_3, ClO_4^-, F_4SO, F_5TeO^-, IF_6^+, $OXeF_6$, etc.) and their "reduced" analogues that have one or more lone pairs on the central atom (SF_4, IF_6^-, ClF_3, etc.), we provide a classification of hypervalent (and many nonhypervalent) molecules. The simple, qualitative bonding concepts for hypervalent molecules developed here supercede the inaccurate and misleading dsp^3 and d^2sp^3 models that are still in widespread use.

I. Introduction

What is the role of d functions in the bonding of "hypervalent" compounds of Si, P, S, and Cl?[1-20] Although the theoretical evidence against the traditional dsp^3, d^2sp^3 bonding models has become substantial,[10-15] recent work by Mayer and others[19,20]

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appears to support strong participation of d orbitals. The resolution of this issue is important, for, as Musher[8] stated in 1969, "The fact that these molecules have never received a good theoretical treatment but have somehow always been considered as exceptions to the rule, has had the unfortunate consequence that many interesting aspects of their chemistry have been almost completely neglected by the modern chemist."

We examine the importance of back-bonding from p-type lone pairs on the ligands into d orbitals on the central atom, especially in view of the fact that inorganic chemists tend to lend more credence to the idea of $(d-p)_\pi$ bonding than to σ-bonding involving d orbitals.[9c,21] The various sulfones and sulfates studied by Mayer[19] lend themselves to the treatment of this very issue and serve as our starting point. The sulfate ion is valence isoelectronic (32 valence electrons) with a wide variety of both nonhypervalent and hypervalent tetracoordinate species of X_3AY type such as CF_4, F_3CO^-, F_3NO, F_3PO, F_3SN, O_3PS^-, etc. On the basis of the short C–O and normal C–F distances, F_3CO^- can be considered to have the structure $[F_3C{=}O]^-$ with a pentavalent carbon atom because the C–O bond length of 1.22 Å is typical of that for ketones.[22] The explanation of the "hypervalency" of F_3CO^- lies in ionic bonding and *negative hyperconjugation* rather than in d-orbital participation.[22] Now, the term "hyperconjugation" was originally employed to denote $\sigma \rightarrow \pi^*$ delocalization,[23] a classic example being the donation from σ_{CH} bonds of the CH_2 group of cyclopentadiene into its π^* orbitals. The complementary interaction with reversed direction of "electron flow" is of $\pi \rightarrow \sigma^*$ type, such as the $\pi_C \rightarrow \sigma^*_{CF}$ interaction in $FCH_2CH_2^-$, and has been often labeled "anionic hyperconjugation", but it is not at all restricted to anions and has been more generally termed "negative hyperconjugation".[24] Both types of hyperconjugation act to build π-bond character into bonds that nominally have only σ character, at the "expense" of weakening adjoining π (σ) bonds through the population of π^* (σ^*) orbitals, respectively. In F_3CO^-, each $p_\pi(O)$ orbital will delocalize into a linear combination of the σ^*_{CF} antibonds of π symmetry. Thus, the shortness of the C–O bond in F_3CO^- derives from $p_\pi(O) \rightarrow p_\pi(C)$ bonding arising from $p_\pi(O) \rightarrow \sigma^*_{CF}$ negative hyperconjugation, whereas $p_\pi(O) \rightarrow d_\pi(C)$ bonding is only of minor importance. F_3NO,[25] with a very short N–O bond length of 1.16 Å, is analogous, and experimental evidence for strong negative hyperconjugation has been obtained by Eyermann et al.[25b] Recently, we have analyzed the roles of partially ionic bonding and negative hyperconjugation in polyfluorinated species such as CF_4 in detail,[26] employing natural population and natural bond orbital analysis.[15] Our studies of fluoramines[27] such as F_2PNH_2 and of polyhydroxylated silanes[28] have shown that $n \rightarrow \sigma^*$ negative hyperconjugation is nearly one order of magnitude greater in importance than $(d-p)_\pi$ bonding in such nonhypervalent species.

A related issue concerns π-bonding between transition metals M and trivalent phosphorus ligands. A combination of theoretical and experimental evidence has challenged the traditional view of $d_\pi(M) \rightarrow d_\pi(P)$ bonding in such coordination complexes. Such bonding is much less important than $d_\pi(M) \rightarrow p_\pi(P)$ bonding through donation from the metal into the empty ligand σ^*_{PX} orbitals.[16] In accord with $d_\pi(M) \rightarrow \sigma^*_{PX}$ donation, the P–X bonds become shorter when metal d_π electrons are removed through oxidation.[16d]

There is thus good reason to suppose that negative hyperconjugation plays an important role in hypervalency, an idea that has

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received very little detailed attention until now. This study augments our analyses of the role of d orbitals in SF_6[13] and of the influence of negative hyperconjugation in nonhypervalent molecules[26-28] to the series of 32-valence-electron X_3AY species. This extends the work of Schmidt and Gordon[29] on neutral 14-valence-electron H_3AY species, since each H is replaced by F or O^-. Schmidt and Gordon[29] found evidence for strong negative hyperconjugation and proposed F_3IC as a candidate for synthesis;[29a] we investigate this species as well as the related possibility, F_3TeC^-.

The plan of our paper is as follows. Methods are summarized in Section II. Section III gives a brief overview of different bonding analysis methods for hypervalent molecules. We focus first on historical aspects and then compare Mayer's bonding analysis (MMA)[19] with natural population analysis (NPA).[13,15] In section IV, we compare the electronic structure of some of the sulfur species discussed by Mayer with both the MMA and NPA methods and examine, in particular, the basis set dependence of the analysis of methylsulfonyl chloride. Section V treats the series of 32-valence-electron X_3AY species. Finally, section VI generalizes our results to systems of coordination number n with $8n$, $8n + 2$, or $8n + 4$ valence electrons.

II. Methods

Ab initio SCF calculations with the 6-31G* basis set[30] were carried out with the GAUSSIAN 82 program[30a] on a Convex C-120 computer. For Te and I, the Huzinaga (433321/43321/431) split-valence basis sets with single-polarization functions were employed.[31] The d functions on F are not very important here and were omitted from the calculations on the Te and I species in order to save computer time (i.e., 6-31G basis on F, 6-31G* on C). Pure d-function sets (5d) were used in the calculations on Te/I species. For all other species, Cartesian d-function sets (6d) were employed, as is standard practice with the 6-31G* basis set.[30] For the basis set dependence study on CH_3SO_2Cl (section IV), the minimal STO-3G and split-valence 4-31G basis sets were also employed, as well as the STO-3G* basis set in which d orbitals are added only to the second-row atoms.[30b] Additional calculations including electron correlation via second-order Møller-Plesset perturbation theory[30b] in the frozen-core approximation were carried out for some of the species.

The calculated wave functions were analyzed with the G82NBO program.[15e] A recent review summarizes the NBO method and its previous applications.[15f] The first step is to carry out natural population analysis (NPA); natural populations are the occupancies of the orthogonal natural atomic orbitals (NAOs).[15b] Natural bond orbitals (NBOs)[15a] are then computed in the NAO basis; these are the localized one- or two-center orbitals that form an orthogonal set. The NBOs correspond to molecular Lewis structures. The NBO Lewis structure is then allowed to delocalize so that all core, lone-pair, and bond orbitals become doubly occupied, forming the natural localized molecular orbitals (NLMOs).[15c] The NLMOs are similar in form to localized molecular orbitals derived by other methods.[15c]

III. Review of the Analysis of Bonding in Hypervalent Molecules

A. History. In order to explain the ability of Si, P, S, and Cl to assume valencies greater than 4, the original Lewis rules[1] need to be modified in one of two ways:[7] (a) Allow violation of the Lewis octet rule through promotion of electrons into vacant higher lying d orbitals.[2] (b) Modify the Lewis rule of localized bonding pairs to allow bonds of 50% or more ionic character, thus preserving the octet rule and circumventing the "necessity" of expanding the valence shell to include the d orbitals.[3-8] The emphasis from 1920–1950 on the newly developed concepts of the two-electron covalent bond ("Lewis bonding pair") and orbital hybridization led to the belief that the Lewis rare-gas rule ("Lewis octet") was violated in ICl_2^-, SF_6, PCl_5, etc., leading to proposal (a) above.[1-2] Pauling[2b] gave a valence bond theory description of PCl_5 and SF_6 in which the wave function was described as a superposition of resonance structures, some of which (of "covalent" type) broke the octet rule and others of which (of "ionic" type) obeyed the octet rule through the delocalization of the excess electrons at the central atom onto the ligands. Pauling thus employed a combination of proposals (a) and (b), leaning more toward (b) for PCl_5 and SF_6, but retaining (a) in other cases such as ICl_2^- and I_3^-. He explained the divalency of hydrogen in FHF^- by considering the H–F bonds to be completely ionic. An important breakthrough came in 1951 with the independent development of the linear 3-center 4-electron (3c–4e) bond model by Pimentel[3a] and by Hach and Rundle.[3b] This molecular orbital model was first applied to the FHF^-, ICl_2^-, I_3^-, and I_5^- cases where the Pauling explanation had been cast in doubt. The 3c–4e bond model involved the delocalization of one of the two bonding electron pairs onto the two ligands and yielded a charge distribution of roughly +1.0 on the central atom and –0.5 on each ligand. This MO model is equivalent to a model involving localized molecular orbitals (LMOs) for each bond that are around 50% ionic and 50% covalent; these LMOs are only very slightly delocalized onto the third center.[4] The 3c–4e bonding model thus lent plausibility to proposal (b) above. Acceptance of proposal (b) occurred only very slowly during the 1950s (even by Rundle), and it was generally applied only to the cases where the d-orbital hybridization model was shown to be untenable, for instance, I_3^-, I_5^-, and various other interhalogen species.[5] The discovery of xenon compounds in 1962 represented an important turning point. It was realized that the Xe 5p to 5d promotion energy is prohibitively large, and the 3c–4e model was favored for XeF_2, XeF_4, etc.[4,6] (this application had been anticipated by Pimentel[3a]). Proposal (b) became more vigorously advocated in the 1960s, and a general theory of hypervalency based on the 3c–4e bonding model was developed by Rundle[7] and by Musher,[8] the model being extended to SF_6, PCl_5, F_2SO, and many other species.

The VSEPR model of Gillespie,[32] on the other hand, emphasizes the differing space requirements of differing ligands and central-atom lone pairs, in connection with the Pauli exclusion principle, and it has proven very useful in rationalizing and predicting valence bond angles of a multitude of species. This pragmatic model, developed at a time when accurate calculations of hypervalent molecules were not possible, makes no direct reference to orbital hybridization and bond ionicity issues.

