(13) The identity of this species, which is most likely solvent coordinated, was established through protonation of $FpCH_3$ in this medium which leads to methane and the $CpFe(CO)_2^+$ species identical by ^1H NMR with that observed here. For a similar protonation, see A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3653 (1962).

(14) The CO resonances in **4** are equivalent down to −40 °C. This suggests a symmetrical geometry in which the C_{ipso}–C_1–H plane bisects the CO–Fe–CO angle (as shown) or an unsymmetrical geometry with rapid rotation about the Fe–C_1 bond. The symmetrical structure is favored by analogy to the contrasting geometries of ethylene and methylene groups in $Cp_2Nb(C_2H_5)(C_2H_4)$[15] and $Cp_2Ta(CH_3)(CH_2)$,[8c] respectively, and the knowledge that the π bond of an olefin bound to $Cp(CO)_2Fe^+$ lies perpendicular to the plane bisecting the CO–Fe–CO angle.[16]

(15) L. J. Guggenberger, P. Meakin, and F. N. Tebbe, *J. Am. Chem. Soc.*, **96**, 5420 (1974).

(16) B. M. Foxman, *J. Chem. Soc., Chem. Commun.*, 221 (1975).

(17) The J_{C_1-H} coupling constants in **4** and **5** (145 and 136 Hz, respectively) are substantially less than might be expected for a trigonal sp^2-hybridized carbon. A speculative explanation for these low values is that the H–C_1–C_{ipso} angle is less than 120° and that the s character of the C_1–H bond has decreased relative to a trigonal sp^2 model. In accord with this view is the report by Schrock of a $J_{C_{carbene}-H}$ of 132 Hz in $Cp_2(CH_3)Ta{=}CH_2$ and correspondingly a H–$C_{carbene}$–H angle of only ~107° (±9).[8b,c]

(18) M. H. Chisholm and S. Godleski, *Prog. Inorg. Chem.*, **20**, 299 (1976).

(19) B. Cetinkaya, M. F. Lappert, and K. Turner, *J. Chem. Soc., Chem. Commun.*, 851 (1972).

(20) The ortho, meta, and para ^{13}C resonances of **3** appear in the range of 124–128 ppm.

(21) G. J. Ray, R. J. Kurland, and A. K. Colter, *Tetrahedron*, **27**, 735 (1971).

(22) (a) J. A. Connor, E. M. Jones, E. W. Randall, and E. Rosenberg, *J. Chem. Soc., Dalton Trans.*, 2419 (1972); (b) O. S. Mills and A. D. Redhouse, *J. Chem. Soc. A*, 642 (1968).

(23) In a typical preparation, 1.0 g of ether **3** in 25 mL of methylene chloride at −20 °C was treated with 1.3 g of trityl hexafluorophosphate. The orange hexafluorophosphate salt of **4** precipitated from solution and additional salt was obtained by treatment with 50 mL of pentane. Filtration and vacuum drying yielded 1.1 g of the hexafluorophosphate salt of **4** (~77% yield).

(24) C. P. Casey and S. W. Polichnowski, *J. Am. Chem. Soc.*, preceding paper in this issue.

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Inversion Barriers of AsH_3 and SeH_3^+

Sir:

The inversion barriers of group 5A molecules have been the subject of many studies.[1] The simplest molecules of this type are the hydrides of general formula AH_3, but, owing to the large magnitude of the inversion barriers in these molecules, only the barrier in NH_3 has been measured experimentally.[2] Several theoretical determinations of the barrier in NH_3 at the Hartree-Fock level are in excellent agreement with experiment.[3] In addition, the inversion barriers for a variety of hydrocarbon-substituted phosphines and arsines have been obtained experimentally;[1] for example, the barriers in $C_6H_5CH_3AR$, where R is an alkyl or aryl group and A is P or As, are ~33 kcal/mol for A = P and ~43 kcal/mol for A = As.[4] Accurate calculations of the barrier in PH_3 give ~36 kcal/mol,[5] which is quite similar to the experimental results for the substituted compounds. Similar results are found for hydrocarbon-substituted amines. The values of the inversion barriers for simple AH_3-type molecules are, therefore, of considerable chemical interest. In this paper we present ab initio SCF calculations using large basis sets on the pyramidal and planar forms of AsH_3 and the isoelectronic SeH_3^+ ion. We estimate the inversion barriers to be 46 and 30 kcal/mol, respectively. In addition, we present optimized minimum basis set exponents and geometries for these molecules and show that the minimum basis set inversion barriers for AsH_3 and SeH_3^+ are 44 and 35 kcal/mol, respectively, in reasonable agreement with the more reliable large basis set calculations.

