Nature of the Semipolar XO Bond. Comparative Ab Initio Study of H_3NO, H_2NOH, H_3PO, H_2POH, $H_2P(O)F$, H_2SO, HSOH, HClO, ArO, and Related Molecules

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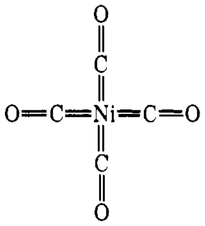
Abstract: Ab initio calculations with various basis sets (of double-ζ quality augmented by polarization functions) were performed on SCF level, and with the inclusion of electron correlation, for the molecules H_3NO, H_3PO, H_2SO, HClO, and ArO, some isomers such as H_2NOH, H_2POH, and HSOH, some fluorine-substituted compounds such as $H_2P(O)F$, and the corresponding oxygen-free molecules. The results are analyzed in terms of binding energies for the XO bonds, contributions of dAOs to the bonds, effective charges, and overlap populations (according to Mulliken and Heinzmann-Ahlrichs). The most relevant geometrical parameters are optimized and computed dipole moments are given. Conclusions are drawn concerning the nature of the XO bond in the various compounds. Although there are large differences, e.g., between H_3NO and H_3PO, all these bonds are essentially semipolar of the type X^+-O^-. dAOs have a significant contribution in H_3PO, $H_2P(O)F$, and H_2SO, but it is not justified to regard them as valence AOs. The isomers H_2NOH, H_2POH, and HSOH are lower in energy than H_3NO, H_3PO, and H_2SO, respectively, although the energy difference of the pair H_2POH/H_3PO is very small. The XO bond is stabilized both by CH_3 and F substitution, though the stabilization mechanisms are quite different. A comparison to bonding in phosphoranes and related compounds is also made. For H_3N, H_3P, H_3NO, and H_3PO the correlation energy is analyzed.

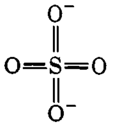
I. Introduction

A two-center, two-electron covalent bond between two partners (atoms or molecules) A and D is called "semipolar" or "dative" if the two binding electrons are contributed by one partner, say A, rather than one electron by either partner as in ordinary covalent bonds. The formation of a semipolar bond is often formulated in two steps: (a) transfer of one electron from the "donor" D to the "acceptor" A, (b) formation of an ordinary bond between A^- and D^+. This two-step picture is borne out in formulations such as

$$H_3P^+{-}C^-H_2;\ R_3N^+{-}O^-;\ {}^-C{\equiv}O^+;\ R_3B^-{-}C^+{=}O$$

For particularly strong semipolar bonds there has recently been some tendency to formulate them as double bonds, e.g., i-iii, as in those days of valence theory when the octet rule was not yet discovered.


i


ii

$R_3P{=}CH_2$

iii

In writing $R_3P{=}O$ rather than $R_3P^+{-}O^-$ one claims that P is in a pentavalent valence state with hybrid AOs that involve dAOs. By reasons of symmetry a P=O "double bond" in $R_3P{=}O$, if it is present, must be basically different from a double bond in, say, H_2CO and it should rather be referred to as a partial triple bond.[1]

There is also a formal analogy between the semipolar bond, say in H_3PO, and the bonding situation in phosphoranes like PH_3F_2 or other electron-rich compounds. In normal-valent compounds one O atom can formally be replaced by two F atoms. If one accepts the same principle for electron-rich compounds, H_3PO and H_3PF_2[2] should be related in the same way as H_2CO and H_2CF_2. Assuming no d participation the axial FPF bond is a three-center, two-electron bond, that in a VB picture can be represented as

$$F^-\ P^+H_3F \leftrightarrow F^+PH_3\ F^-$$

or

$$F^{-1/2}\ldots P^{+1}H_3\ldots F^{-1/2}$$

which is, in fact, in close analogy to the semipolar bond in the formulation H_3P^+-O^- and shows that O^- is formally replaced by $2F^{-1/2}$.

As for the bonding in phosphoranes there are two extreme views to describe the bond in phosphine oxides and related compounds: (a) in terms of semipolar bonds (analogous to the three-center, four-electron bonds) without referring to dAOs of P; (b) in terms of ordinary covalent bonds constructed from appropriate hybrids that involve dAOs.

Since the situation (a) corresponds to zero population of dAOs and (b) to a dAO population equal to unity, the actual dAO population is an important parameter for a characterization of the bonding situation. We have seen[2] that in the phosphoranes the dAO contribution is significant but much smaller than required by the hybridization model. For phosphine oxides and related systems the following questions arise: (1) Which is the best description for the bonds that are conventionally called semipolar? In particular, are these bonds single, double, or what else? (2) How important is dAO participation? (3) How can one explain differences between "weak" bonds as in H_3NO or HClO and "strong" bonds as in H_3PO or H_2SO or even very strong bonds as in F_3PO, etc.? (4) Do all members of the isoelectronic series H_3PO, H_2SO, HClO, and ArO exist?

The recipe of this study is similar to our previous one.[2] We performed ab initio calculations with and without dAOs on the X atom (X = N, P, S, etc.) and compared both the energies and the population analyses from the respective calculations. We also looked carefully at differences between X atoms from the first row (N) and the second row (P).

Both the energy increments due to dAOs and the Mulliken[3] populations are to some extent basis dependent. Hence we used different reference basis sets and tried to get "stable" results. Nevertheless absolute figures should not be taken too literally and trends should be regarded as more important. In addition to the Mulliken-population analysis, we have also used the recent population analysis of Heinzmann and Ahlrichs,[4] the results of which depend much less on the basis size.

We also tried to get reliable values for the binding energies of the molecules that we studied. We have optimized the relevant geometrical parameters and have also calculated some physical properties such as dipole moments.

II. Review of Previous Studies

A few studies concerning the role of dAOs on phosphorus

0002-7863/79/1501-2804$01.00/0

in phosphine oxides or sulfur in sulfoxides have been published. The state of this problem up to 1963 has been reviewed by Hudson.[5] Early model calculations were mainly concerned with the problem that spectroscopic 3d AOs of P or S are too "diffuse" in order to overlap appropriately with orbitals of the partners. So mechanisms were looked for that allow for a "contraction" of the d AOs.[6,7] Semiempirical EHT calculations including d AOs were performed[8,9] before ab initio quantum chemistry attacked the problem of the nature of the XO bond and of d AO participation in amine oxides,[10,11] phosphine oxides,[12-18] sulfoxides,[19,20] and related compounds such as methylenephosphorane,[21] sulfate and phosphate ions,[22,23] and esters.[24] Two CNDO studies[11,20] are included in this list, because they are somewhat related to the ab initio work.

Comparative studies of the bonding situation in different semipolar XO bonds have so far been limited to investigations of the effect of fluorine[16,17] or methyl substitutions[13,18] on the PO bond, to a comparison of the PO bond in H_3PO with the PB bond in H_3PBH_3,[15] to the comparison of the NO bonds in H_3NO, H_2NO, and HNO,[10] or to a comparison of H_3PCH_2 and $H_3PCH_3^+$.[21] Several investigators were interested in H_3PO or F_3PO as model systems for the bonding of PH_3 or PF_3 to transition-metal ions.[12-17]

It is known that, if one wants to get significant results concerning the effect of d AOs, both on the energy and on the populations, one has to start from a reference basis which is sufficiently close to saturation in its s and p parts. Otherwise the d AOs try to compensate defects of the s-p basis and the role of d AOs is overestimated owing to spurious contributions. Unfortunately most of the previous studies do not satisfy the requirement of a near-saturated (sp) basis; e.g., Hillier et al.[12,13,17] use a "minimal" sp basis and get for H_3PO a total SCF energy of −412.690 au. The basis set of van Wazer et al.[14,18] is slightly larger and yields −414.356 au for H_3PO. These total energies for H_3PO differ from that of the Veillard group[15,16] of −417.317 au by ~5 (~3000 kcal/mol) and ~3 au, respectively. The total SCF energies obtained in the present paper differ from those of the Veillard group by 0.1 au and in fact only these two sets of calculations are directly comparable and liable to be free from spurious d effects.

In previous studies the differences and relations between the NO, the PO, and the SO semipolar bonds were not analyzed, nor were the pairs of isomers H_2NOH/H_3NO and H_2POH/H_3PO compared. Geometry optimizations of the molecules studied have not been performed so far; in particular the influence of d AOs on the geometry was not analyzed. Alternatives to the Mulliken population analysis[3] were only considered by Lischka[21] in his study of H_3PCH_2; the Heinzmann-Ahlrichs[4] population analysis has not been used so far. Previously to this paper binding energies of the XO bonds have not been calculated. Only in ref 14 and 19 SCF atomization energies are reported, but they have hardly any relation to measurable quantities. Finally, in the present paper for the first time calculations are reported that go beyond the SCF approximation, i.e., that take account of correlation effects. Such studies have so far been limited to the parent hydrides NH_3,[25] PH_3, H_2S, etc.[26]

III. Method and Basis Sets

Most calculations were done in the SCF approximation, a few selected calculations also with the inclusion of electron correlation in the CEPA-PNO and PNO-CI schemes.[27,28] The PNO-CI is a configuration interaction method including all doubly excited Slater determinants with respect to a leading configuration that can be constructed within a given basis. This is done in terms of pair natural orbitals (PNOs) which allow a considerable reduction of the secular problem. The CEPA-PNO method corrects the incorrect particle number dependence of the CI method. It is no longer strictly variational, but gives usually better results than CI. The computer program described in ref 28 was used.