Before the mid-1970s, the theoretical discussion of proposals (a) and (b) was of a more speculative nature due to the infeasibility of calculating sufficiently accurate wave functions, e.g., for SF_6.[9] But this is now routine. Such wave functions are of sufficient quality to reproduce geometries and provide bonding interpretations. One hopes that the controversy could be settled finally. The literature up to 1984 in this area has been reviewed by Kutzelnigg,[10] who drew together conclusive evidence favoring proposal (b) over proposal (a). Since then, more refined theoretical analyses of hypervalent molecules, employing shared electron number and occupation number analysis,[11] electron density analysis,[12] and natural population analysis (NPA),[13-15] have been carried out. In accord with Kutzelnigg,[10] these analyses[11-15] have concluded that, though d orbitals on second-row elements often give large energetic contributions in hypervalent species, the traditional dsp^3 and d^2sp^3 models are invalid: total d-orbital occupancies are at most 0.3e, and the d orbitals act primarily not as valence but as polarization functions, or, equivalently, as acceptor orbitals for back-donation from the ligands. These studies[11-15] emphasize the importance of partial ionic bonding in second-row hypervalent species (proposal (b) above) and reinforce the essential conclusions of Rundle[7] and Musher.[8] Due to the ionic character of the bonding, the *electronic* octet rule is far from being violated. This emphasizes the robustness of the Lewis octet concept stemming from 1902.[1a,13]

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It is indisputable, however, that extra-valence d orbitals must be employed in order to obtain qualitatively correct bond lengths and energies of hypervalent (and indeed, many nonhypervalent) species of second-row and higher row atoms.[33] In particular, Mezey and Haas[33c] have shown that it is impossible to construct an sp basis set for the dimethyl sulfoxide molecule that is able to yield qualitatively correct geometry, charge distribution, and energy. The role of d functions in preferential stabilization of hypervalent species is apparent from the increase in the absolute energy contribution of sulfur d functions from −52 to −138 to −246 kcal/mol along the series SF_2, SF_4, SF_6, with a corresponding increase in S 3d population (NPA) from 0.060 to 0.148 to 0.235 (double-ζ basis set with d orbitals added to S).[15d] The total S 3d population is however distinctly smaller than that required by the dsp^3/d^2sp^3 models. The role of the d functions in hypervalent molecules is to provide "orbital space" at the central atom to accept electron charge from the ligands (back-bonding). The resulting energy stabilization overcomes the strong ligand–ligand repulsion at the hypervalent atom.[13] The d-orbital polarization functions also improve the overlap of the central-atom valence sp hybrids with the ligand orbitals.

We have questioned the importance of central atom d orbitals in σ-bonding. What about π-bonding? Proposal (b) is just as applicable to π-bonding in hypervalent molecules. In SO_4^{2-}, for instance, symmetry dictates that each S–O bond should have triple- and not double-bond character (one σ_{SO} and two equivalent π_{SO} bonds). Sulfur thus should participate in 12 "bonds", many more than could even be formed by hybridization with all of the S 3d orbitals (d^5sp^3). Clearly, in accord with proposal (b), the π_{SO} bonds are far from being "covalent".

Despite the increasing experimental and (especially) theoretical evidence for proposal (b),[3,5–8,10–16] many chemists still employ proposal (a) in rationalizing experimental results[17] or in teaching.[18] Apparent support for retaining proposal (a) is given by the recent theoretical work of Mayer.[19] His analysis method represents an extension of Mulliken population analysis (MPA) and involves the computation of bond order and valency numbers.[19b] We shall refer to MPA and the Mayer bond orders and valencies collectively as Mayer–Mulliken analysis (MMA). A number of research groups have recently applied the MMA method to hypervalent species.[20] Taken literally, the MMA method appears to support the validity of the traditional dsp^3 and d^2sp^3 models for bonding in hypervalent sulfur species.

Several months after this article was submitted, a special journal issue appeared on the structure and bonding of organic sulfur compounds.[34] Mayer[34a] and Angyan[34b] have presented simplified algebraic models of bonding in hypervalent species and have acknowledged the importance of electronegative substituents and ionic bonding components in stabilizing hypervalent species (3-center 4-electron bonding models). They have backed away somewhat from the literal dsp^3 and d^2sp^3 hybridization models, while still emphasizing the importance of d orbitals. Several groups speak of a "decet" or "duodecet" rule instead of the octet rule for second-row compounds, without discussing the role of d orbitals or the details of the bonding.[34c] Volatran[34d] presented a qualitative valence bond analysis of sulfuranes that avoids d-orbital participation and emphasizes the importance of mixing with a excited configuration of $p \rightarrow \sigma^*$ type. Volatran's model is therefore related to the negative hyperconjugation model presented here. By contrast, a qualitative valence bond description of hypervalent sulfur species given by Harcourt[34e] invokes participation of d orbitals as valence orbitals. In other recent relevant work, Gronert et al.[35] have emphasized the importance of ionic bonding in the $FSiH_4^-$ anion.

B. Comparison of Mayer–Mulliken and Natural Population Analysis Methods. The basis set artifacts of Mulliken population analysis (MPA) have been known for some time.[15b] Baker[36] has shown that these deficiencies also carry over to the bond orders and valencies of Mayer–Mulliken analysis (MMA).[19,20] As an extreme example, Baker found that the MMA valency of one of the carbon atoms in $C_3H_3^-$ changes from +3.39 to −4.86 on adding diffuse functions to the 3-21G basis set, with one of the diffuse functions acquiring a negative Mulliken population of −1.98! By contrast, natural population analysis[15b] converges as the basis set expands and does not exhibit basis set artifacts (for example, addition of diffuse functions alters the analysis only minimally). In addition, the orbital populations in NPA are strictly bounded between 0 and 2, whereas Mulliken populations can vary from $-\infty$ to $+\infty$, though they are commonly in the range of about −0.5 to 2.02. An argument brought forth in favor of MMA is that the MMA bond order appears in a first-order, point charge approximation to the molecular exchange energy, as given in Mayer's "Chemical Hamiltonian" analysis.[19] However, since atomic orbitals on adjacent centers overlap strongly, this multipole expansion of the exchange energy will converge very slowly. As higher order terms will contribute strongly to the exchange energy, the advantage of this relation is questionable. The fact that these bond orders can assume the *wrong sign* for covalent bonds[36a] provides ample evidence that these higher order terms can dominate over the first-order term.

In addition to the numerical instability of MMA evidenced by such negative valencies and populations, there are other theoretical grounds for criticism. Atomic orbitals (AOs) are only strictly definable in the SCF wave functions of corresponding isolated atoms. Furthermore, AOs in molecules are artificial constructions enabling the discussion of molecular electronic structure in terms of atomic building blocks. The electronic states of these atomic building blocks within the molecule are compared with those of the isolated atoms. Clearly, then, a population analysis of a molecular wave function that partitions the electrons among "atomic orbitals" should assign electrons *preferentially* to the core and valence AOs that are occupied in the ground-state configuration of the respective isolated atoms. Conversely, a population analysis should assign electrons to extra-valence AOs (i.e., those sets of AOs that are unoccupied in the ground-state configuration of the isolated atoms) only when these *cannot* be assigned to the core and valence AOs of any of the atoms of the molecule. Otherwise, the population analysis of "atoms in molecules" cannot be compared meaningfully with that of the isolated atoms as a reference point. This is the problem with both MPA and its MMA extension: Since electrons shared between two nonorthogonal AOs are divided equally between them, regardless of whether they are valence or extra-valence orbitals, the *high-energy* extra-valence orbitals can acquire significant occupancy at the expense of the *lower energy* valence orbitals. In the NPA[15b] and SEN[11] analysis methods, in contrast, optimum sets of valence AOs are constructed as linear combinations of the available basis functions, and no electrons are assigned to extra-valence orbitals that cannot be assigned to the optimum valence AO set. (For an abbreviated description of the NPA method and how it compares with SEN, see the Appendix of ref 13.) The electron density analysis method of Cruickshank and co-workers[12] operates in an analogous fashion.

As is clear from the discussion, both NPA and MMA assume that the basis set consists of atom-centered orbitals. A basis set involving only orbitals at a *single* center for a polyatomic molecule (single-center expansion), or involving bond functions, would lead to a breakdown of both procedures. In the case of NPA, however, this breakdown can be circumvented by using the non-atom-

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(33) See, e.g.: (a) Collins, J. B.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1976**, *64*, 5142. (b) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039. (c) Mezey, P. G.; Haas, E.-C. *J. Chem. Phys.* **1982**, *77*, 870.

(34) See: *THEOCHEM* **1989**, 186. (a) Mayer, I. *THEOCHEM* **1989**, *186*, 43–52. (b) Angyan, J. G. *THEOCHEM* **1989**, *186*, 61–68. (c) Innes, E. A.; Csizmadia, I. G.; Kanada, Y. *THEOCHEM* **1989**, *186*, 1–8. Robinson, E. A. *THEOCHEM* **1989**, *186*, 9–28. (d) Volatron, F. *THEOCHEM* **1989**, *186*, 167–184. (e) Harcourt, R. D. *THEOCHEM* **1989**, *186*, 131–166. (f) Mezey, E. G.; Flakus, H. *THEOCHEM* **1989**, *186*, 117–129.

(35) Gronert, S.; Glaser, R.; Streitwieser, A. *J. Am. Chem. Soc.* **1989**, *111*, 3111–3117.

(36) (a) Baker, J. *Theor. Chim. Acta* **1985**, *68*, 221. (b) For a comparison of the changes in NPA and MMA charges upon addition of diffuse functions, see Table VII in: Reed, A. E.; Weinhold, F.; Weiss, R.; Macheleid, J. *J. Phys. Chem.* **1985**, *89*, 2688–2694.

Table I. Basis Set Dependence of Natural Population (NPA) and Mayer–Mulliken (MMA) Analyses for SO_2Cl_2, CH_3SO_2Cl, and $(CH_3)_2SO_2$

			NPA					MMA				
basis set	total energy[a]	E(d)[b]	q_S	q_O	q_{Cl}	q_{CH_3}	3d(S)[c]	q_S	q_O	q_{Cl}	q_{CH_3}	V_S[d]
					SO_2Cl_2[e]							
6-31G*	−1466.078 59		+2.29	−0.97	−0.18		0.213	+1.24	−0.55	−0.07		5.10
					CH_3SO_2Cl[e]							
STO-3G	−1034.203 25		+1.42	−0.54	−0.36	+0.03		+1.28	−0.50	−0.34	+0.04	3.73
STO-3G*[S(0d)]	−1034.232 75		+1.46	−0.56	−0.36	+0.02		+1.36	−0.51	−0.38	+0.05	3.76
STO-3G*	−1034.655 15	−265	+1.58	−0.61	−0.31	−0.03	0.377	+0.51	−0.22	−0.22	+0.16	6.00
4-31G	−1044.809 28		+2.13	−0.94	−0.24	+0.00		+1.55	−0.79	−0.10	+0.13	3.73
6-31G	−1045.867 30		+2.17	−0.96	−0.26	−0.01		+1.38	−0.69	−0.08	+0.08	3.93
6-31G*[S0d)]	−1046.031 47		+2.30	−1.00	−0.27	−0.03		+1.84	−0.85	−0.16	+0.02	4.04
6-31G*	−1046.241 99	−132	+2.38	−1.01	−0.26	−0.09	0.213	+1.33	−0.61	−0.16	+0.04	5.02
6-31G*[S(2d)]	−1046.267 81	−148	+2.34	−1.01	−0.25	−0.08	0.228	+0.98	−0.53	−0.07	+0.17	5.59
6-31G*[S(3d)]	−1046.281 64	−157	+2.34	−1.01	−0.25	−0.08	0.233	+0.94	−0.55	+0.02	+0.15	5.62
					$(CH_3)_2SO_2$[f]							
6-31G*			+2.43	−1.07		−0.15	0.172					

[a] Energy in atomic units. [b] Energetic contribution of d orbitals on sulfur, in kilocalories per mole. [c] Total occupancy of sulfur 3d orbitals by NPA. [d] Mayer–Mulliken valency of sulfur. [e] At experimental geometry from ref 38. [f] At optimized 3-21G$^{(*)}$ geometry from ref 33b.

centered basis set to construct atom-centered basis functions.[37] The analysis can then be carried out using the atom-centered basis set. Baker's example[36] concerning the failings of MMA arising from addition of diffuse functions to the basis set might be considered unfair. The diffuse functions of each atom extend over the whole molecule, and hence, the atomic nature of the basis set might be called into question (as was done by one of the reviewers). However, this very example illustrates the strength of NPA over MMA. In MMA, the diffuse functions are treated as independent orbitals, which compete with the valence-shell orbitals for electron occupancy on an unbiased basis. By contrast, in NPA, the "best possible" valence orbitals are constructed (the "natural minimal basis set"[15b] as optimal linear combinations of all orbitals of the same symmetry on a particular atom), and the valence orbitals acquire Slater-like tails through the diffuse functions.[36b] The primary role of the diffuse functions in the wave function in building long-reaching tails into the valence AOs is thus made clear through NPA. Baker's reluctant suggestion,[36a] to carry out a full symmetric (Löwdin) orthogonalization of the basis set, suffers from the same problem as MMA, namely the overestimated occupancy of high-energy atomic orbitals. This has been shown in the paper that introduced the NPA method.[15b]

The difference between MMA and three alternative population analysis methods (NPA, SEN, and that of Cruickshank) is especially apparent in hypervalent species. The d orbitals of the central atom have significant overlap with the valence s and p orbitals of the ligands and are significantly higher in energy. As a result, the d orbitals, though unoccupied in the atomic ground-state configuration, "steal" electrons from the ligand valence orbitals when MMA analysis is applied. The MMA "definition" of AOs in hypervalent molecules is thus inconsistent with the isolated atom reference points. The valency at the central atom is thus overestimated in MMA; it can have a value 5 or 6 or more, in rough correspondence with the dsp^3 and d^{2}sp^3 hybridization models.[19,20] Additionally, the positive charge at the central atom is greatly reduced due to the overestimated central-atom d-orbital occupancy.

In the Appendix, we propose and apply a new definition of bond order and valency based on natural population analysis of localized molecular orbitals.

IV. Electronic Structure of Sulfones and Sulfates

Mayer focused on the basis set dependence of the analysis of the bonding in methylsulfonyl chloride (CH_3SO_2Cl),[19] and we have extended his work. The experimental geometry determined by electron diffraction[38] was used throughout, and Table I shows how the MMA and NPA results change with basis set, from a minimal basis set with and without d functions on the second-row atoms (STO-3G* and STO-3G, respectively) to a good split-valence basis set with and without one set of Cartesian d functions[39] on all heavy atoms (6-31G* and 6-31G, respectively).[30b] To add functional flexibility to the sulfur 3d orbitals, we split the sulfur d orbitals into two [6-31G(2d)] and into three [6-31G(3d)] sets in the standard manner.[30b] The d orbitals on the other heavy atoms, being of lesser importance, were left unsplit (6-31G*), and we denote the two extended basis sets as 6-31G*[S(2d)] and 6-31G*[S(3d)], respectively. In order to evaluate the energetic importance of the sulfur d orbitals, calculations were also done with basis sets where the sulfur d functions were omitted (6-31G basis on S), leaving the basis set on the other atoms unchanged (at 6-31G*). We denote this basis set as 6-31G*[S(0d)]. We carried out a similar procedure with the STO-3G* basis set, leaving out the sulfur d functions to give a basis set that we denote as STO-3G*[S(0d)]. (For studies of the dependence of NPA and MPA on the form of d functions in SF_6, see ref 13 and 15d.)

The NPA results are very similar among the 6-31G* basis set and its extensions, there being a slight increase in the total d-orbital occupancy on S from 0.213 (1d) to 0.228 (2d) to 0.233 (3d). By contrast, the total d population on S with the STO-3G* basis set is much larger, at 0.377. This is due to the poor quality of the sp part of the STO-3G* basis set; the d orbitals on sulfur strongly act as superposition functions for the valence (and core) shells of C, O, and Cl. This judgement is supported by the energetic contributions E(d) of the sulfur d orbitals given in Table I: The contribution of 265 kcal/mol at the STO-3G* level is twice as large as that at the 6-31G* level. Though, with the 6-31G* basis set, the energetic contribution of the sulfur d orbitals (as well as the d-orbital population) increases steadily from 132 to 148 to 157 kcal/mol on going from 1 to 2 to 3 sets of sulfur d orbitals, the basis set has been expanded in an unbalanced manner, exaggerating the importance of these d functions. In all basis sets at or beyond the 6-31G level, the charge on oxygen is around −1 and that on sulfur greater than +2.

In the Mayer–Mulliken analysis, by contrast, a significant portion of the electron density that could have been assigned to the low-energy valence s and p orbitals of O and Cl is assigned instead to the high-energy 3d orbitals on sulfur. As a result, the atomic charges are reduced greatly and "valencies" of 5–6 are derived for sulfur (see Table I). The sulfur MMA valency attains the classical value of 6 only with the STO-3G* basis set, however.

A more nearly complete picture of the nature of the bonding in hypervalent species can be obtained through natural population analysis of the localized molecular orbitals (LMOs). The LMO procedure directly related to NPA is the NLMO procedure (see section II).[15c] We have previously presented an NPA/NLMO

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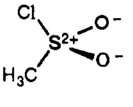
(37) See ref 7 in ref 15b.

(38) Hargittai, M.; Hargittai, I. *J. Chem. Phys.* **1973**, *59*, 2513. See the "note added in proof" for the experimental geometry of $(CH_3)_2SO_2$.

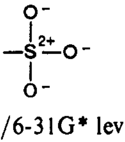
(39) A previous study on SF_6 showed the difference between pure and Cartesian d basis functions on sulfur to be only about 1.5 kcal/mol and thus negligible.[15d]

analysis of SF_6.[13] The NLMOs are formed by delocalization of the NBOs; hence, we first describe the NBOs for CH_3SO_2Cl. The set of NBOs automatically found by the NBO program (in all basis sets) for CH_3SO_2Cl include three C–H, two S–O, one C–S, and one S–Cl σ bonds, three lone pairs on chlorine and on each oxygen, and core orbitals on C, S, O, and Cl. Rather than a hexavalent sulfur with two S=O double bonds, the NBO Lewis structure points to a tetravalent sulfur atom with two $S–O^-$ bonds, which is in accordance with the natural charge (from NPA) on each oxygen of around -1. However, the π-type oxygen lone-pair (π_O) NBOs are highly depleted, having occupancies of 1.84e and 1.80e. The four π_O NBOs donate strongly into vicinal σ^*_{SO}, σ^*_{SC}, and (especially) σ^*_{SCl} NBOs, as well as into the NBOs for the sulfur d orbitals. With the formation of the NLMOs from the NBOs, the oxygen lone pairs delocalize by 6–8% onto hybrids on sulfur of 19–27% d character (depending on how many d functions are added to the 6-31G basis on sulfur). By contrast, the % d character on sulfur in the σ_{SCl}, σ_{SO}, and σ_{SC} orbitals is only 2–3%, both in the NBOs and in the NLMOs (delocalization of these σ NBOs is only slight). The chlorine π-type lone pairs delocalize much more weakly, as the π_{Cl} NBOs have fairly high occupancies (1.972).

Note that the π_O lone pairs donate into π-type sulfur hybrid orbitals that are *only* of 19–27% 3d character and thus of 73–81% valence 3p character. This $\pi_O \rightarrow 3p(S)$ donation arises from $\pi_O \rightarrow \sigma^*_{SX}$ negative hyperconjugation and is connected with the generalized anomeric effect, which we have recently analyzed extensively.[26-28] The ratio of importance of negative hyperconjugation to d_π bonding is thus in the range of 81:19 (4.3:1) to 73:27 (2.7:1). Thus, we are led to a rather simple picture of the bonding in CH_3SO_2Cl, represented by



modified by strong $\pi_O \rightarrow \sigma^*_{SX}$ negative hyperconjugation and, to a lesser extent, by $\pi_O \rightarrow S(3d_\pi)$ back-bonding. Results for SO_2Cl_2 and $(CH_3)_2SO_2$, which were also examined by Mayer,[19] are similar (see Table I). Since $\pi_O \rightarrow \sigma^*_{SCl}$ hyperconjugation is stronger than $\pi_O \rightarrow \sigma^*_{SC}$, the average occupancy of the π_O NBO decreases progressively from 1.850 to 1.821 to 1.800 on going from $(CH_3)_2SO_2$ to CH_3SO_2Cl to SO_2Cl_2. This is also consistent with the experimentally observed decrease in the S–O bond length along this series, from 1.435 to 1.424 to 1.404 Å.[38] The corresponding Lewis structure for the sulfate ion SO_4^{2-} would be:[15d]



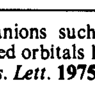
Calculations at the 6-31G*//6-31G* level (section V) confirm this description. Natural charges were found to be +2.92 on sulfur and -1.23 on oxygen. The π_O NBOs were found to have occupancies of 1.901, much greater than in $(CH_3)_2SO_2$, consistent with the much longer S–O bond length of 1.48 Å in SO_4^{2-} (average crystal structure[40]). The total delocalization from π_O orbitals in SO_4^{2-} is 0.79e; of this, 0.61e goes into the σ^*_{SO} orbitals and only 0.18e (less than 25%) into sulfur $3d_\pi$ orbitals.

V. General Study of X_3AY Species

Each of the tetracoordinate species $(CH_3)_2SO_2$, CH_3SO_2Cl, SO_2Cl_2, and SO_4^{2-} treated in section IV have 32 valence electrons and analogous electronic structures. In carrying out a general study of tetracoordinate 32-electron species, it is simplest to employ only monoatomic ligands (F, Cl, O^-, S^-, N^{2-}, etc., but not H_3C) and to restrict three of the ligands to be the same. Such X_3AY species have high symmetry (C_{3v}) and only three geometrical parameters, simplifying the analysis of geometric trends. When all four substituents are identical, the structure is exactly tetrahedral, and the negative hyperconjugative $n \rightarrow \sigma^*$ interactions are symmetric with respect to the four ligands. Each $n \rightarrow \sigma^*$ interaction strengthens (shortens) one of the A–X bonds in AX_4 but weakens (lengthens) the remaining A–X bonds, resulting in little net influence on A–X bond length.[26,28] In X_3AY species, by contrast, the ligand lone pairs have differing donor strengths, the angles are no longer tetrahedral, and $n \rightarrow \sigma^*$ interactions exert a greater influence on the structure;[27] this constitutes an additional advantage of studying X_3AY systems.

For our study, we start with a number of experimentally known X_3AY species: CF_4, F_3CO^-, NF_4^+, F_3NO, F_3PO, F_3PS, PF_4^+, F_3SN, O_3PS^{3-}, PO_4^{3-}, SO_4^{2-}, ClO_4^-, and O_3ClF.[41] We then extend this series to include the hypothetical species F_3PN^-, F_3SC^-, F_3ClC, F_3TeC^-, and F_3IC. For the latter four species and for F_3SN, we also considered the isomers with the A and Y atoms exchanged (X_3YA) in order to determine which is more stable (the remaining species are unlikely to have any X_3YA isomers). Optimized structures are given in Table II, along with those of various species useful for comparison of the bond lengths (H_3Cl, H_3COH, F_3CH, etc.). Experimental structures, given in Table II where available, are generally in good correspondence with theory, except for the N–F bond lengths in F_3N and F_3NO (inclusion of electron correlation is necessary in order to obtain correct N–F lengths[22c]) and the P–S bond length and S–P–O angle in O_3PS^{3-} (which may be influenced by counterions in the crystal). Isomerization energies are given in Table III. Where available, 6-31G* structures were taken from the CMU and FAU-Erlangen archives.[42] Comparison of the A–X and A–Y bond lengths with those in reference species is presented in Table IV. Key features of the NPA and NBO analysis are also given in Table IV: the atomic charges, the occupancies and total depletion of the ligand π-type lone pairs, and the total central-atom d-orbital population. We have already presented an analysis of negative hyperconjugation in CF_4.[26] Though weaker than in SO_4^{2-} (the π_Y occupancies are 1.952 and 1.901, respectively; cf. Table IV), negative hyperconjugation in CF_4 is nevertheless of great importance with respect to the strengthening of the C–F bonds.[26]

If atom Y is less electronegative than atom X, n_Y will normally be a better electron donor than n_X, and σ^*_{AX} will be a better electron acceptor than σ^*_{AY}. Thus, the $n_Y \rightarrow \sigma^*_{AX}$ interaction will be stronger and have greater influence on the molecular geometry. Now, $n_Y \rightarrow \sigma^*_{AX}$ hyperconjugation favors an *increased* X–A–Y bond angle,[26] due to the unfavorable overlap of n_Y with the hybrid orbital contribution to σ^*_{AX} from atom X; this unfavorable overlap is maximized at a bond angle of 90°. Therefore, in a species of X_3AY type, the X–A–Y angle will be greater than tetrahedral if Y is a better π-electron donor than X (discussion of exceptions to this rule, and of other factors influencing the angle, is given further below and in ref 26). For example, the F–C–O angle in F_3CO^- is *much* larger than tetrahedral: It is 116.6 and 116.3° in the theoretically optimized (6-31G*) structure and in the averaged crystal structure,[22a] respectively:



In accordance with dominant $\pi_O \rightarrow \sigma^*_{CF}$ interaction, the C–F bonds are lengthened by 0.069 Å with respect to F_3CH and the C–O bond is contracted by 0.182 Å with respect to H_3COH (Table IV). In F_3CO^-, the $p_\pi(O)$ orbitals are much more depleted than the $p_\pi(F)$ orbitals; their occupancies (Table IV) are 1.805 and

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[40] Gelius, U.; Roos, B.; Siegbahn, P. *Theor. Chim. Acta* **1971**, *23*, 59.