Chart I

N	O	F	P	S	Cl	Ar
0.60	0.60;[a] 1.25	0.50	0.57 1.0; 0.3	0.55	0.60	0.70

[a] 0.60 was used in semipolar bonded oxygen compounds.

The basis sets are of similar quality as those in our previous study of the phosphoranes.[2] The basis sets without polarization functions were a 3s Huzinaga[29] basis for H in the contraction (2,1) for H_3N, H_2NOH, and H_3NO and a 4s basis in the contraction (3,1), otherwise, a (7s/3p) basis in the contraction (4,1,1,1/2,1) for N, O, and F and a (10s/7p) basis in the contraction (4,6 × 1/3,1,1,1) for P, S, Cl, and Ar. In view of the partial negative charges on O and F the basis sets for these atoms were augmented by flat s and p functions ($\eta = 0.1$).

As polarization functions[30] a p set with $\eta = 0.65$ was used for H ($\eta = 0.50$ for SH bonds) and d sets for N, O, F, P, S, Cl, and Ar with η varying between 0.5 and 0.7; only for O in H_2POH and HSOH $\eta = 1.25$ was used. The d exponents are collected in Chart I.

Basis sets of different size differ in the number of polarization functions.

IV. Total Energies and Calculation of Binding Energies

All total energies calculated with various basis sets are collected in Tables IA (SCF energies) and IB (CEPA energies). We are particularly interested in the binding energy of the XO bond in the different compounds and it might have been desirable to compute potential curves as functions of the XO distances. At first glance this should not be too difficult since on dissociation of the XO bond no electron pair is broken (it always remains with X) and SCF calculations should be sufficient. However, such a computed potential curve dissociates to X (e.g., PH_3) in its ground state and to O in a $1s^22s^22p_x{}^22p_y{}^2$ quasi-closed-shell valence state (z is the XO axis), which is a linear combination of the lowest ^1D_g and the ^1S_g states of oxygen. One could, on performing MC-SCF calculations (which we plan), enforce the dissociation to ^1D_g (the lowest singlet state). The ground state of O is, however, ^3P_g and the ground state of, say, H_3PO is a triplet state (probably repulsive) for large R but a singlet state (attractive) for small R. These two curves cross somewhere unless the crossing is avoided by spin-orbit coupling.

Anyhow, calculation of a potential curve does not really help to compute the binding energy which has to be referred to both H_3P and O in their ground states. Now, among the species H_nX, H_nXO, and O the most difficult one to compute is the oxygen atom with its ^3P ground state, whereas both H_nXO and H_nX are usually (except for ArO) good closed-shell singlet states.

In the reactions

$$R_nX + O \rightarrow R_nXO \tag{1}$$

a significant change of the correlation energy occurs and one ought to know the correlation energy very accurately or be able to extrapolate the computed correlation energies to 100%. In order to avoid these difficulties we rather considered the reaction

$$R_nXO + H_2 \rightarrow R_nX + H_2O \tag{2}$$

in which only closed-shell species occur and where the correlation energy does not change much. From the energy of reaction 2 we can deduce that of reaction 1 by comparing it with the known D_e of the reaction

$$O + H_2 \rightarrow H_2O \tag{3}$$

Table I. Total Energies (Negative, in au)

basis	H_3N	H_2NOH	H_3NO	H_3P	H_2POH	H_3PO	H_2PF	H_2POF	H_2S	H_2SO	HSOH	HCl	HClO
A. SCF													
without pol fctns	56.0906^{e}	130.7675^{e}	130.7307^{d}	342.3332^{d}					398.5533^{d}			459.9482^{d}	
p(O),p(F)^{g}	56.0906	130.7880^{e}	130.7713^{d}	342.3332	417.0866^{d}	417.0090^{d}	441.0653^{d}	515.7687^{d}	398.5533	473.1632^{d}	473.2689^{d}	459.9482	534.5319^{d}
p(H)	56.1278^{e}	130.8058^{e}	130.7636^{d}	342.3785^{a}					398.5902^{a}			459.9710^{a}	
p(O),p(F), p(H)	56.1278	130.8270^{e}	130.8042^{a}	342.3785	417.1357^{d}	417.0763^{a}	441.0981^{d}	515.8084^{d}	398.5902	473.2335^{a}	473.3093^{d}	459.9710	534.5565^{d}
p(O),p(F), d(X)^{h}	56.1091^{e}	130.8175^{e}	130.7882^{d}	342.3776^{d}			441.1394^{d}		398.5874^{d}			459.9679^{d}	
p(O),p(F), d(X),d(O), d(F)	56.1091	130.8378^{e}	130.8073^{d}	342.3776	417.1686^{d}	417.1770^{d}	441.1478^{d}	515.9726^{d}	398.5874	473.2998^{d}	473.3325^{d}	459.9679	534.5860^{d}
p(O),p(H), p(F),d(X)	56.1311^{e}	130.8454^{e}	130.8157^{d}	342.3967^{b} 342.3971^{c}	417.1818^{d}	417.1657^{d}	441.1615^{a}	515.9301^{a}	398.6019^{a}	473.2848^{d}	473.3399^{d}	459.9780^{a}	534.5831^{d}
p(O),p(H), p(F),d(X), d(O),d(F)	56.1311	130.8574^{e}	130.8287^{a}	342.3967 342.3971	417.1946^{a}	417.1976^{a}	441.1615	515.9874^{f}	398.6019	473.3143^{a}	473.3586^{a}	459.9780	534.5967^{a}
p(O),p(H), 2d(X),d(O)				342.4012^{f}	417.2007^{f}	417.2123^{f}							
B. CEPA													
without pol fctns	56.213 35	131.007 71	130.962 41	342.418 76					398.628 38			460.009 44	
p(O),p(F)	56.212 35	131.038 41	131.021 54	342.418 76	417.29065	417.222 52	441.264 18	516.066 39	398.628 38	473.366 71	473.464 21	460.009 44	534.710 24
p(H)				342.494 58									
p(O),p(F), p(H)				342.494 58							473.526 40		
p(O),p(F), d(X)	56.282 48			342.504 41					398.734 10			460.120 97	
p(O),p(F), d(X),d(O), d(F)	56.282 48	131.183 96	131.151 99	342.504 41	417.472 66	417.467 06	441.418 13	516.40731	398.734 10	473.613 62	473.658 83	460.120 97	534.905 10
p(O),p(H), p(F),d(X)				342.555 07	417.453 77	417.436 84					473.623 27		
p(O),p(H), p(F),d(X), d(O),d(F)				342.555 07		417.517 24					473.686 97		
p(O),p(H), 2d(X),d(O)				342.569 99	417.542 62	417.537 78							

[a] Geometry optimized in the respective basis. [b] At the CEPA minimum. [c] At the SCF minimum. [d] Geometry as in the next larger basis. [e] Geometry from Pople et al. See ref 32. [f] Geometry as in the next smaller basis. [g] p(O) and p(F) refer to "flat" functions on O and F. [h] X = N, P, S, Cl.

Table II. XO Binding Energies[a] (kcal/mol)

		H_3NO	H_2NOH	H_3PO	H_2POH	H_2POF	H_2SO	HSOH	HClO
without[b] d on X	SCF[d]	37	47	34	83	51	−7	59	−24
	IEPA[d]	44	51	43	82	59	−3	59	−29
	IEPA[e]	43	51	42	82	59	−3	58	−29
	CEPA[d]	*42*	*52*	*38*	*81*	*54*	*−3*	*58*	*−27*
	CI[d]	36	48	34	78	48	−6	56	−29
with[c] d on X	SCF[d]	45	64	108	103	124	54	74	−5
	IEPA[d]	57	75	116	115	132	62	89	3
	IEPA[e]	54	72	113	113	129	60	86	0
	CEPA[d]	*53*	*73*	*111*	*114*	*127*	*59*	*87*	*−1*
	CI[d]	45	64	105	108	118	51	79	−9

[a] These binding energies refer to the removal of an O atom in its ^3P ground state; they are based on the minima of the potential surfaces rather than the zero-point levels. [b] These basis sets include flat functions on F and O. [c] As *b* but additionally one d set on X and O. [d] Calculated indirectly as explained in section IV. [e] Calculated directly.