[41] SCF calculations on dianions such as SO_4^{2-} have questionable meaning when some of the occupied orbitals have eigenvalues ϵ greater than zero; see: Ahlrichs, R. *Chem. Phys. Lett.* **1975**, *34*, 570. The 6-31G* HOMO of SO_4^{2-} has a slightly positive ϵ (+0.02 au, triply degenerate); these positive eigenvalues disappear when diffuse (+) functions were added (6-31+G* basis of ref 30b), but the NPA/NBO analysis of the wave function remained essentially unchanged. The wave functions for PO_4^{3-} and O_3PS^{3-} are rather questionable, though, since the 11 top MOs have positive ϵ values; extremely diffuse or continuum functions would be required for these trianions. For an analysis of the trends in the bonding, however, the 6-31G* basis should be adequate.

[42] (a) Whiteside, R. A.; Frisch, M. J.; Pople, J. A. *The Carnegie-Mellon Quantum Chemistry Archive*, 3rd ed.; Carnegie-Mellon University: Pittsburgh, PA, 1983. (b) Friedrich-Alexander Universität Erlangen-Nürnberg Quantum Chemistry Archive, unpublished.

Table II. Comparison of Optimized HF/6-31G* Geometrical Parameters of the X_3AY Species with Those of Related Species X_3AH, X_3A, etc. (Experimental Values in Paretheses)

species	R(XA)	R(AY)	θ(XAY)	θ(XAX)
$H_3CH^{a,b}$	1.084 (1.094)	1.084 (1.094)	109.5 (109.5)	109.5 (109.5)
$H_3CF^{a,b}$	1.082 (1.110)	1.365 (1.383)	109.8 (110.6)	109.1 (108.3)
$H_3CCl^{a,b}$	1.078 (1.086)	1.785 (1.778)	108.4 (108.2)	110.5 (110.7)
$H_3CI^{b,c,d}$	1.076 (1.084)	2.168 (2.132)	107.5 (107.7)	111.4 (111.2)
$H_2CO^{a,b}$	1.092 (1.108)	1.184 (1.206)	122.1 (121.7)	
$H_3CO^{-\,c}$	1.133	1.310	116.5	101.6
$H_3CO^{-\,c,e}$	1.121[e]	1.330[e]	115.0[e]	103.4[e]
$H_3COH^{a,b}$		1.400 (1.425)		
$H_3CSH^{a,b}$		1.818 (1.819)		
$H_3CTeH^{c,d}$		2.171		
$F_3CH^{a,b}$	1.317 (1.332)	1.074 (1.098)	110.4 (110.1)	108.5 (108.8)
$F_3CF^{f,g}$	1.302 (1.320)	1.302 (1.320)	109.5 (109.5)	109.5 (109.5)
F_3CCl^{h}	1.306 (1.325)	1.747 (1.752)	110.3 (110.4)	108.7 (108.6)
$F_3CO^{-\,i}$	1.386 (1.391)	1.218 (1.227)	116.6 (116.3)	101.5 (101.9)
F_3CS^-	1.350	1.756	114.9	103.6
$F_3CTe^{-\,d}$	1.344	2.181	114.3	104.3
$F_3CI^{d,j}$	1.311 (1.328)	2.154 (2.144)	110.7 (110.5)	108.2 (108.4)
$H_3N^{a,b}$	1.002 (1.012)			107.2 (106.7)
$H_3NH^{+\,f}$	1.013	1.013	109.5	109.5
$H_3NF^{+\,f}$	1.015	1.333	107.8	111.1
H_2NOH^{b}	1.003 (1.016)	1.389 (1.453)	103.8 (103.2)	
HNO^{b}	1.032 (1.063)	1.175 (1.212)	108.8 (108.6)	
H_3NO	1.010	1.376	111.7	107.1
$F_3N^{b,f}$	1.328 (1.365)			102.7 (102.4)
$F_3NH^{+\,f}$	1.289	1.023	110.1	108.9
$F_3NF^{+\,f,k}$	1.280 (1.30)	1.280 (1.30)	109.5	109.5
F_3NO^{l}	1.350 (1.431)	1.172 (1.158)	116.3 (117.1)	101.8 (100.8)
F_3NS	1.319	1.776	114.9	103.5
$H_3P^{a,b}$	1.403 (1.420)			95.4 (93.3)
$H_3PH^{+\,f}$	1.380	1.380	109.5	109.5
$H_3PF^{+\,f}$	1.375	1.523	108.3	110.6
$H_2PNH_2{}^{a}$	1.405	1.706	103.7	99.5
H_2POH^{c}	1.408	1.643		
$HPO^{b,c}$	1.431	1.460 (1.512)	105.4 (104.7)	
H_3PO	1.393	1.465	116.9	101.1
H_2PSH^{c}	1.399	2.127		
HPS	1.414	1.914	102.9	
H_3PS^{c}	1.391	1.954	117.0	101.0
$F_3P^{b,f}$	1.564 (1.561)			97.3 (97.7)
$F_3PH^{+\,f}$	1.491	1.364	110.9	108.0
$F_3PF^{+\,f}$	1.480	1.480	109.5	109.5
F_3PO^{m}	1.526 (1.524)	1.425 (1.436)	117.2 (116.8)	100.7 (101.3)
F_3PS^{m}	1.535 (1.538)	1.874 (1.866)	118.1 (118.1)	99.6 (99.6)
F_3PN^-	1.594	1.460	123.1	93.0
$O_3PO^{3-\,n}$	1.567 (1.56)	1.567 (1.56)	109.5 (109.5)	109.5 (109.5)
$O_3PS^{3-\,o}$	1.530 (1.519)	2.260 (1.992)	106.4 (110.6)	112.4 (108.3)
$HSNH_2{}^{c}$	1.326	1.710	97.9	
SNH^{c}		1.539		
$SN^{+\,c}$		1.397		
$HSOH^{c}$	1.328	1.654	98.6	
$SO^{a,b}$		1.465 (1.481)		
$SO_2{}^{a,b}$		1.414 (1.435)	118.8 (119.4)	
H_2SO^{c}	1.343	1.479	109.2	
$F_2S^{b,f}$	1.586 (1.589)			97.9 (98.3)
F_3SN^{p}	1.544 (1.522)	1.388 (1.416)	122.9 (122.2)	93.3 (94.0)
F_3SC^-	1.649	1.477	127.6	86.6
$O_3SO^{2-\,q}$	1.487 (1.48)	1.487 (1.48)	109.5 (109.5)	109.5 (109.5)
$Cl_2O^{b,c}$	1.671 (1.700)			113.0 (110.9)
$ClF^{c,g}$		1.613 (1.628)		
F_3ClC	1.654	1.444	127.5	86.8
O_3ClO^-	1.450	1.450	109.5	109.5
O_3ClF^{m}	1.402 (1.404)	1.580 (1.619)	102.7 (101.5)	115.3 (116.6)
$F_3TeC^{-\,d}$	1.976	1.867	130.6	82.2
FI^{b}	(1.910)			
F_3IC^{d}	1.941	1.840	130.8	82.0

[a] Optimized 6-31G* geometry from CMU Archive.[42a] [b] Exptl: Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, E. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* **1979**, *8*, 619–671. Effective values were chosen, except when equilibrium values were available. [c] Optimized 6-31G* geometry from FAU Archive.[42b] [d] See text for basis set for species containing Te and I. [e] 6-31+G* optimized geometry, FAU Archive.[42b] [f] Optimized 6-31G* geometry from ref 26. [g] Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1. [h] Exptl: Typke, V.; Dakkouri, M.; Oberhammer, H. *J. Mol. Struct.* **1978**, *44*, 85. [i] Exptl: Reference 22a. [j] Exptl: Cox, A. P.; Duxbury, G.; Hardy, J. A.; Kawashima, Y. *J. Chem. Soc., Faraday Trans. 2* **1980**, *76*, 339–350. [k] Exptl: Chirste, K. O.; Lind, M. D.; Thorup, N.; Russell, D. R.; Fawcett, J.; Bau, R. *Inorg. Chem.* **1988**, *27*, 2450–2454. [l] Exptl: reference 25a. [m] Exptl: Callomon, J. H.; Hirota, E.; Kuchitsu, K.; Lafferty, W. J.; Maki, A. G.; Pote, C. S. Structure Data on Free Polyatomic Molecules. *Landolt-Bornstein, New Series*; Hellwege, K. H., Hellwege, A. M., Eds.; Springer-Verlag: Berlin, 1976; Group II, Vol. 7. [n] Exptl: Fraser, B. C.; Pepinsky, R. *Acta Crystallogr.* **1953**, *6*, 273. [o] Exptl: Goldstein, B. M. *Acta Crystallogr. B* **1982**, *38*, 1116–1120. [p] Exptl: Reference 44a. [q] Exptl: Reference 40.

Table III. Total and Relative Energies of F_3AY Species, HF/6-31G* Level, and Geometry[a]

"normal" isomer[b]		"inverted" isomer[b]		ΔE^c
F_3CS^-	−733.735 73	F_3SC^-	−733.447 31	+181
F_3CTe^-	−6943.062 21	F_3TeC^-	−6942.806 78	+160
	−6943.649 43[d]		−6943.488 60[d]	+101[d]
F_3CCl	−795.663 20	F_3ClC	−795.054 44	+382
F_3CI	−7249.014 78	F_3IC	−7248.561 36	+285
F_3NS	−749.972 27	F_3SN	−750.084 70	−71
	−750.777 52[d]		−750.923 02[d]	−91[d]
	−749.828 92[e]		−749.757 39[e]	+45[e]

[a] For species containing Te and I, see text for basis set. [b] Total energy in atomic units. [c] E(inverted) − E(normal), in kilocalories per mole. [d] MP2 energy (in frozen core approximation) at HF level geometry. For the Te species, only the four lowest energy MOs were frozen. [e] HF/6-31G energy at HF/6-31G optimized geometry of Table V.

1.968, respectively. In H_3CO^-, by contrast, the $p_\pi(O)$ orbitals have much greater occupancy (1.903), and the contraction of the C–O bond with respect to H_3COH is accordingly smaller (0.070 Å).[43]

A similar trend is seen in the 6-31G* and experimental structures[25,44,45] for F_3NO, F_3PO, F_3PS, and F_3SN in Table II, and the A–Y bonds of all of these F_3AY species are strongly contracted in comparison with reference species (see Table IV). Just as in CH_3SO_2Cl, significant ionic bonding and strong p_π lone-pair occupancy depletion is present. However, in contrast to the first-row species F_3CO^- and F_3NO in which A–F bond lengthening is found, the A–F bonds are *shortened* in F_3PO, F_3PS, and F_3SN. Other factors must influence the A–F bond lengths besides negative hyperconjugation. One important factor, brought out in our analysis of the C–F bond shortening in the fluoromethane series,[26] is the stepwise shrinkage of the effective central-atom covalent bond radius induced by electronegative substituents through charge withdrawal. Clearly, the effective covalent radius of sulfur in F_3SN will be significantly smaller than in F_2S. Another important factor promoting A–F bond contraction might be the greater importance of d orbitals for second-row atoms as opposed to first-row atoms, since d functions generally lead to much greater bond-length contractions in the case of hypervalent as opposed to normal-valent second-row compounds.[33] We tested this idea directly by reoptimizing these species with the 6-31G basis set, which is identical with 6-31G* except for the absence of d functions.

The 6-31G results in Table V show that the omission of d orbitals leads to dramatic increases in the A–F bond length

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(43) For H_3CO^-, the only anion that we have considered in which only one electronegative ligand is present, diffuse (+) functions (6-31+G* basis set)[30b] are essential for describing the oxygen lone pairs. Comparison of the 6-31G* and 6-31+G* values in Tables II and IV reveal less lone-pair delocalization, shorter CH bonds, a longer CO bond, and smaller HCO angles when diffuse functions are added. In the other anions, the influence of diffuse functions should be smaller, as the anionic charge can be distributed over all four electronegative ligands.

(44) (a) Kirchhoff, W. H.; Wilson, E. B., Jr. *J. Am. Chem. Soc.* **1962**, *84*, 334–336. (b) Glemser, O.; Mews, R. *Angew. Chem.* **1980**, *92*, 904.

(45) Moritani, T.; Kuchitsu, K.; Morino, Y. *Inorg. Chem.* **1971**, *10*, 344–350.

Table IV. Natural Population Analysis of X_3AY Species, HF/6-31G* Level, and Geometry[a]

X_3AY	q_X	q_A	q_Y	$p_\pi(X)$[b]	$p_\pi(Y)$[b]	$\Delta n(p_\pi)$[c]	3d(A)[d]	$\Delta R(XA)$[e]	$\Delta R(AY)$[e]
H_3CF	+0.17	-0.08	-0.43		1.979	0.042	0.012	-0.002 (H_3CH)	
F_3CF	-0.40	+1.62	-0.40	1.952	1.952	0.384	0.027	-0.015 (F_3CH)	-0.063 (H_3CF)
H_3CO^-	+0.04	-0.09	-1.03		1.891	0.218	0.010	+0.049 (H_3CH)	-0.090 (H_3COH)
H_3CO^-[f]	+0.05	-0.11	-1.04		1.903	0.194	0.013	+0.037 (H_3CH)	-0.070 (H_3COH)
F_3CO^-	-0.51	+1.47	-0.95	1.968	1.805	0.582	0.024	+0.069 (F_3CH)	-0.182 (H_3COH)
F_3CS^-	-0.46	+1.04	-0.66	1.963	1.914	0.394	0.023	+0.033 (F_3CH)	-0.062 (H_3CSH)
F_3CCl	-0.40	+1.23	-0.04	1.951	1.957	0.380	0.028	-0.011 (F_3CH)	-0.038 (H_3CCl)
F_3CTe^-[a]	-0.45	+0.91	-0.56	1.961	1.961	0.312	0.025	*g*	+0.010 (H_3CTeH)
F_3CI[a]	-0.40	+1.04	+0.16	1.950	1.972	0.356	0.031	*g*	-0.014 (H_3CI)
F_3NF^+	-0.09	+1.36	-0.09	1.951	1.951	0.391	0.034	-0.009 (F_3NH^+)	-0.053 (H_3NF^+)
H_3NO	+0.40	-0.46	-0.74		1.959	0.082	0.015	+0.008 (H_3N)	-0.013 (H_2NOH)
F_3NO	-0.24	+1.20	-0.48	1.971	1.738	0.698	0.036	+0.022 (F_3N)	-0.217 (H_2NOH)
F_3NS	-0.20	+0.79	-0.20	1.967	1.906	0.386	0.027	-0.009 (F_3N)	+0.066 (H_2NSH)
F_3PF^+	-0.53	+3.11	-0.53	1.943	1.943	0.456	0.115	-0.011 (F_3PH^+)	-0.053 (H_3PF^+)
H_3PO	-0.12	+1.51	-1.16		1.839	0.322	0.106	-0.010 (H_3P)	-0.178 (H_2POH)
F_3PO	-0.60	+2.93	-1.14	1.959	1.809	0.628	0.120	-0.038 (F_3P)	-0.218 (H_2POH)
H_3PS	-0.05	+0.80	-0.64		1.834	0.332	0.091	-0.012 (H_3P)	-0.173 (H_2PSH)
F_3PS	-0.60	+2.41	-0.61	1.957	1.776	0.706	0.128	-0.029 (F_3P)	-0.253 (H_2PSH)
F_3PN^-	-0.66	2.50	-1.52	1.970	1.589	1.002	0.116	+0.030 (F_3P)	-0.246 (H_2PNH_2)
O_3PS^{3-}	-1.38	+2.54	-1.41	1.897	1.976	0.666	0.100	-0.113 (H_2POH)	+0.133 (H_2PSH)
O_3PO^{3-}	-1.44	+2.75	-1.44	1.919	1.919	0.648	0.102	-0.076 (H_2POH)	-0.076 (H_2POH)
F_3SC^-	-0.61	+1.80	-0.97	1.979	1.066	1.994	0.141	+0.063 (F_2S)	-0.341 ($HSCH_3$)
F_3SN	-0.52	+2.60	-1.03	1.965	1.441	1.328	0.185	-0.042 (F_2S)	-0.322 ($HSNH_2$)
O_3SO^{2-}	-1.23	+2.92	-1.23	1.901	1.901	0.792	0.185	-0.167 (HSOH)	-0.167 (HSOH)
O_3ClO^-	-0.97	+2.87	-0.97	1.882	1.882	0.944	0.261	-0.221 (OCl_2)	-0.221 (OCl_2)
O_3ClF	-0.81	+2.91	-0.46	1.817	1.976	1.146	0.276	-0.269 (OCl_2)	-0.033 (ClF)
F_3ClC	-0.47	+1.63	-0.22	1.982	0.796	2.516	0.174	+0.041 (FCl)	-0.341 ($ClCH_3$)
Fe_3TeC^-[a]	-0.71	+2.18	-1.05	1.980	1.168	1.784	0.096		-0.304 ($HTeCH_3$)
F_3IC[a]	-0.61	+2.41	-0.57	1.979	0.980	2.166	0.140		-0.328 (ICH_3)

[a] For species containing Te and I, see text for basis set. [b] Average occupancy of each p_π NBO. [c] Total loss of occupancy of ligand p_π NBOs, on atoms X and Y (relative to double occupancy). [d] Total occupancy of 3d orbitals on atom A, by NPA. [e] Bond length change in comparison to reference molecule in parentheses, in angstroms (data from Table II). [f] 6-31+G* basis set and geometry. [g] Cannot be compared with 6-31G* F_3CH because no d orbitals were put on the F atoms.

Table V. Comparison of Optimized HF/6-31G Geometrical Parameters of X_3AY Species with Those of the Related Species X_3AH, X_3A, etc.[a]

species	R(XA)	R(AY)	θ(XAY)	$\Delta R(XA)$[b]
F_3CH	1.358 (+0.041)	1.067 (-0.007)	110.6 (+0.2)	
F_3CO^-	1.423 (+0.037)	1.238 (+0.020)	116.9 (+0.3)	+0.065 (F_3CH)
F_3N	1.380 (+0.052)		102.7 (+0.0)[c]	
F_3NO	1.405 (+0.055)	1.203 (+0.031)	116.6 (+0.3)	+0.025 (F_3N)
F_3NS	1.369 (+0.050)	1.946 (+0.170)	114.7 (-0.2)	-0.011 (F_3N)
F_3P	1.663 (+0.099)		95.9 (-1.4)[c]	
F_3PO	1.628 (+0.102)	1.540 (+0.115)	118.4 (+1.2)	-0.035 (F_3P)
F_3PS	1.641 (+0.106)	2.036 (+0.162)	119.4 (+1.3)	-0.022 (F_3P)
F_2S	1.692 (+0.106)		96.6 (-1.3)[c]	
F_3SN	1.690 (+0.146)	1.508 (+0.120)	124.2 (+1.3)	-0.002 (F_2S)

[a] Bond lengths in angstroms; angles in degrees. Values in parentheses denote changes in bond lengths and angles with respect to the 6-31G* basis set. [b] Bond length change in comparison to reference molecule in parentheses, in angstroms, with 6-31G basis set. [c] θ(XAX).

(0.04–0.05 Å for first-row species and 0.10–0.15 Å for second-row species). With the exception of the sulfur species, however, the increase in the A–F bond length is about the same for reference species (F_3A, F_3AH) as for the hypervalent species, and thus the values of ΔR(XA) in Table V are about the same as those in Table IV. Thus, the P–F bond in F_3PO is contracted by 0.035 Å over that in F_3P at 6-31G, whereas the 6-31G* contraction is 0.038 Å. The exception is F_3SN, whose S–F bond in comparison to F_2S is 0.042 Å shorter at 6-31G* but only 0.002 Å shorter at 6-31G. But even in this case, the bond lengthening expected on the basis of negative hyperconjugation does not occur at 6-31G.

A useful criterion for judging the relative importance of negative hyperconjugation and d-orbital participation in these species is the ratio between the total p_π lone-pair occupancy depletion in a molecule (represented by $\Delta n(p_\pi)$) and the total d-orbital population at the central atom. If the magnitude of this ratio is less than 2, one could attribute most of the lone-pair occupancy depletion to π-bonding with the d orbitals on atom A. The data in Table IV show that this is not the case and point to a more important role of negative hyperconjugation than of d orbitals in these "hypervalent" species. The values of $\Delta n(p_\pi)$ in Table IV far exceed the total occupancy of the central-atom d orbitals, by factors of 3–25. The ratio is largest in first-row species with strong hyperconjugation (0.582:0.024 in F_3CO^-), smaller both in first-row species with weaker hyperconjugation (0.042:0.012 in H_3CF) as well as in second-row species with strong hyperconjugation (0.628:0.120 in F_3PO). It is smallest in second-row species with weaker hyperconjugation (0.322:0.106 in H_3PO). The total 3d population on the central atom A in the X_3AY species is only a fraction of that required by dsp^3/d^2sp^3 models. As seen by the values in Table IV, the 3d(A) occupancy increases from 0.02–0.04 for A = C or N to 0.09–0.13 for A = P, to 0.14–0.18 for A = S, to 0.17–0.28 for A = Cl, whereas an occupancy on the order of 1.0 is required by the dsp^3/d^2sp^3 hybridization models.

On the basis of our new NPA/LMO definition of bond order and valence (see the Appendix), the A atoms in all X_3AY species have valencies less than 4. The octet rule is thus obeyed in all cases.