Table III. Geometrical Parameters[a]

	H_3N	H_2NOH	H_3NO	H_3P	H_2POH	H_3PO
r(XH)	1.000	1.044	1.038	*1.416*	1.418	1.418
∠(HXH)	107.20	103.29	105.90	*92.51*	*93.49*	*101.6*
∠(HXO)		104.50			*99.09*	
∠(HOX)		101.41			*110.35*	
r(XO)		1.427	*1.383*		*1.669*	*1.469*
r(OH)		0.995			*0.949*	

	H_2PF	H_2POF	H_2S	HSOH	H_2SO	HCl	HClO	ArO
r(XH)	1.418	1.390	*1.337*	*1.337*	1.330	*1.274*	1.260	
∠HXH	93.83	105.30	*93.59*		93.00			
∠HXO		108.30		100.00	106.00		100.00	
∠HOX				*107.85*				
r(XO)		*1.467*		*1.686*	*1.515*		*1.737*	*2.532*
r(XF)	*1.608*	*1.578*						
r(OH)				*0.949*				
∠FXO		117.30						
∠dihedral				*94.25*				

[a] Parameters optimized in this study are given in italics. Distances in ångstroms; angles in degrees.

Table IV. Energy Lowering through d AOs[a] (au)

	H_3N	H_2NOH	H_3NO	H_3P	H_2POH	H_3PO	H_2PF	$H_2P(O)F$	H_2S	HSOH	H_2SO	HClO	ArO
d on N, P, S, etc.	0.0033	0.0184	0.0115	0.0186	0.0393	0.0820	0.0413	0.1217	0.0117	0.0306	0.0513	0.0266	0.0004
d on all atoms		0.0304	0.0245		0.0534	0.1142	0.0634	0.1790		0.0493	0.0808	0.0402	0.0007

[a] Referred to calculations without d AOs but with p AOs on H included.

The binding energies in Table II have mainly been obtained in this way. For these calculations the basis set for the hydrogen atoms in H_2 and H_2O always contained a p set with $\eta = 0.65$.

We have also computed the energy of reaction 1 directly, but only on the IEPA level, because SCF calculations of this difference would be meaningless and CI or CEPA calculations of open-shell states such as the ^3P_g state of oxygen are at present not possible with our computer program. The results are also included in Table II.

We point out that the CEPA values have to be regarded as the most reliable ones.

V. Comparison of H_3NO with H_3N and H_2NOH

For "ordinary" molecules of first-row atoms d AOs have usually only a very small effect on the geometry, such that calculations without d AOs[31] are meaningful. H_3NO is not an "ordinary" molecule in this sense, since the NO bond length from a calculation without d AOs is 1.58 Å[31] but with d AOs only 1.38 Å. (We have not tried to decompose the reduction of the NO bond length from that predicted by a single STO-3G into contributions of the different polarization functions that are included in our basis.)

For $(CH_3)_3NO$ an experimental bond length of 1.41 Å was reported,[32] while a typical value for genuine NO single bonds is 1.36 Å.[33] The geometrical parameters of our calculations are summarized in Table III.

In spite of the strong influence of the d AOs on the NO distance the energy lowering due to d AOs is rather small (see Table IV) and even smaller than in the "ordinary" isomer H_2NOH. The derivative of the energy contribution with respect to the distance need hence not go parallel to the actual value of this contribution.

Polarization functions on hydrogen and flat p functions on oxygen lower the energy more (see Table IA), but have little effect on the NO bond length and on the binding energy of H_3NO or H_2NOH compared to NH_3 plus O.

The Mulliken populations of d AOs which are collected in Table V support the conclusion reached from the energy lowerings, namely, that d AOs have to be regarded as essentially "polarization functions", i.e., that no valence state involving d-type valence AOs is realized. Note that d AOs on O have similar populations as those on N.

In all calculations that we have performed for H_3NO and H_2NOH, hydroxylamine had a lower energy than amine oxide. The difference in SCF calculations varied between 0.02 and 0.04 au for different basis size. The best value for this difference is probably that from a CEPA calculation and a large basis. It amounts to 0.032 au ≈ 20 kcal/mol.

From Table II one sees that the CEPA value (large basis)

Table V. Mulliken Gross Populations of d AOs

	H_3N	H_2NOH	H_3NO	H_3P	H_2POH	H_3PO	H_2PF	$H_2P(O)F$	H_2S	HSOH	H_2SO	HClO	ArO
on N, P, S, etc.	0.01	0.05	0.08	0.08	0.15	0.30	0.13	0.36	0.05	0.11	0.26	0.08	0.00
on O		0.05	0.05		0.01	0.05		0.05		0.01	0.05	0.03	0.00

Table VI. Total Effective Charges from the Mulliken Populations

		H_2N	H_2NOH	H_3NO	H_3P	H_2POH	H_3PO	H_2PF	$H_2P(O)F$	H_2S	HSOH	H_2SO	HClO	ArO
calcd	$q(O)$		−0.37	−0.57		−0.63	−0.83		−0.98		−0.51	−0.58	−0.48	−0.06
without	$q(X)$[a]	−0.08	+0.01	+0.18	+0.52	+0.77	+1.25	+0.78	+1.73	+0.25	+0.47	+0.78	+0.41	+0.06
d	$q(F)$							−0.54	−0.47					
calcd	$q(O)$		−0.48	−0.76		−0.56	−0.97		−1.01		−0.44	−0.92	−0.57	−0.06
with	$q(X)$	−0.16	+0.08	+0.39	+0.34	+0.58	+1.33	+0.76	+1.82	+0.05	+0.28	+1.05	+0.43	+0.06
d	$q(F)$							−0.60	−0.60					

[a] X = N, P, S, Cl, Ar.

Table VII. Overlap Populations According to Mulliken

		H_3N	H_2NOH	H_3NO	H_3P	H_2POH	H_3PO	H_2PF	$H_2P(O)F$	H_2S	HSOH	H_2SO	HClO	ArO
calcd	$p(XO)$		0.54	−0.01		0.20	0.19		0.33		0.17	−0.02	−0.16	0.06
without	$p(XH)$	0.77	0.74	0.73	0.60	0.61	0.63	0.58	0.72	0.59	0.54	0.55	0.62	
d	$p(XF)$							0.02	−0.16					
calcd	$p(XO)$		0.60	0.35		0.35	0.71		0.80		0.31	0.47	0.11	0.07
with	$p(XH)$	0.74	0.74	0.79	0.63	0.64	0.75	0.61	0.82	0.66	0.65	0.63	0.69	
d	$p(XF)$							0.09	0.21					

Table VIII. Effective Charges from MAO Populations According to Heinzmann[a] and Ahlrichs

		H_2NOH	H_3NO	H_2POH	H_3PO	$H_2P(O)F$	H_2SO	HClO	H_3NF_2[b]	H_3PF_2[b]	PH_5[c]
analysis	$q(O)$	−0.23	−0.76	−0.40	−0.94	−0.92	−0.92	−0.61			
without	$q(X)$	+0.04	+0.53	+0.49	+1.31	+1.66	+1.12	+0.55			+1.15
d	$q(F)$					−0.67					−0.45[e]
	$q(H)$	+0.07	+0.10	−0.13	−0.20	−0.19	−0.12	+0.06			−0.19
	uac[d]	0.018	0.024	0.005	0.050	0.054	0.070	0.017			0.046
	$q(O)$				−0.78	−0.77	−0.84				
analysis	$q(X)$				+1.12	+1.40	+1.03		+0.90	+1.26	+0.81
with d	$q(F)$					−0.61			−0.62	−0.49	−0.24[e]
	$q(H)$				−0.16	−0.19	−0.10		+0.13	−0.10	−0.10
	uac[d]				0.036	0.052	0.055		0.020	0.033	0.035

[a] Based on calculations with polarization functions on all atoms. [b] From F. Keil. Thesis, Karlsruhe, 1976. [c] R. Ahlrichs and C. Zirz, private communication. [d] Unassigned charge. [e] Axial H atom.

Table IX. Bond Populations According to Heinzmann and Ahlrichs

		H_2NOH	H_3NO	H_2POH	H_3PO	$H_2P(O)F$	H_2SO	HClO	H_3NF_2[a]	H_3PF_2[a]
analysis	$p(XO)$	1.08	1.11	1.09	1.50	1.63	1.27	0.70		
without	$p(XH)$	1.29	1.28	1.25	1.16	1.18	1.17	1.25		
d	$p(XF)$					0.54				
analysis	$p(XO)$				1.78	1.94	1.41			
with	$p(XH)$				1.20	1.18	1.19		1.36	1.34
d_π	$p(XF)$					0.66			0.35	0.35

[a] See Table VIII, footnote *b*.

for the binding energy of H_2NOH with respect to H_3N and $O(^3P)$ is $D_e = 73$ kcal/mol. Taking care of the change in zero-point energy, D_0 would be obtained and be a few kilocalories per mole smaller. The experimental value of D_0 is 60 kcal/mol (as calculated from data in ref 34 and 35). For H_3NO with respect to H_3N and $O(^3P)$ we get $D_e = 53$ kcal/mol.

From the Mulliken (M) overlap populations (MOP) in Table VII one concludes that—with d AOs included—the NO bond in H_3NO is somewhat weaker than in H_2NOH whereas according to the Heinzmann-Ahlrichs (HA) analysis the NO bond populations in the two molecules are nearly the same. Since the MOP become problematic for highly polar bonds the HA bond populations deserve more credit.[36] (For more details concerning the HA analysis see section XIII.)