The role of d functions in π_{AY} bonding in X_3AY species is best described as that of polarization functions. These modify the σ^*_{AX} orbital so that overlap with the π_Y donor orbital is enhanced. At the same time, the unfavorable overlap between the A and X atoms

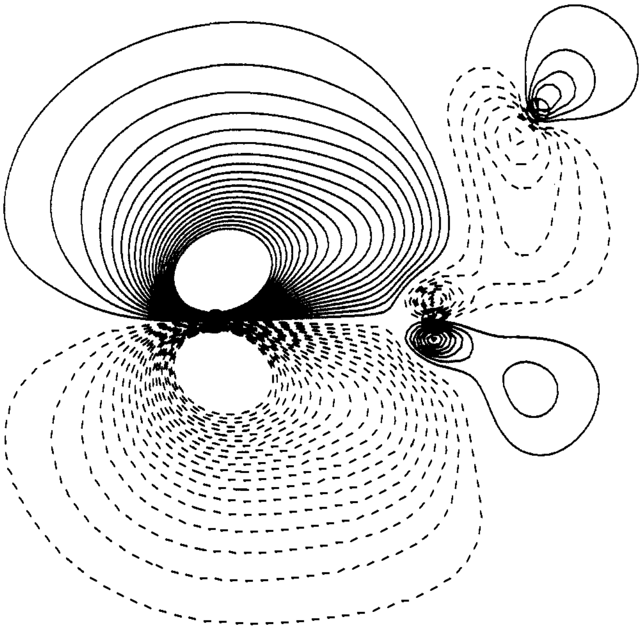

Figure 1. Contour plot of the natural localized molecular orbital (NLMO) for the delocalization of the π_O lone-pair orbital that is coplanar with one of the fluorine atoms of F_3PO, derived from a calculation with 6-31G* basis set at the 6-31G* optimized geometry. The lowest contour corresponds to an orbital value of 0.016. Atomic positions in the O-P-F plane are marked by circled crosses, the oxygen atom being at the left.

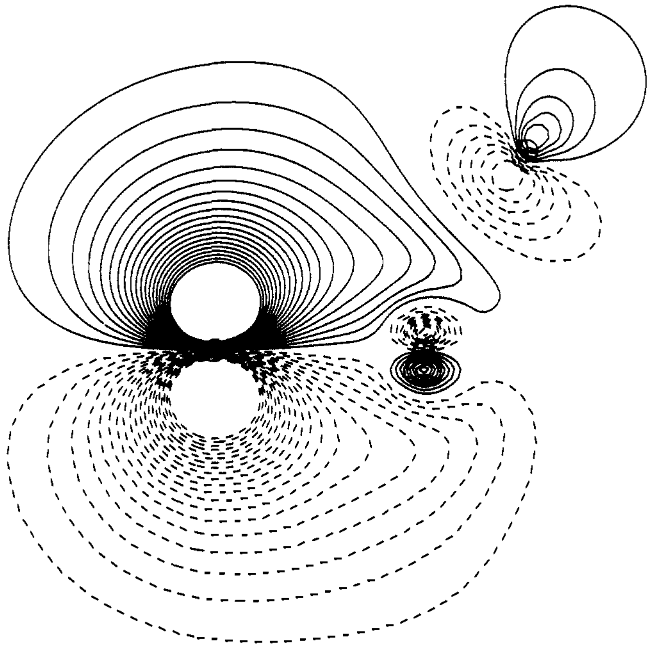

Figure 2. Same orbital and molecular geometry as Figure 1 but derived from a calculation not including d orbitals (6-31G basis set). Note the increased P-F antibonding character compared to Figure 1.

in this antibond is decreased.[46] This is illustrated by the orbital contour plots in Figures 1 and 2, which show the NLMO for one of the $p_\pi(O)$ lone pairs in F_3PO at the 6-31G* geometry, calculated with the 6-31G* and 6-31G basis sets, respectively. Figure 3 shows the contribution to the oxygen lone-pair NLMO from d orbitals on P in the 6-31G* basis set (the P d orbital has nearly perfect π symmetry about the P-O axis and is slightly rotated toward the in-plane fluorine atom). The d orbitals thus play an essential role in polarizing the valence orbitals of the central atom, both to enhance bonding and to diminish antibonding interactions.

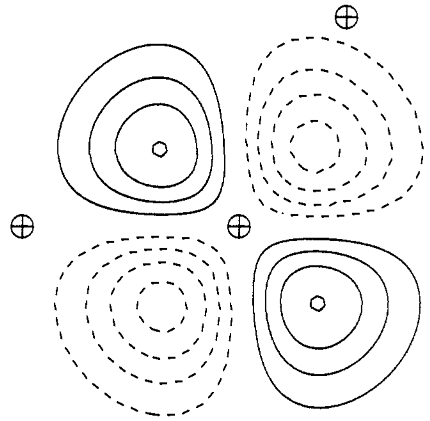

Figure 3. Same as Figure 1, except that only the contribution to the NLMO from the phosphorus d atomic orbitals is plotted. Addition of the contours of this plot to those of Figure 2 would give approximately the same contours as in Figure 1. Note the small polarization of the d orbital toward the fluorine atom (upper right).

An alternative explanation for the bond angles in X_3AY species[45] focuses not on π-bonding (hyperconjugation) but on σ-bonding and Bent's rule:[47] one expects smaller bond angles between electronegative substituents because the central atom tends to direct bonding hybrids of greater p character toward its more electronegative substituents. For instance, the experimental bond angles in NH_3 and NF_3 are 106.7 and 102.4°, respectively. This explanation is insufficient for F_3NO, however: The difference between the electronegativities of F and O is much less than that between F and H, yet the calculated F-N-F angle in F_3NO is much smaller than that in F_3NH^+ (101.8 vs 108.9°). Indeed, by both experiment and theory, the F-N-F angle in F_3NO is about 1 deg smaller than that of F_3N (in F_3N, the absent fourth substituent can be assigned an "electronegativity" of zero). Our previous analyses[26] of F_nAH_m species have shown that, when n $\rightarrow$ σ^* interactions are excluded (by calculational adjustment described in ref 26), Bent's rule is consistently correct (i.e., F-A-F angles considerably less than tetrahedral). However, n $\rightarrow$ σ^* hyperconjugation pushes the F-A-F angles significantly back toward tetrahedral values. Hence, the bond angle of F_3P is 4.4° greater than that of PH_3, *contrary* to Bent's rule. Clearly, however, *both* σ (Bent's rule) and π (n $\rightarrow$ σ^*) interactions favor wide Y-A-X angles in X_3AY species, in contrast to the behavior of the X_3A cases.

Even more extreme Y-A-X angles are observed in the five hypothetical species F_3PN^-, F_3SC^-, F_3ClC, F_3TeC^-, and F_3IC; these range from 123.1 to 130.8°. The corresponding X-A-X angles range from 93.0 to 82.0°. Schmidt and Gordon[29a] had previously optimized H_3ClC, finding an H-Cl-C angle of 127.6° at the 3-21G basis set level, which is similar to the F-Cl-C angle of 127.5° in F_3ClC at 6-31G*. For four of these five species, the "normal" isomers of X_3YA type need to be considered as well. The fifth one, F_3PN^-, is unlikely to have an alternative X_3YA isomer (the nonhypervalent form F_2PNF^- is probably lower in energy, however). As Table III shows, the normal F_3CA isomers with tetracoordinate carbon are favored in all cases over the "inverted" possibilities F_3AC with monocoordinate carbon. The best possibility is F_3TeC^-, which is 160 kcal/mol above F_3CTe^- at the SCF level. With inclusion of electron correlation, this energy difference decreases to 101 kcal/mol. From Table III, we may conclude that the isomers F_3ClC and F_3IC are highly unlikely to exist. The isomer F_3TeC^- is also unlikely, but more sophisticated levels of theory would be needed to determine this with certainty. Since distortion of F_3TeC^- from C_{3v} to C_s symmetry at the SCF level results in an energy lowering, F_3TeC^- is not a minimum at this level. Certain stable species with monocoordinate carbon do occur, such as CN^-, CO (these can have no isomers), and H_3CNC, but these involve π-bonding between two first-row atoms and not

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[46] This general idea was suggested by one of the reviewers.

[47] Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

the intrinsically weaker π-bonding between carbon and higher elements such as S or Te. Thus, π_{CS} and π_{CTe} bonding is probably not strong enough to stabilize monocoordinate carbon with respect to tetracoordinate carbon. Monocoordinate nitrogen is much easier to stabilize, and we find (Table III) that F_3SN is 71 and 91 kcal/mol lower in energy than F_3NS at the SCF and MP2 levels, respectively. The structure F_3SN has been known since 1962; it is a stable molecule.[44] However, omission of d orbitals (6-31G basis set) incorrectly leads to a preference of F_3NS over F_3SN by 45 kcal/mol (Table III).

The smaller (and more depleted) the populations of the p_π lone-pair orbitals on atom Y, the stronger atom Y acts as an electron donor. Examination of trends in the $p_\pi(Y)$ populations among the X_3AY species in Table IV, setting A and X constant and varying Y, leads to the following orderings of electron donor strength of atom Y:

$$\text{for } X = F;\ A = C, N: \quad I < Te^- < Cl < F < S^- < O^-$$

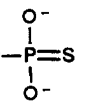
$$\text{for } X = F;\ A = P, S: \quad F < O^- < S^- < N^{2-} < C^{3-}$$

$$\text{for } X = O^-;\ A = P, Cl: \quad F < O^-, S^- < O^-$$

The trends are in line with expectation, except for the reversal between O^- and S^- based on the comparison of F_3PO and F_3PS. Though puzzling, the greater delocalization from lone pairs on sulfur than from lone pairs on oxygen in F_3PY is consistent with the greater F–A–Y angle in F_3PS than F_3PO (118.1 vs 117.2°). In the comparisons of Y = O and S for F_3CY^-, F_3NY, and O_3PY^{3-}, both the greater F–A–Y angle (Table II) and greater depletion of the $p_\pi(Y)$ orbital (Table IV) in the species with Y = O speak for stronger delocalization from oxygen than from sulfur lone pairs. One comparison is possible from Table IV where A and Y are constant: F_3PO vs O_3PO^{3-}. The populations of the $p_\pi(O)$ orbitals in these two species are 1.809 and 1.919, respectively, showing that delocalization from $p_\pi(O)$ into σ^*_{PF} is roughly twice as effective as into σ^*_{PO}.

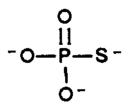
The tetrahedral oxyanions PO_4^{3-}, SO_4^{2-}, and ClO_4^- exhibit nearly constant natural charges at the central atom (in the range of +2.75 to +2.92). The A–O electronegativity difference in AO_4^q becomes progressively smaller as one goes along this series, resulting in progressively smaller charges at the oxygen atoms, which is also in line with the decrease in net molecular charge from −3 to −1.