These data support the idea that the NO bond in H_3NO is essentially "single", but also that without d AOs the bond is much weaker than a single bond.

One sees from Tables VI and VIII that the difference in the effective charges on N and O in H_3NO (from calculations with d AOs) is 1.15 in the M and 1.29 in the AH analysis; the respective values for H_2NOH are 0.56 and 0.27. If we regard the latter values as representative of the charge transfer due to the difference in electronegativity we can conclude that an extra charge difference of 0.59 or 1.02 occurs in H_3NO. Again, this is in agreement with the picture of a semipolar bond, though a literal semipolar bond would require a charge difference of 2.

If one likes an illustration in terms of resonance structures one has to think of a resonance between a semipolar bond and no bond at all:

$$H_3N^+{-}\overline{\underline{O}}|^- \leftrightarrow H_3N|\quad \overline{\underline{O}}|$$

Polarization functions stabilize the semipolar structure, probably in allowing for induction (i.e., polarization of the electrons by the electric charges), and raise its "weight". There is no indication for back-bonding. One can also regard H_3NO as a charge transfer complex between H_3N and O in its quasi-closed-shell valence state (see section IV).

The computed dipole moments of the three molecules are given in Table X. Since these were obtained from SCF calculations the agreement with experiment is not fully satisfactory. Nevertheless we expect that the predicted rather large dipole moment of 5.9 D for H_3NO is not in error by more than 0.5 D. Millie and Berthier[10] calculated a dipole moment of 5.67 D, which—in their calculation—is practically identical with the bond moment of the NO bond. They estimated that, due to the bond moments of the NC bonds, $(CH_3)_3NO$ should have a dipole moment smaller by about 0.3 D, while the experimental dipole moment of $(CH_3)_3NO$ is ~5 D.[37]

VI. Study of PH_3, H_3PO, and H_2POH

The equilibrium geometry of PH_3 was optimized with the large basis on both SCF and CEPA level. The CEPA result (see Table III) agrees well with experiment.[38] For hydroxyphosphine H_2POH and phosphine oxide H_3PO the experimental PH distance of PH_3[38] was assumed, while the other geometrical parameters were optimized in the large basis on SCF level, considering C_{3v} symmetry for H_3PO. In order to get an idea of the influence of d AOs on the PO bond in H_3PO, it was optimized additionally without d AOs. The geometrical parameters are collected in Table III. (Calculations for H_3PO without or with d AOs are compared at the respective optimum PO distances.)

From Table IV we see that the energy lowering due to d functions is larger by about a factor of 5–8 in H_3PO as compared to H_3NO, whereas the respective numbers of H_2POH and H_2NOH differ only by a factor of 2. The energy lowering due to the d AOs on P in H_3PO amounts to 52 kcal/mol and is hence quite significant.

Inclusion of the d AOs reduces the PO bond length in H_3PO by 8% (see Table III). This reduction is, in spite of the larger d contribution in H_3PO, smaller than the corresponding one in H_3NO (13%). The PO bond length in H_2POH (1.67 Å) is close to that of the bridge bonds in P_4O_{10} (1.63 Å)[33] and can be regarded as representative for a P-O single bond, whereas that in H_3PO (1.47 Å) is much shorter. (Note that the NO bond length in H_3NO is not very different from that in H_2NOH). The PO bond length optimized without d AOs (1.60 Å) is close to that of a single bond, which indicates that without d AOs the PO bond would be just single. The bond length optimized with d AOs (1.47 Å) is in good agreement with the experimental value of r_0 for $(CH_3)_3PO$ (1.48 Å) and not very different from the bond length in the PO molecule (1.45 Å)[38] in which one can assume a bond order between 2 and 2.5.

It is not so easy to decide whether H_3PO or H_2POH is lower in energy. The most refined calculations (with two d sets on P, one d set on O, and one p set on H, on CEPA level, i.e., with electron correlation) yield D_e = 114 kcal/mol for H_3PO and D_e = 117 kcal/mol for H_2POH, both values with respect to $H_3P + O(^3P)$. We expect a larger zero-point energy for H_3PO such that H_2POH should be slightly more stable than H_3PO. Neither of the two isomers has so far been isolated.

If one omits d AOs on P (or N) the binding energy of the PO bond is only 38 kcal/mol in H_3PO and 81 kcal/mol in H_2POH and rather close to that of the NO bond (42 and 52 kcal/mol, respectively). The difference between the N and P compounds is hence essentially due to the different role of d AOs.

Table X. Dipole Moments (D)

basis	H_3N	H_2NOH	H_3NO	H_3P	H_2POH	H_3PO	H_2PF	$H_2P(O)F$	H_2S	HSOH	H_2SO	HCl	HClO
without pol functions	2.088	0.780	5.240	1.130					1.803			1.805	
p(O)	2.088	1.148	6.141	1.130	1.677	5.042	2.612	5.014	1.803	2.585	5.435	1.805	4.299
p(H)	1.680	0.746	5.069	0.837					1.421			1.602	
p(O),p(H)	1.680	1.098	5.819	0.837	1.566	5.439	2.589	4.979	1.421		5.227	1.602	4.263
d(X),p(O)	1.590	1.160	5.841	0.669					1.296			1.376	
d(X),p(O),d(O)	1.590	0.959	5.927	0.669	1.292	4.433	1.709	4.152	1.296	2.104	4.584	1.376	4.155
d(X),p(O),p(H)	1.528	1.087	6/	6	0.618^e 0.690^f	1.381	4.845	2.222	4.476	1.177		4.883	1.324
4.249													
d(X),p(O),d(O),p(H)	1.528	0.947	5.907	0.618 0.690	1.190	4.451	1.727	4.141	1.177	1.925	4.516	1.324	4.151
2d(X),p(O),d(O),p(H)				0.525	1.104	4.302							
exptl[a]	1.47	0.59^b	5.0^c	0.55		4.34^d			0.97		3.96^g		

[a] If not indicated otherwise, from "Selected Values of Electric Moments for Molecules in the Gas Phase", U.S. Department of Commerce, National Bureau of Standards, 1967. [b] S. Tsunekawa, *J. Phys. Soc. Jpn.*, **33**, 167 (1972). [c] Value for $(CH_3)_3NO$ from ref 37. [d] Value for $(CH_3)_3PO$ from ref 46. [e] At the CEPA minimum. [f] At the SCF minimum. [g] Value for $(CH_3)_2SO$ from ref 49.

We have not performed calculations on $(CH_3)_3PO$. However, we expect a significant stabilization of the PO bond in this molecule compared to the one in H_3PO. We know, both from a theoretical study by Koch and Ahlrichs[41] and from experimental gas-phase electron affinities,[42,43] that trimethyl substitution stabilizes PH_4^+ relative to PH_3 by 33[41] or even 40 kcal/mol.[42,43] This is partially due to a stabilization of the positive charge on P through methyl substitution, partially to a destabilization of $P(CH_3)_3$ as compared to PH_3 via steric hindrance of the methyl groups and opening of the CPC angle[41] (see also section XIII).

Since the phosphorus atom carries a partial positive charge in $(CH_3)_3PO$ and since the steric hindrance argument for $(CH_3)_3P$ applies as well, a stabilization of $(CH_3)_3PO$ vs. $(CH_3)_3P$ by ~20 kcal/mol as compared to H_3PO vs. H_3P is expected. We hence predict a binding energy for the PO bond in $(CH_3)_3PO$ of roughly 135 kcal/mol. An experimental value of ~140 kcal/mol has been reported.[40]

In H_3PO the Mulliken population (see Table V) of the d AOs on P is 0.30 and hence comparable to that in PH_3F_2 (0.20). However, the d population in H_2POH is only smaller by a factor of 2 and the energy lowering due to the presence of d AOs is roughly proportional to the d AO populations (see Tables IV and V).

The results of the Mulliken (M) and Heinzmann-Ahlrichs (HA) population analyses are again found in Tables VI and IX. The effective charges of both schemes are consistent with the picture that about one electron is transferred from P to O. The polarity of the PO bond is significantly larger in H_3PO than in H_2POH, where it is only determined by the difference of electronegativity. As in H_3NO the charge transfer is not attenuated by the presence of d AOs. This is at first glance in disagreement with the idea that d AOs are mainly involved in back-bonding which is accompanied by a charge transfer in the direction opposite to that in the σ bond.

The effect of the d AOs on the σ and π bonds in H_3PO has been analyzed by Demuynck and Veillard.[15] They found a population of 0.14 for $d\sigma$ and 0.22 for $d\pi$. A total charge transfer of 0.7 electron from P to O was composed of a σ transfer of 1.2 electrons and an opposite π transfer of 0.5 electron. (Their total d population of 0.36 differs from ours (0.30, see Table V) because the basis sets are not identical; with different basis sets our values varied between 0.29 and 0.35).

The presence of significant back-bonding—unlike in H_3NO—is evident from the overlap population. In the M analysis (Table VII) H_2POH and H_3PO have practically the same overlap population for the PO bond (0.2) if no d AOs are included, whereas that of H_3PO is twice as large as that of H_2POH if d AOs are present.

In the HA analysis the factor between the bond populations of the two molecules is only ~1.5, but significant as well.

Bond length, bond energy, and bond population indicate that the PO bond in H_3PO is significantly stronger than a single PO bond, though it is hard to formulate this result quantitatively. On the other hand, this bond has all the properties that one requires for a semipolar bond.

The picture that the two "limiting" structures $H_3P{=}O$ and $H_3P^+{-}O^-$ are exclusive, i.e., that the bond is either semipolar or multiple must hence be given up. The presence of back-bonding does not seem to attenuate the charge transfer characteristic of a semipolar bond.

With the large basis we find a force constant for PO stretch of 11.23 mdyn/Å in H_3PO and of 4.83 mdyn/Å in H_2POH. An experimental force constant of 8.25 mdyn/Å has been reported for $(CH_3)_3PO$. It is well-known[44,45] that Hartree-Fock calculations overestimate force constants of multiple bonds.

The computed dipole moments are given in Table X. Our values of 4.1 D for H_3PO (it is rather basis dependent; without d AOs on O we get 4.5 D) can be compared with the 4.7 D of ref 15. The experimental dipole moment of $(CH_3)_3PO$ is 4.34 D.[46]

VII. Substitution by Fluorine. H_2PF and $H_2P(O)F$

For H_2PF we took the PH distances and angles from the experimental geometries of H_3P and F_3P. The PF distance was optimized in the large basis. For $H_2P(O)F$ we started from the experimental geometry of $H_2PO_2^-$ and optimized the PO and PF distances. The geometrical parameters are collected in Table III.

The energy lowering due to d AOs (Table IV), the d populations (Table V), and the overlap populations (Tables VI-IX) in H_2PF are very similar to those in H_2POH. The energy lowering due to d AOs in $H_2P(O)F$ is approximately the sum of the respective values for H_3PO and H_2PF. Even the d population in $H_2P(O)F$ is to a rough approximation additive from the values in H_3PO and H_2PF. The binding energy of the PO bond in $H_2P(O)F$ is larger than that in H_3PO (see Table I). The overlap population or bond order (Tables VII and VIII) is significantly (25%) larger in $H_2P(O)F$ than in H_3PO, which confirms that fluorine substitution stabilizes the PO bond.

Somewhat surprising are the MOP for the PF bond. In H_2PF it is nearly zero; in $H_2P(O)F$ it is negative if no d AOs are included and slightly positive with d AOs. The reason for this is obviously that the PF bonds are highly ionic and have only a small covalent contribution. The HA bond orders (Table VI) are somewhat smaller than for ordinary single bonds but are otherwise not exceptional.

The PO bond length and the PO force constant (11.55 mdyn/Å) in $H_2P(O)F$ are comparable to those in H_3PO. The PF bond length is slightly reduced in $H_2P(O)F$ with respect to H_2PF; hence there is a mutual strengthening of PO and PF bonds.

In the doubly fluorine substituted compound $HP(O)F_2$ a still shorter PF distance (1.54 Å) was observed.[47] Since the PF distance (experimental[48]) in HPF_2 is 0.02 Å smaller than the (computed) PF distance in H_2PF it is not unexpected that the PF distance in $HP(O)F_2$ is 0.04 Å smaller than in $H_2P(O)F$. Dipole moments of H_2PF and $H_2P(O)F$ are given in Table X.

The trend of the effect of fluorine substitution is comparable to that found for triple substitution by Serafini et al.[16] They observed an increase of the d population from 0.26 (H_3PO) to 0.50 (F_3PO), a decrease of the σ charge transfer (from 1.2 to 0.9 electrons), and an increase of the π back-transfer (from 0.5 to 0.7 electron).

VIII. Study of H_2S, H_2SO, HSOH, HCl, and HClO

The experimental geometry of H_2S was used for the H_2S unit in H_2SO; the SO distance was energy optimized both with and without d AOs. For H_2S the geometry was fully optimized with and without d AOs, for HSOH only with d AOs. The HCl distance in HClO was taken as the experimental distance in HCl, an HClO angle of 100° was assumed, and the ClO distance was optimized with d AOs. Without d AOs the potential energy curve turned out to be repulsive everywhere. The HCl distance in HCl was optimized with and without d AOs. The geometrical parameters are collected in Table III. (We have not studied the isomeric hypochlorous acid ClOH.)

One sees from Tables IV and V that the energy lowering due to d AOs as well as the d population is somewhat smaller in H_2SO than in H_3PO but of the same order of magnitude, while HSOH behaves much like H_2POH.

The binding energy of the SO bond in H_2SO (Table II) is comparable to that of the PO bond in H_3PO. The analogy between H_3PO and H_2SO is also found for the effective charges (Tables VI and VIII) and the overlap populations from the calculations in which d AOs are included. If we rely more on the HA analysis we have to conclude that the charge transfer in H_2SO is nearly the same as in H_3PO and that the bond order is only slightly smaller. Hence like in H_3PO the bond is at the same time semipolar and partially multiple.

The SO bond in HSOH is an ordinary (though polar) single bond as is the PO bond in H_2POH. In all calculations HSOH is lower in energy (by ~20 kcal/mol with d AOs and ~70 kcal/mol without d AOs) than H_2SO. Like for H_3PO, methyl substitution should stabilize H_2SO significantly. In fact $(CH_3)_2SO$ is a stable compound while H_2SO and HSOH are unknown.

In going from H_2SO to HClO the bonding situation changes. Energy lowering, d population, charge transfer, and XO bond orders are much closer to those in H_3NO than to those in H_2SO or H_3PO.

The binding energy of the ClO bond is extremely small. While the XO bonds in H_3PO and H_2SO are shorter than single XO bonds the ClO bond in HClO (1.74 Å) is longer than a ClO single bond (1.71 Å).[38]

A pictorial description of bonding in HClO would therefore, as in H_3NO, rather be a superposition of a "structure" with a semipolar bond and one with no bond. One sees from Table VII that in the calculations without d AOs on S (or Cl) negative MOP for H_2SO and HClO are found, and also that the MOP for the SO bond (as for the NO bond in H_3NO) is practically zero. Negative overlap populations for semipolar (dative) bonds have been observed previously by other authors,[50-53] probably first by Valdemoro[50] in a study of the N→O bond as a two-electron, two-center problem. Inclusion of d AOs changes the MOP to positive ones (Table VII). We have already mentioned that (without d AOs) we get a negative MOP even for the PF bond in $H_2P(O)F$.

IX. Concerning the Possible Existence of ArO

While for HClO a distinct local minimum of the energy was found in SCF calculations, which indicates that HClO is at least stable with respect to dissociation into HCl + oxygen in its quasi-closed-shell $1s^22s^22p_x{}^22p_y{}^2$ valence state, only a very shallow minimum was found for ArO. In order to be sure that this minimum was not artifact due to basis superposition errors, we performed "counterpoise" calculations in which for each subsystem the full supersystem basis was used and the sum of these energies was subtracted from the supersystem values. A flat local minimum of the energy at ~2.53 Å with a depth of 0.44 kcal/mol still remained.

We then performed an SCF calculation for the lowest triplet state of ArO for which a fully repulsive curve was obtained. At the singlet minimum of 2.53 Å the triplet state was lower than the singlet state by 69 kcal/mol. With the same basis the SCF energy of the ^3P state of O is 30 kcal below the ^1D state and 75 kcal/mol below the quasi-closed-shell valence state.

We conclude with some certainty that ArO, if it exists, is not stable with respect to dissociation into Ar and O in their ground states, not even with respect to dissociation into the lowest singlet states of both Ar and O. We cannot exclude that the lowest singlet potential curve has a local minimum near 2.53 Å and a barrier at some larger distance before the potential curve goes down to approach the limit Ar (^1S) + O(^1D). More refined calculations, best of MCSCF type, are necessary to settle this question. We note that the sum of the van der Waals radii of Ar and O is 4.74 Å; a local energy minimum near 2.53 Å, if it turns out to be correct, would correspond to a chemical bond (though in a metastable state) rather than to a van der Waals interaction.

In the context of the present study we are interested in the importance of d AOs. One can see from Tables IV and V that the energy lowering due to d AOs is extremely small and the d population is practically negligible (though without d AOs there would be no local energy minimum in our potential curve). The charge transfer (0.06 electron) is small, but nonnegligible; the same is true for the overlap population (0.07).