In O_3PS^{3-} and O_3ClF, Y is a poorer π-electron donor than X and the Y–A–X angles are *reduced* from tetrahedral to 106.4 and 102.7°, respectively. This is consistent with the negative hyperconjugation model, as discussed above, but the O–P–S angle in O_3PS^{3-} is opposite to that expected by Bent's rule. Interestingly, the negative charge on sulfur in O_3PS^{3-} is greater than that on O (−1.41 vs −1.38), in spite of the fact that the σ_{PS} bonds are less polarized than are the σ_{PO} bonds (71% toward S for σ_{PS} vs 79% toward O for σ_{PO} by NBO analysis). The explanation is that the hyperconjugative depletion of the sulfur lone pairs is only about one-fourth that of the oxygen lone pairs in O_3PS^{3-} (totals from Table IV are 0.048e for S but 0.206e from each O atom). The π_{PO} bond order is thus significantly greater than the π_{PS} bond order. This finding would not be expected on the basis of traditional arguments, which favor resonance structure **1a** that places all three of the formal negative charges on the more electronegative oxygen atoms and imply much more π_{PS}- than π_{PO}-bonding. We therefore concur with the conclusion of Frey and Sammons[48] that phosphorothioate anions are better represented by resonance structure **1b** than **1a**:



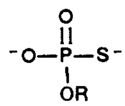
$$^{-}O-\overset{O^-}{\underset{O^-}{P}}=S$$

1a



$$^{-}O-\overset{O}{\underset{O^-}{P}}-S^{-}$$

1b



$$^{-}O-\overset{O}{\underset{OR}{P}}-S^{-}$$

2b

Their conclusions were based on crystal structure, NMR, IR, and pK_a measurements for various O-substituted derivatives, e.g., **2** (such species are of importance in certain biochemical experiments). When looking at representations such as **1a** and **1b**, it is important to realize that P is not forming five full covalent bonds. Our results indicate only 0.10e in the P 3d orbitals (i.e., no dsp^3 hybridization) and four very polar σ bonds, with some π_{PO} and much less π_{PS} bond character arising mainly through $p_\pi \rightarrow \sigma^*$ negative hyperconjugation. Preference of resonance structure **1b** over **1a** should be interpreted to mean that (1) the π_{PS} bond order is small compared to π_{PO} and (2) the sulfur atom is much more negatively charged than would be expected on the basis of structure **1a**.

The question of π_{PS}-bonding in phosphorothioate anions has been examined recently theoretically by Liang and Allen,[49] who also concur with the conclusions of Frey and co-workers.[48] Their work cannot be considered definitive, however, for the P–O and P–S bond orders that they derive are built upon unfounded assumptions such as, "phosphorus is assumed to maintain five bonds in all of its anions, four fixed σ bonds plus one π bond...". Thus, the Mulliken and electrostatic potential charges from which they derive bond orders are "scaled" to fit a preconceived notion of the π-bonding in PO_4^{3-} (i.e., that the total π_{PO} bond order is 1). Basis set extension to 3-21+G* reduces the difference between their P–O and P–S bond orders in O_3PS^{3-} to only 0.06 (1.28 vs 1.22).[50] Deviation of the bond angles from tetrahedral values (only bond lengths are given) and negative hyperconjugation are not considered by Liang and Allen.

VI. Conclusion and Extension to Other Coordination Numbers

We have found bonding in the 32-valence-electron tetracoordinate species such as F_3CO^-, F_3SN, O_3PS^{3-}, and SO_2Cl_2 to be quite analogous. The simple picture shows partially ionic σ bonds and partial π-bonding through strong $n \rightarrow \sigma^*$ negative hyperconjugation (just as in CF_4[26]). The d orbitals on the central atom play only a secondary role in the π-bonding. Claims of dsp^3 or d^2sp^3 hybridization in such species, which have been revived recently by Mayer,[19] are quite misleading. Our conclusion that π-bonding occurs mainly through negative hyperconjugation and only secondarily through overlap with extra-valence-shell d orbitals is in line with recent experimental and theoretical investigations of transition-metal-trivalent phosphorus π-bonding.[16] Indeed, evidence for stereoelectronic effects (negative hyperconjugation) in sulfate diesters and sulfuric acid has been recently published.[51] We emphasize, however, that d orbitals are nevertheless essential for a qualitatively correct description of the bonding, structure, and energy of these species. They serve as additional central-atom acceptor functions, which polarize already existing valence orbitals. Superimposed upon the σ^*_{AX} orbitals of X_3AY species, they enhance the π_{AY}-bonding and diminish the σ^*_{AX}-antibonding character of the $\pi_Y \rightarrow \sigma^*_{AX}$ delocalization.

It is instructive to extend these conclusions to systems with other coordination numbers. The tetracoordinate 32-valence-electron molecules discussed above are a special case (n = 4) of the series of n-coordinate $8n$-valence-electron AL_n^q species, some examples of which are listed in Table VI. Conceptually, such species are built up from "octet ions":[15d] a cationic central atom A with *no* valence electrons (i.e., Li^+, S^{6+}, I^{7+}, etc.) and n (anionic) ligands L that have full octets of valence electrons (i.e., F^-, O^{2-}, H_3C^-,

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[48] Frey, P. A.; Sammons, R. D. *Science* **1985**, *228*, 541–545. See also: Frey, P. A.; Reimschlüssel, W.; Paneth, P. *J. Am. Chem. Soc.* **1986**, *108*, 1720–1722.

[49] Liang, C.; Allen, L. C. *J. Am. Chem. Soc.* **1987**, *109*, 6449–6453.

[50] These values are derived from Table V of ref 49, according to the recipe given in Table VII in that work. At 3-21G*, their P–O and P–S bond orders are 1.33 and 1.06, respectively. Indeed, their 3-21+G* Mulliken charges in HPO_3S^{2-} from Table V lead to a larger P–S than P–O bond order and thus, by the logic of that article, to a larger π_{PS} than π_{PO} bond order. (We have found diffuse (+) functions to exert little effect on the natural populations in these species; see also ref 36b.) We have carried out NBO analysis of the bonding in HPO_3S^{2-} and found that, although the natural charge on S is less negative than on the two nonbonded oxygens, the π_{PS} bond order is much less than the π_{PO} bond order, just as we found in O_3PS^{3-}.

[51] Lowe, G.; Thatcher, G. R. J.; Turner, J. C. G.; Waller, A.; Watkin, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 8512–8520.

Table VI. Examples of *n*-Coordinate, 8*n*-Valence-Electron Species of AL_n[b] Type, as Well as Examples of Corresponding 2-, 4-, and 6-Electron-Reduced Species[a]

n	AL_n[b]
0	H^+, Li^+, Mg^{2+}, Al^{3+}, Ti^{4+}, V^{5+}, Cr^{6+}, Mn^{7+}, Os^{8+}
1	HF, LiF, BeO, BN
1, $+2e^-$	CO
1, $+6e^-$	IO^-, XeF^+
2	HF_2^-, LiF_2^-, BeF_2, CO_2, FCN, FNC, NO_2^+
2, $+2e^-$	SiF_2, NO_2^-, NSF, SO_2, ClO_2^+, TiF_2
2, $+4e^-$	SCl_2, ICl_2^+, FClO, ClO_2^-
2, $+6e^-$	ICl_2, XeF_2
3	BO_3^{3-}, BF_3, CF_3^+, F_2CO, CO_3^{2-}, F_2NO^+, NO_3^-, SO_3, CrO_3, UO_3
3, $+2e^-$	$SnCl_3^-$, NF_3, SeF_3^+, F_2SO, SO_3^{2-}, $FClO_2$, IO_3^-, XeO_3
3, $+4e^-$	ClF_3, XeF_3^+, F_2XeO
4	BeF_4^{2-}, BF_4^-, CF_4, SiO_4^{4-}, F_3NO, PF_4^+, $F_2PO_2^-$, FPO_3^{2-}, PS_4^{3-}, F_3SN, SO_4^{2-}, $FClO_3$, XeO_4, Cl_3VO, CrO_4^{2-}, MnO_4^-, OsO_4, O_3OsN^-, UO_4^{2-}
4. $+2e^-$	SF_4, F_2XeO_2
4, $+4e^-$	BrF_4^-, XeF_4
5	$InCl_5^{2-}$, SiF_5^-, PF_5, F_4SO, IO_4^{3-}, VF_5
5, $+2e^-$	SbF_5^{2-}, TeF_5^-, ClF_5, F_4ClO^-, XeF_5^+, F_4XeO
5, $+4e^-$	$MnCl_5^{2-}$
6	AlF_6^{3-}, SiF_6^{2-}, SnO_6^{8-}, PF_6^-, SbO_6^{7-}, SF_6, F_5SO^-, TeO_6^{6-}, IF_6^+, F_5IO, IO_6^{5-}, F_4XeO_2, XeO_6^{4-}, TiF_6^{2-}, TaF_6^-, CrF_6, ReO_6^{5-}, UF_6
6, $+2e^-$	$SbBr_6^{3-}$, $SeBr_6^{2-}$, IF_6^-, F_5IO, XeF_6, F_5XeO^-, $RuCl_4O_2$, $OsNCl_5^{2-}$
6, $+4e^-$	OsF_6^{2-}
7	TeF_7^-, IF_7, F_6XeO, ZrF_7^{3-}, NbF_7^{2-}, ReF_7
7, $+2e^-$	XeF_7^-, UF_7^{3-}
8	TeF_8^{2-}, TaF_8^{3-}, ReF_8^{2-}
8, $+2e^-$	XeF_8^{2-}
9[a]	TcH_9^{2-}, ReH_9^{2-}

[a] Species taken from ref 21, 52, 53; related species where one or more atoms are replaced by elements in the same column of the periodic table are not listed; e.g., BrF_4^- is given but ICl_4^- is not. [b] For *n* = 9, only *n*-coordinate, *n*-valence-electron species are given.

etc.). CH_3SO_2Cl, for instance, can be constructed conceptually from H_3C^-, S^{6+}, $2O^{2-}$, and Cl^-. Though this decomposition overemphasizes the ionic character of these species, it aids in electron counting. Many of the species listed in Table VI are quite familiar,[21] such as LiF, CO_2, CO_3^{2-}, IO_4^-, PF_5, SF_6, and IF_7. Species with even higher *n* exist:[21] TeF_8^{2-} and ReH_9^{2-} (the latter species has only 9 valence electrons, however, and there are no lone pairs that could delocalize). Many anionic species of the type listed in Table VI can be generated by fluoride ion exchange in the gas phase.[52] In linear dicoordinate species, $p_\pi \rightarrow \sigma^*$ hyperconjugation is not possible due to symmetry. Delocalization interactions are nevertheless important in such species. The FHF^- anion can be described as a very strong $F^-\cdots HF \leftrightarrow FH\cdots F^-$ hydrogen bond with a $\sigma_F \rightarrow \sigma^*_{HF}$ charge-transfer interaction of 0.20e (at 6-31G* level);[15d,f] the natural charges are thus −0.80 (F) and +0.60 (H). The CO_2 molecule can be envisioned as resonating between $O^-{-}C{\equiv}O^+$ and $O^+{\equiv}C{-}O^-$ structures due to strong $\pi_O \rightarrow \pi^*_{CO}$ delocalization amounting to 0.33e per oxygen lone pair; the 6-31G* natural charges are −0.62 (O) and +1.24 (C).[15d]

Many potential cationic 8*n*-electron species are found in reduced form (Table VI) and acquire 1, 2, or 3 pairs of extra electrons, which bond to the central atom as lone pairs. Examples of two-electron-reduced species are CO (from CO^{2+}), NO_2^- (from NO_2^+), F_2SO, SF_4, ClF_5, and XeF_6. Four-electron-reduced species include SF_2, ClF_3, and ICl_4^-, whereas ICl_2 and XeF^+ represent six-electron-reduced species. Conversely, many potential anionic 8*n*-electron species are found in their protonated forms, e.g., the potential species F_5TeN^{2-} is found as F_5TeNH_2. Protonation of a lone pair turns off most of the π_{AY}-bonding interaction of that lone pair, however. Due to the strong stabilization of the ligand lone pairs through σ^* delocalization, many corresponding protonated species are strong acids, such as F_5SeOH and F_5TeOH, and even F_5TeNH_2 shows some acidic character.[53] Similarly, F_3COH is not a typical alcohol but an acid that forms salts with, for instance, Me_3N. Interestingly, the ligands F_5SeO^- and F_5TeO^- appear to be more electronegative than fluorine.[53b] These chemical properties cannot be explained solely by inductive effects.[53]

The geometries of the species of Table VI follow the VSEPR rules[32] and do not need to be discussed here, except to underscore the fact that negative hyperconjugation leads to wider bond angles. Caution is advised however for cases where the central atom A is not significantly more electropositive than the ligands, for then other isomers must be considered (F_3CI will be more favored than F_3IC, F_2PNF^- over F_3PN^-, etc.). An unusual case along these lines is $TeTe_4^{2-}$, which is planar instead of tetrahedral.[54] It occurs in certain solid-state structures. This 32-electron species, where neither ionic σ-bonding nor strong $p_\pi \rightarrow \sigma^*$ (π) bonding can be expected, is beyond the range of our discussion.

In summary, our simple, qualitative insights are suitable replacements for the traditional dsp^3 and d^2sp^3 models of hypervalent species. Table VI provides a scheme for classifying various hypervalent (and many related nonhypervalent) molecules.

Appendix

We propose here an alternative definition of bond order and valence based on NPA. After much effort, no suitable definition based solely on the density and overlap matrices could be devised. A straightforward, easy-to-interpret definition based on covalent electron sharing within the localized molecular orbitals (LMOs) can be given, however. We analyze the LMOs according to the NPA partitioning, by expressing the LMOs in the basis set of the natural atomic orbitals (NAOs),[15b] each LMO having the form

$$\phi_i^{\rm LMO} = \sum_{j=1}^{N} c_{ij} \chi_j^{\rm NAO} \tag{1}$$

N being the total number of basis functions. Since the NAOs form an orthogonal set, the following normalization relation holds:

$$\sum_{j=1}^{N} c_{kj}^2 = 1 \tag{2}$$

For closed-shell SCF wave functions, each LMO is doubly occupied. The number of electrons n_{iA} assigned to atom A within LMO *i* is obtained by summing over the squares of the coefficients from NAOs on atom A:

$$n_{iA} = 2\sum_{j\epsilon A} c_{ij}^2 \tag{3}$$

Now, the number of covalently shared electron *pairs* between atoms A and B is given by the minimum of n_{iA} and n_{iB}, b_{iAB}:

$$b_{iAB} = \min(n_{iA}, n_{iB}) \tag{4}$$

The reasonableness of eq 4 is demonstrated by the following simple examples. If, for instance, the LMO is 50% on A and 50% on B, corresponding to an apolar two-electron bond, then n_{iA} and n_{iB} are each 1.0, and b_{iAB} is also 1.0. If, however, n_{iA} = 2.0 and n_{iB} = 0.0, corresponding to a fully ionic bond, b_{iAB} is 0.0. And if n_{iA} = 1.5 and n_{iB} = 0.5, then b_{iAB} is 0.5, corresponding to a bond that is 50% covalent and 50% ionic. It is necessary to distinguish between bonding and antibonding interactions; this is done by examining the sign of the overlap integral between the hybrid orbitals on atoms A and B within the LMO, S_{iAB}:

$$S_{iAB} = \langle h_{iA}^{\rm LMO} | h_{iB}^{\rm LMO} \rangle \tag{5}$$

$$h_{iA}^{\rm LMO} = \Big[\sum_{j\epsilon A} c_{ij}^2\Big]^{-1/2} \sum_{j\epsilon A} c_{ij} \chi_j^{\rm NONAO} \tag{6}$$

where the "nonorthogonal NAO" (NONAO) functions $\chi_j^{\rm NONAO}$ differ from the $\chi_j^{\rm NAO}$ functions through the omission of the NAO interatomic orthogonalization steps. As discussed in the Appendix of ref 26, this "omission" is carried out by replacing the NAO transformation T_N by the preorthogonal NAO transformation *N*, in the notation of ref 15b. (Use of the NAOs instead of the NONAOs in eq 6 would lead to zero overlap integrals because

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(52) Larson, J. W.; McMahon, T. B. *Inorg. Chem.* **1987**, *26*, 4018–4023.

(53) (a) Klöter, G.; Seppelt, K. *J. Am. Chem. Soc.* **1979**, *101*, 347–349. (b) Lentz, D.; Seppelt, K. *Angew. Chem.* **1978**, *90*, 390–391.

(54) Böttcher, P. *Angew. Chem.* **1988**, *100*, 781–794.

Table VII. NPA/NLMO Bond Order Analysis of X_3AY Species, HF/6-31G* Level, and Geometry[a]

X_3AY	X	A	Y	XA	AY	XY	σ_{AY}[b]	π_{AY}[b]
H_3CO^-	0.81	3.49	0.73	0.88	0.85	−0.04	0.75 (0.73)	0.05 (0.39)
F_3CO^-	0.40	2.39	0.87	0.47	0.97	−0.03	0.66 (0.79)	0.15 (0.44)
H_3NO	0.54	2.54	0.78	0.56	0.84	−0.02	0.82 (0.59)	0.01 (0.34)
F_3NO	0.59	3.50	1.10	0.73	1.31	−0.07	0.98 (0.75)	0.17 (0.45)
F_3NS	0.68	2.79	0.39	0.77	0.48	−0.03	0.37 (0.59)	0.06 (0.31)
H_3PO	0.82	3.36	0.63	0.88	0.73	−0.04	0.53 (0.74)	0.10 (0.40)
F_3PO	0.34	1.95	0.75	0.38	0.81	−0.02	0.49 (0.76)	0.17 (0.40)
H_3PS	0.90	3.97	1.01	0.95	1.13	−0.04	0.95 (0.67)	0.09 (0.38)
F_3PS	0.34	2.49	1.32	0.38	1.37	−0.02	0.96 (0.70)	0.22 (0.37)
F_3SN	0.37	3.21	1.77	0.44	1.91	−0.05	0.85 (0.79)	0.55 (0.45)

[a] Listed are the valence numbers of the X, A, and Y atoms, the total XA, AY, and XY bond orders, and the individual σ_{AY} and π_{AY} bond order components. See the Appendix for definition. [b] In parentheses, the overlap between the hybrids on atoms A and Y participating in the given bond. The total AY bond order is roughly equal to the sum of the σ_{AY} bond order and twice the π_{AY} bond order.

the NAOs are orthogonal to each other.) We therefore modify eq 5 in the following manner:

$$b_{iAB} = \mathrm{sgn}(S_{iAB}) \min(n_{iA}, n_{iB}) \qquad (7)$$

In the above, $\mathrm{sgn}(S_{iAB})$ is the sign of S_{iAB}; b_{iAB} can now be defined as the A–B covalent bond order within LMO *i*. The bond order of eq 7 varies linearly with the number of electrons covalently shared between a pair of atoms and linearly with the polarity of the bond. This definition was previously employed in discussing the π_{SN} bond order in $FSNH_2$.[27] In the LMO basis set, the density matrix is diagonal, so the sum of the b_{iAB} bond orders over the M occupied LMOs yields the total bond order:

$$B_{AB} = \sum_{i=1}^{M} b_{iAB} \qquad (8)$$

The total valency of atom A is then found by summing over all atoms:

$$V_A = \sum_{B \neq A} B_{AB} \qquad (9)$$

While we employ the "natural LMOs" (NLMOs)[15c] that are associated with NPA/NBO analysis, similar results would be obtained from LMOs derived by other methods. We tested the proposed method on ethane, ethylene, and acetylene with the 6-31G* basis set, finding values for B_{CC}, the C–C bond order, of 1.02, 2.03, and 3.01, respectively (the deviations from integer values are due to small contributions from hyperconjugation).

Table VII shows the calculated NPA/NLMO bond orders in various X_3AY species. The atomic valencies are all less than 4, with the maximum value of 3.97 occurring in H_3PS. The AY bond order varies from 0.47 in F_3NS to 1.91 in F_3SN. The XY bond orders are all negative, reflecting the antibonding interaction between atoms X and Y in the π_{AY} LMOs, as seen in Figures 1 and 2. Also given in Table VII are the individual "b_{iAY}" values for the AY bond order from the LMOs representing the σ_{AY} and π_{AY} bonds, as well as the corresponding overlap integrals S_{iAY}. For comparison, the values S_{iCC} for the σ_{CC} and π_{CC} LMOs in ethylene are 0.82 and 0.48, respectively.

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Note Added in Proof. Very recently, the bonding in SO_2 was considered in detail qualitatively by Purser (Purser, G. H. *J. Chem. Educ.* **1989**, *66*, 710–713). The author favored a "structure containing two, covalent S=O bonds", which would require the formation of two pd π-bonding hybrid orbitals on S. NPA/NBO analysis of the 6-31G* wave function of SO_2 disagrees sharply. The charges (O −0.928 and S +1.856) suggest $O^-{-}S^{2+}{-}O^-$ as the main resonance structure. Though significant π(S–O) bonding is present, this is almost exclusively (95%) of O(2pπ)–S(2pπ) type. Each of the two doubly occupied O(2pπ) orbitals in SO_2 delocalizes into the *formally empty* S(3pπ) orbital by 0.38e, but only by 0.02e into the S(3dπ) orbitals. The total S(3dπ) population is thus rather minimal, at 0.04e, which is comparable with the "unique" S(3dπ) population of 0.030e given by Cruickshank and Eisenstein in 1987 (ref 12). The NLMOs corresponding to the two π(S–O) bonds are thus quite polar (80% on O, 20% on S). The σ(S–O) bonds are also quite polar (71% on O, 29% on S). The fact that the bond angle of SO_2 is greater than that of O (119 vs 117°), in contradiction to Bent's rule (as noted by Purser), can be rationalized on the basis of the in-plane negative hyperconjugative O(2pσ) → σ*(S–O) interaction, which acts to increase the O–S–O angle.

Registry No. H_3CH, 74-82-8; H_3CF, 593-53-3; H_32CCl, 74-87-3; H_3Cl, 74-88-4; H_2CO, 50-00-0; H_3CO^-, 3315-60-4; H_3COH, 67-56-1; H_3CSH, 74-93-1; H_3CTeH, 25284-83-7; F_3CH, 75-46-7; F_3CF, 75-73-0; F_3CCl, 75-72-9; F_3CO^-, 57178-38-8; F_3CS^-, 83193-05-9; F_3CTe^-, 123903-49-1; F_3Cl, 2314-97-8; H_3N, 7664-41-7; H_3NH^+, 14798-03-9; H_3NF^+, 53768-39-1; H_2NOH, 7803-49-8; HNO, 14332-28-6; H_3NO, 38544-48-8; F_3N, 7783-54-2; F_3NH^+, 14720-69-5; F_3NF^+, 30494-78-1; F_3NO, 13847-65-9; F_3NS, 15930-75-3; H_3P, 7803-51-2; H_3PH^+, 16749-13-6; H_3PF^+, 64306-13-4; H_2PNH_2, 13598-67-9; H_2POH, 25756-87-0; HPO, 13817-06-6; H_3PO, 13840-40-9; H_2PSH, 13965-74-7; HPS, 109306-51-6; H_3PS, 35280-73-0; F_3P, 7783-55-3; F_3PH^+, 62779-06-0; F_3PF^+, 29075-80-7; F_3PO, 13478-20-1; F_3PS, 2404-52-6; F_3PN^-, 123903-50-4; O_3PO^{3-}, 14265-44-2; O_3PS^{3-}, 15181-41-6; $HSNH_2$, 14097-00-8; SNH, 14501-19-0; SN^+, 27954-72-9; HSOH, 62607-44-7; SO, 13827-32-2; SO_2, 7446-09-5; H_2SO, 25540-60-7; F_2S, 13814-25-0; F_3SN, 15930-75-3; F_3SC^-, 123903-51-5; O_3SO^{2-}, 14808-79-8; Cl_2O, 7791-21-1; ClF, 7790-89-8; F_3ClC, 75-72-9; O_3ClO^-, 14797-73-0; O_3ClF, 7616-94-6; F_3TeC^-, 123933-26-6; FI, 13873-84-2; F_3IC, 2314-97-8.