X. Orbital Energies and Ionization Potentials

Since in this study we performed systematic calculations on a series of related molecules with basis sets of equal and rather good quality we regard it as worthwhile to publish the orbital energies (Table XI). In view of Koopmans' theorem[54] they can be correlated with experimental ionization potentials and they may be useful for other purposes. Table XI is self-explanatory and we do not want to discuss the interrelation of the orbital energies in the various molecules. We do, however, want to make one comment on the inner-shell ionization potentials (especially those of the 2p electrons of P) in H_3P and H_3PO. Perry et al.[55] have recently claimed that the observed shifts of these ionization potentials allow the conclusion that d AOs on P do not play a significant role. We have therefore studied to which extent the 2p orbital energies are affected by d AOs. One sees from Table XI that the 2p orbital energies in H_3P are not changed significantly by the inclusion of d AOs in the basis. In H_3PO d AOs on P decrease the 2p orbital energies by about 1 eV, although with d AOs the P atom has a slightly larger positive charge. The shift from H_3P to H_3PO is 3.7 eV without d AOs and 2.8 with d AOs. For the shift from $(CH_3)_3P$ to $(CH_3)_3PO$ Perry et al.[55] observed 1.9 eV. Although the pairs H_3P/H_3PO and $(CH_3)_3/(CH_3)_3PO$ are not directly comparable (see section VI), we conclude that d AOs are necessary to account correctly for the chemical shift, but also that it is very dangerous to base conclusions concerning the d participation in bonds on observed shifts in the inner-shell ionization potentials.

XI. Localized Orbitals and Discussion of Pair Correlation Energies

For all the molecules studied the canonical Hartree–Fock orbitals were transformed to localized orbitals according to the criterion of Boys.[56] As expected localized MOs for the same bonds in different molecules are very similar. As is well-known (see, e.g., ref 44) straightforward application of the Boys criterion to multiple bonds leads to banana-type bent bonds unless one imposes some σ–π separation. Lischka[21] in his study of H_3PCH_2 had a natural choice of symmetry plane in terms of which σ and π MOs of the PC bond could be defined. He found that the highest occupied MO (HOMO) was of π type and mainly localized in the PC bond. He then applied the Boys criterion only to the remaining MOs.

In H_3PO there is no such natural plane of symmetry and no reason to leave the HOMO out of the localization procedure. We therefore got three equivalent banana bonds between P and O (rather than two as in the case of H_3PCH_2 if one includes the HOMO) somewhat like in acetylene, but with the difference that all three bananas are localized mainly on the oxygen atom such that they could as well be classified as lone-pair AOs of an O^{2-} subunit. There is an additional genuine lone pair of O opposite to the PO bond. This result is consistent with the picture that there is a partial triple PO bond, although it should not be taken too literally. In H_3NO, where back-bonding is unimportant, only a partial single bond should be present, and in fact Boys localization yields a localized MO of the NO bond, localized mainly on N and three lone pairs of O opposite to the NO bond. The localized orbitals are illustrated schematically in Figure 1.

The total valence shell correlation energy can be represented as a sum of orbital pair contributions (that sum up to the IEPA correlation energy) plus pair coupling terms. We have collected the IEPA pair contributions for NH_3, H_3NO, PH_3, and H_3PO in Table XII. Unfortunately our results are not directly comparable to those given by Lischka for H_3PCH_2 because he imposed a σ–π separation and because he included p AOs on the H atoms in his correlation calculations.

One sees, especially from the smallness of the interorbital contributions, that the localized MOs are rather well localized on H_3N (H_3P) or O. Only interpair contributions between two MOs of the same subunit contribute significantly to the correlation energy.

XII. Comparison of H_3NO and H_3PO with H_3NF_2 and H_3PF_2

Comparison of the populations collected in Table V with those of Table V of ref 4 shows striking similarities of the va-

Table XI. MO Energies (eV) of H_3P and H_3PO with and without d AOs[a]

H_3P (C_{3v})	with d[b]	without d[c]	H_3PO (C_{3v})	with d[b]	without d[c]
1a$_1$ (1sP)	−2175.28	−2175.19	1a$_1$(1sP)	−2198.54	−2178.18
2a$_1$(2sP)	−203.75	−203.61	2a$_1$(1sO)	−559.91	−559.47
1e (2pP)	−146.24	−146.10	3a$_1$(2sP)	−207.40	−206.31
	−146.24	−146.10	4a$_1$(2pP)	−149.97	−148.89
3a$_1$(2pP)	−146.19	−146.07	1e (2pP)	−149.92	−148.88
4a$_1$	−23.57	−23.29		−149.92	−148.88
2e	−14.26	−14.18	5a$_1$	−35.12	−35.96
	−14.26	−14.18	6a$_1$	−24.71	−23.58
5a$_1$	−10.23	−10.36	2e	−16.49	−16.38
				−16.48	−16.38
			7a$_1$	−14.46	−15.39
			3e	−11.85	−12.49
				−11.85	−12.49

C_{3v}	H_3N	C_s	H_2NOH	C_{3v}	H_3NO
		1a′	−561.47	1a$_1$	−558.62
1a$_1$	−422.76	2a′	−425.33	2a$_1$	−428.30
2a$_1$	−30.85	3a′	−38.14	3a$_1$	−37.39
		4a′	−29.09	4a$_1$	−29.79
1e	−16.67	1a″	−18.19	1e	−20.21
	−16.67	5a′	−18.09		−20.21
		6a′	−16.74	5a$_1$	−15.91
		2a″	−12.75	2e	−10.53
3a$_1$	−11.14	7a′	−11.25		−10.53

C_s	H_2PF	C_s	$H_2P(O)F$	$C_{\infty v}$	HCl	C_s	HClO
1a′	−2177.09	1a′	−2179.74	1σ		1a′	
2a′	−717.76	2a′	−719.26			2a′	−560.90
		3a′	−559.82	2σ	−287.24	3a′	−290.47
3a′	−205.31	4a′	−207.70	3σ	−218.08	4a′	−221.29
4a′	−147.81	5a′	−150.31	1π	−217.99	5a′	−221.24
1a″	−147.78	6a′	−150.27		−217.99	1a″	−221.20
5a′	−147.75	1a″	−150.26			6a′	−35.79
6a′	−44.15	7a′	−45.97	4σ	−30.05	7a′	−30.21
		8a′	−36.37	5σ	−16.60	8a′	−19.12
7a′	−23.78	9a′	−24.47	2π	−12.53	2a″	−15.85
8a′	−18.90	10a′	−20.63		−12.53	9a′	−15.36
2a″	−18.60	2a″	−20.39			10a′	−12.48
9a′	−18.03	11a′	−19.51			3a″	−11.72
		3a″	−16.86				
3a″	−14.24	12a′	−15.53				
10a′	−10.43	13a′	−13.16				
		4a″	−12.45				

C_{2v}	H_2S	C_s	H_2SO	C_1	HSOH
1a$_1$	−2502.12	1a′	−2505.99	1	−2503.49
		2a′	−559.49	2	−561.78
2a$_1$	−243.70	3a′	−247.29	3	−244.95
1b$_2$	−180.38	4a′	−183.98	4	−181.63
3a$_1$	−180.36	1a″	−183.97	5	−181.58
1b$_1$	−180.30	5a′	−183.92	6	−181.53
		6a′	−36.69	7	−37.83
4a$_1$	−26.50	7a′	−26.84	8	−25.94
		2a″	−18.46	9	−19.02
		8a′	−16.85	10	−16.71
2b$_2$	−15.85	9a′	−15.01	11	−15.23
5a$_1$	−13.29	3a″	−11.96	12	−12.59
2b$_1$	−10.20	10a′	−10.81	13	−10.79

[a] At the respective equilibrium geometries. [b] p(O), p(H), d(P), d(O) (see Table IA). [c] p(O), p(H).

lence AO populations of phosphorus in H_3PO and H_3PF_2 (in both molecules referring to the largest basis):

$$H_3PO\text{: } s^{1.14}\, p^{2.23}\, d^{0.30}$$
$$H_3PF_2\text{: } s^{1.15}\, p^{2.03}\, d^{0.34}$$

which means that the "valence state" of P must be rather similar in these two electron-rich molecules.

The analogy between H_3NO and H_3NF_2 is somewhat less pronounced:

$$H_3NO\text{: } s^{1.27}\, p^{3.25}\, d^{0.08}$$
$$H_3NF_2\text{: } s^{1.22}\, p^{2.98}\, d^{0.06}$$

There is one important difference in the pairs H_3NO/H_3PO and H_3NF_2/H_3PF_2. Without d AOs H_3NO and H_3PO have nearly the same binding energy for the XO bond; that in H_3PO is stabilized by d AOs by about 70 kcal/mol (40 kcal/mol by d AOs on P alone), that of H_3NO by only ~10 kcal/mol (7

Table XII. Pair Correlation Energies[a]

	H_3N	H_3NO	H_3P	H_3PO
h	0.0240 (3×)	0.0262 (3×)	0.0198 (3×)	0.0209 (3×)
n	0.0221 (1×)	0.0274 (1×)	0.0247 (1×)	0.0188 (1×)
^{1}hh′	0.0068 (3×)	0.0077 (3×)	0.0026 (3×)	0.0028 (3×)
^{1}hn	0.0083 (3×)	0.0068 (3×)	0.0046 (3×)	0.0006 (3×)
^{3}hh′	0.0109 (3×)	0.0115 (3×)	0.0045 (3×)	0.0043 (3×)
^{3}hn	0.0127 (3×)	0.0103 (3×)	0.0063 (3×)	0.0011 (3×)
o		0.0209 (3×)		0.0208 (3×)
^{1}ho		0.0006 (6×)		0.0012 (6×)
^{1}ho′		0.0007 (3×)		0.0006 (3×)
^{1}no		0.0081 (3×)		0.0102 (3×)
^{1}oo′		0.0110 (3×)		0.0127 (3×)
^{3}ho		0.0012 (6×)		0.0019 (6×)
^{3}ho′		0.0014 (3×)		0.0011 (3×)
^{3}no		0.0133 (3×)		0.0149 (3×)
^{3}oo′		0.0159 (3×)		0.0181 (3×)

[a] These sum up to the IEPA correlation energy. The following abbreviations have been used for the localized MOs: h = XH bond, n = lone pair of X or X–O bond, o = lone pair of O. a means intraorbital contribution of the MO a, ^{1}ab and ^{3}ab singlet and triplet interorbital contributions of the MOs a and b.

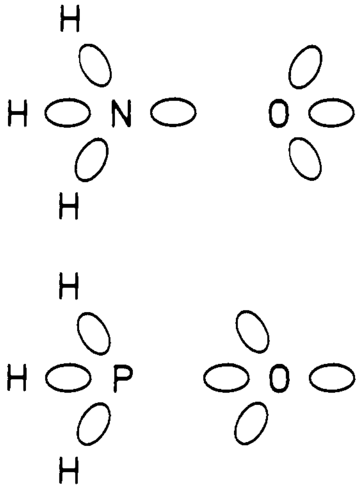


Figure 1. Schematic representation of the localized MOs in H_3NO and H_3PO.

kcal/mol by d AOs on N). The d AO contribution is hence decisive for the difference between H_3NO and H_3PO.

The binding energies of H_3NF_2 and H_3PF_2 (with respect to planar NH_3 or PH_3) differ already by ~120 kcal/mol if no d AOs are included while the extra stabilizing effects of d AOs on P are similar as in H_3PO and H_3NO.

Some other effect hence plays a more important role than the difference in the d AO contribution. The difference in the ionization potentials of planar PH_3 and NH_3 may account for a difference of ~70 kcal/mol[2] but ~50 kcal/mol (120 − 70) still lack an explanation. If one remembers[2] that NH_3F_2 has only a saddle point for D_{3h} geometry (with r(NF) = 1.7 Å) and is stabilized by relaxation to a C_{3v} structure (essentially an ion pair NH_3F^+/F^-) with only one F atom in the first coordination sphere (r(PH) = 1.40 Å) and the second F atom at a distance of 2.00 Å from the P atom, one realizes that there is not enough space around N for five ligands and that steric reasons are mainly responsible for the nonexistence of pentavalent nitrogen. For F_3NO there are, of course, no serious steric problems even if the NO bond can be regarded as multiple.[57]

XIII. Discussion and Conclusions

The difference in stability of H_nXO and H_nYO depends on the difference in the ionization potentials (IP) of H_nX and H_nY and on the different contribution of the d AOs. The former is responsible for the different ability of X or Y to carry a positive charge, the latter for the amount of back-bonding. Since the IPs of H_3N (10.6 eV) and H_3P (8.9) in their tetrahedral equilibrium configurations differ little, the different d AO contribution is the dominating effect for the difference in the pair H_3NO/H_3PO. (For the pair H_3NF_2/H_3PF_2 where the IPs of planar H_3N (~10 eV) and planar PH_3 (~7 eV) are relevant, the difference in the IPs has a larger effect.[4])

The stabilization of the semipolar PO bond by both the electron-donating CH_3 group and the electron-withdrawing F is based on two different mechanisms. The CH_3 stabilizes the R_3P^+ part of the molecule, as it lowers the IP (H_3P, 10.6 eV; $(CH_3)_3P$, 8.6 eV) and as it stabilizes R_3PH^+, and thus makes the charge transfer easier, without much affecting the PO bond (i.e., its bond length, force constant, etc.). The fluorine substitution destabilizes the R_3P^+ part of the molecule (IP of F_3P, 12.3 eV[58]), but by withdrawing electrons from P it lowers the energy of d AOs and enhances the possibility of back-bonding, which does strengthen the PO bond.

In forming a semipolar bond between R_3X and O one has to consider that only R_3X is, in its ground state, "prepared" for bonding, while O has formally first to be promoted from the ^3P state to its quasi-closed-shell valence state. This "promotion energy" is of the order of 75 kcal/mol. The conditions for the possibility of the formation of a charge-transfer complex (semipolar bond) between R_nX and O are therefore more severe than between R_nX and BH_3. For BH_3 or other electron acceptors even a small charge-transfer interaction with the lone pair of R_nX leads to complex formation.[59,60] For O this is only possible if the charge-transfer interaction is larger than the promotion energy. If the energy gain does not allow oxygen to be promoted to its valence state it can only react in its lowest ^3P or ^1D states as electron acceptor in which state it is much less effective than in the quasi-closed-shell valence state. The reason for the possible nonexistence of HClO and ArO lies probably there.

Although R_nX does not need electronic promotion in order to form the complex, there is nevertheless some kind of promotion energy, namely, one associated with a change of internal geometry. In fact the HPH angle is ~92.5° in H_3P, but ~102° in H_3PO. Opening of the HPH angles from their value in H_3P to that in H_3PO requires ~20 kcal/mol. There is practically no change in the CPC angle on going from $(CH_3)_3P$ to $(CH_3)_3PO$ and hence no promotion energy of $(CH_3)_3P$ necessary.

This is another way of looking at the difference in the binding energies in these two molecules, namely, as essentially a difference in promotion energy. The relevance of this idea due to Gibbs[61] for explaining the differences in the proton affinity of $(CH_3)_3P$ and $(CH_3)_3PO$ has been analyzed in the original context by Ahlrichs and Koch.[4]

The decreasing stability of the XO bonds in the series H_3PO, H_2SO, HClO, ArO is obviously related to the increasing ionization potentials and decreasing proton affinities in the series H_3P, H_2S, HCl, Ar. All these oxides can, however, be stabilized by substitution with CH_3 or—to a larger extent—with F, OH, or O^-. This is convincingly demonstrated by the existence and stability of orthophosphoric acid, $(HO)_3PO$, the sulfite ion, SO_3^{2-}, and chlorous acid, (HO)ClO. Moreover, it seems that two semipolar XO bonds attached to the same X as in $(CH_3)_2SO_2$, $(HO)_2SO_2$, or $HOClO_3$ stabilize each other. The mechanism of this extra stabilization would deserve a special quantum-chemical study.

In the discussion of the importance of d AOs the question whether they should be regarded as "valence AOs" or just as "polarization functions"[30] has played a big role. Of course, the d AOs are just basis functions chosen such as to minimize the energy. They are localized in the same region of space as the s and p AOs with which they interact and are very different from the rather "diffuse" spectroscopic d AOs.

The question whether the d AOs only serve to allow for a deformation (polarization) of the s- or p-type valence AOs or whether they are valence AOs themselves can to some extent be answered by application of the Heinzmann-Ahlrichs population analysis.[4] This analysis has two main features.

1. Different basis sets are used for the calculation of the electron density (via a conventional ab initio SCF method) and its analysis. For the analysis a special minimal basis set of MAOs (modified atomic orbitals) is constructed (the members of which are linear combinations of the original basis functions). The actual charge distribution cannot be expressed exactly in terms of the MAOs; there always remains an "unassigned charge". The MAOs are, however, determined such as to minimize the unassigned charge.

2. In the analysis only quantities are used that are expectation values of the density operator, which guarantees optimum independence of the original basis set.

If the unassigned charge is sufficiently small (i.e., $\ll 1$) one can say that the chosen set of MAOs is sufficient to describe the bonding situation in the given molecule. If, on the other hand, the unassigned charge gets close to 1 or even larger, this is an indication that the MAO basis has to be extended to include additional valence AOs.

We see from Table VIII that for a minimal MAO basis the unassigned charge is 0.02 electron in H_2NOH, H_3NO, H_2POH, and HClO but close to 0.05 in H_3PO, H_2POF, H_2SO, and PH_5. When one extends the MAO basis to include a d AO on P (or S) the unassigned charge is only insignificantly reduced (while the populations of the other MAOs are, of course, changed). We conclude that the traditional valence AOs of s and p type are, when appropriately deformed, able to describe the bonding in all molecules studied in this paper. They are slightly poorer for the electron-rich molecules, but even for them there is no indication of a "valence extension". "Back-bonding" then means simply that the π AOs of O^- are strongly polarized toward H_nX^+.

We finally want to comment on the isoelectronic series H_3PO, H_3PNH, H_3PCH_2, H_3PBH_3. Several published calculations[15,60,62] have confirmed that in H_3PBH_3 a rather pure semipolar σ bond without noticeable π back-bonding is realized; the same is true for $H_3PCH_3^+$.[21] In H_3PCH_2 there is back-bonding between the lone pair of the -CH_2^- group and d AOs on P, hence there is a partial double bond. In H_3PO the two lone pairs of O can participate in back-bonding with corresponding d AOs of P, hence there is a partial triple bond. H_3PNH should be somewhere in between. The effect of d AOs in H_3PO is, according to this qualitative argument, expected to be twice as large as in H_3PCH_2. Comparison of our results for H_3PO with Lischka's for H_3PCH_2 shows, however, nearly the same energy lowerings due to d AOs on P and very similar total d populations. The relatively higher d contribution in methylenephosphorane is probably due to the fact that the RCH_2^- ion has a stronger tendency to get rid of part of the negative charge than RO^-.

Acknowledgment. The authors are grateful to Professor Dr. R. Ahlrichs, Dr. H. Kollmar, and Dr. V. Staemmler for interesting discussions and valuable suggestions, to a referee for useful comments, and to Professor Ahlrichs also for the HA population analysis program. The numerical calculations were partly done on the Telefunken TR 440 of the computer center of the Ruhr University and partly on the Interdata 8/32 minicomputer, sponsored by Deutsche Forschungsgemeinschaft.

References and Notes

(1) W. Kutzelnigg, *Pure Appl. Chem.*, **49**, 981 (1977).
(2) F. Keil and W. Kutzelnigg, *J. Am. Chem. Soc.*, **97**, 3623 (1975).
(3) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).
(4) R. Heinzmann and R. Ahlrichs, *Theor. Chim. Acta*, **42**, 33 (1976).
(5) R. F. Hudson, *Adv. Inorg. Chem. Radiochem.*, **5**, 347 (1963).
(6) D. P. Craig and C. Zauli, *J. Chem. Phys.*, **37**, 609 (1962).
(7) K. A. R. Mitchell, *Can. J. Chem.*, **46**, 3499 (1968).
(8) L. S. Bartell, L. S. Su, and H. Yow, *Inorg. Chem.*, **9**, 1903 (1970).
(9) R. Hoffmann, D. B. Boyd, and S. Z. Goldberg, *J. Am. Chem. Soc.*, **92**, 3930 (1970).
(10) P. Millie and G. Bertheir, *Colloq. Int. CNRS*, **191**, 31 (1970).
(11) J. F. Labarre and C. Leibovici, *J. Chim. Phys. Phys.-Chim. Biol.*, **68**, 1618 (1971).
(12) B. J. Barsett, D. R. Lloyd, I. H. Hillier, and V. R. Saunders, *Chem. Phys. Lett.*, **6**, 253 (1970).
(13) I. H. Hillier and V. R. Saunders, *J. Chem. Soc. A*, 2475 (1970).
(14) H. Marsmann, L. C. D. Groenwegh, L. J. Schaad, and J. R. van Wazer, *J. Am. Chem. Soc.*, **92**, 6107 (1970).
(15) J. Demuynck and A. Veillard, *Chem. Commun.*, 873 (1970).
(16) A. Serafini, J. F. Labarre, A. Veillard, and G. Vinot, *Chem. Commun.*, 996 (1971).
(17) M. F. Guest, I. H. Hillier, and V. R. Saunders, *J. Chem. Soc., Faraday Trans. 2*, **68**, 867 (1972).
(18) I. Absar and J. R. van Wazer, *J. Am. Chem. Soc.*, **94**, 6294 (1972).
(19) J. R. van Wazer and I. Absar, *Adv. Chem. Ser.*, **No. 110**, 20 (1972).
(20) G. Robinet, C. Leibovici, and J. F. Labarre, *Theor. Chim. Acta*, **25**, 257 (1972).
(21) H. Lischka, *J. Am. Chem. Soc.*, **99**, 353 (1977).
(22) U. Gelius, B. Roos, and G. Siegbahn, *Theor. Chim. Acta*, **23**, 59 (1971).
(23) J. A. Connor, I. H. Hillier, V. R. Saunders, and M. Barber, *Mol. Phys.*, **23**, 81 (1972).
(24) D. Perahia, A. Pullman, and H. Berthod, *Theor. Chim. Acta*, **40**, 47 (1975).
(25) R. Ahlrichs, F. Driessler, H. Lischka, V. Staemmler, and W. Kutzelnigg, *J. Chem. Phys.*, **62**, 1235 (1975).
(26) R. Ahlrichs, F. Keil, H. Lischka, W. Kutzelnigg, and V. Staemmler, *J. Chem. Phys.*, **63**, 455 (1975).
(27) W. Meyer, *Int. J. Quantum Chem., Symp.*, **5**, 59 (1971); *J. Chem. Phys.*, **58**, 1017 (1973).
(28) R. Ahlrichs, H. Lischka, V. Staemmler, and W. Kutzelnigg, *J. Chem. Phys.*, **62**, 1225 (1975).
(29) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965); "Approximate Atomic Functions II", Technical Report, The University of Alberta, 1971.
(30) The term "polarization function" is currently used in a twofold meaning: (a) formally for atomic orbital type basis functions with $l > 0$ for H and $l > 1$ for first- and seond-row atoms, (b) as contrasted to genuine valence AOs—for formal polarization functions that only serve to account for deformation of the traditional AOs. See also section XIII.
(31) W. A. Lathan, L. A. Curtiss, W. H. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11**, 175 (1974).
(32) F. Chopling and G. Kaufman, *Spectrochim. Acta, Part A*, **26**, 2113 (1970).
(33) C. B. Colburn, "Developments in Nitrogen Chemistry", Elsevier, Amsterdam, 1966.
(34) S. W. Benson, *Chem. Rev.*, **69**, 279 (1969).
(35) "IANAF Thermochemical Tables", 2nd ed., 1971.
(36) The difference of the MOP for the NO bond in H_3NO with and without d AOs is an illustration of the strong basis dependence of the MOP. Even the HABP depend somewhat on the basis, though to a much lesser extent. While for four different basis sets MOP for the NO bond of +0.08, −0.01, −0.12, and +0.35 were found, the respective HABP were 0.69, 0.84, 0.79, and 1.11. For the NH bond the MOP varied between 0.73 and 0.79, the HABP between 1.27 and 1.29. Some dependence of the NO bond population on the basis is to be expected since the bond lengths and the binding energies are sensitive to the basis too.
(37) N. Hacket and R. J. W. Fevre, *J. Chem. Soc.*, 1612 (1961).
(38) L. E. Sutton et al., "Interatomic Distances", *Chem. Soc., Spec. Publ.* (1958–1965).
(39) H. K. Wang, *Acta Chem. Scand.*, **19**, 879 (1965).
(40) From the data given in S. B. Hartley, W. S. Holmes, J. K. Jacques, M. F. Mole, and J. C. McCoubrey, *Q. Rev., Chem. Soc.*, **17**, 204 (1963).
(41) R. Ahlrichs and W. Koch, private communication.
(42) R. H. Staley and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96**, 6252 (1974).
(43) D. H. Ane, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **94**, 4826 (1972).
(44) R. Ahlrichs, H. Lischka, B. Zurawski, and W. Kutzelnigg, *J. Chem. Phys.*, **63**, 4685 (1975).
(45) R. Jaquet, H. Kollmar, and W. Kutzelnigg, unpublished.
(46) R. S. Armstrong et al., *J. Chem. Soc. A*, 2735 (1969).
(47) L. F. Centofanti and P. L. Kuczkowski, *Inorg. Chem.*, 7, 2582 (1968).
(48) R. L. Kuczkowski, *J. Am. Chem. Soc.*, **90**, 1705 (1968).
(49) H. Dreizler and G. Dendl, *Z. Naturforsch. A*, **19**, 512 (1964).
(50) C. Valdemoro, Thesis, Madrid, 1964.
(51) P. E. Stevenson and W. N. Lipscomb, *J. Chem. Phys.*, **50**, 3306 (1969).
(52) G. Berthier, *Adv. Quantum Chem.*, **8**, 183 (1974).
(53) G. Berthier, *Bull. Soc. Chim. Belg.*, **85**, 977 (1976).
(54) T. Koopmans, *Physica (Utrecht)*, **1**, 104 (1933).
(55) W. B. Perry, T. F. Schaaf, and W. L. Jolly, *J. Am. Chem. Soc.*, **97**, 4899 (1975).
(56) S. F. Boys in "Quantum Theory of Atoms, Molecules and the Solid State", P. O. Löwdin, Ed., Interscience, New York, 1967, p 252.
(57) V. Plato, W. D. Hartford, and K. Hedberg, *J. Chem. Phys.*, **53**, 3488 (1970).
(58) H. Bock, *Pure Appl. Chem.*, **44**, 343 (1975).
(59) K. Hoheisel and W. Kutzelnigg, *J. Am. Chem. Soc.*, **97**, 6971 (1975).
(60) H. Umeyama and K. Morokuma, *J. Am. Chem. Soc.*, **98**, 7208 (1976).
(61) J. H. Gibbs, *J. Chem. Phys.*, **22**, 1460 (1954).
(62) C. Aslangul, A. Veillard, R. Daudel, and F. Gallais, *Theor. Chim. Acta*, **23**, 211 (1971).