All calculations employed Slater orbital basis sets and computer programs previously described.[3] The large basis sets (Table I) were of the "polarized double zeta" type augmented by one additional 3d function on the central atom to ensure adequate treatment of the 3d orbitals. The inner shell exponents on the central atom were taken from best atom double zeta results,[6] while the 3d and valence orbital exponents were optimized for the ground state of the free atom. The exponent for the 4d polarization function on As and Se was chosen by analogy to an optimized value of the corresponding polarization function in PH_3.[5b,7] The hydrogen basis sets were chosen as that of PH_3 for AsH_3 and that of SH_3^+ for SeH_3^+.[8] Similar quality basis sets are known to yield calculated barriers within 1-2 kcal/mol of the Hartree-Fock limit for PH_3. For instance, polarized double zeta Slater orbital calculations on PH_3 yield a calculated barrier of 37 kcal/mol,[5a] compared with a very large gaussian lobe basis (including f functions) of 38 kcal/mol.[5d]

Table I. Large Basis Set Geometries and Exponents

Molecule	Symmetry	Geometries Bond length, Å	 Bond angle, degree
AsH_3	C_{3v}	1.520	91.6
	D_{3h}	1.480	120
SeH_3^+	C_{3v}	1.450	93.0
	D_{3h}	1.434	120

	Basis sets As	 Se
1s	34.0214	35.0365
1s′	23.6356	24.3614
2s	16.2147	16.5867
2s′	13.2611	13.7371
3s	7.55246	7.95809
3s′	5.31126	5.66700
4s	2.931	3.188
4s′	1.736	1.918
2p	21.7642	22.4336
2p′	13.3553	13.8318
3p	7.0563	7.27814
3p′	4.50827	4.68101
4p	2.493	2.699
4p′	1.403	1.503
3d	11.961	12.018
3d′	6.544	6.611
3d″	3.482	3.658
4d	2.270	2.440
H1s	1.331	1.431
H2s	1.4054	1.7054
H2p	1.500	1.340

For the large basis set calculations, the geometry of AsH_3 was taken from experiment,[9] while the bond length for the planar molecule was shortened 0.04 Å by analogy to accurate geometry optimizations for PH_3.[5] This bond-length shortening is also consistent with optimized minimum basis set results described below. Estimates of the possible errors in the calculated barrier for AsH_3 due to inaccuracies in the transition state bond length can best be made by comparison with PH_3. For PH_3, the P-H stretching force constants in the planar form calculated at the minimum basis set SCF and the polarized double zeta SCF-CI levels of approximation differ by only ~15%. Calculation of the corresponding minimum basis set force constant for planar AsH_3 allows us to estimate a maximum error of 1.0 kcal/mol in our calculated barrier owing to inaccuracies in the bond length in the planar form, assuming the estimated transition state bond length of 1.480 Å is within 0.030 Å of the correct value and the minimum basis set force constant is accurate to within 30%. For pyramidal SeH_3^+, the bond length and angle were assumed to be 1.45 Å and 93°, respectively, and the bond length of the planar molecule was fixed at 1.434 Å. These values were obtained from optimized minimum basis set results (see below) along with estimates of minimum basis set errors associated with several other AH_3 molecules.[3,5b,10] We expect that all geometries are accurate

Table II. Total Energies and Inversion Barriers

Molecule	Basis set	Symmetry	Energy[a]	Inversion barrier[b]
AsH_3	Large	C_{3v}	−2235.9713	46.4
	Large	D_{3h}	−2235.8974	
	Minimum	C_{3v}	−2229.0258	43.8
	Minimum	D_{3h}	−2228.9560	
SeH_3^+	Large	C_{3v}	−2401.3096	29.8
	Large	D_{3h}	−2401.2621	
	Minimum	C_{3v}	−2394.2406	35.3
	Minimum	D_{3h}	−2394.1844	

[a] Atomic units. [b] Kilocalories/mole.

Table III. Minimum Basis Set Geometries and Exponents

		Geometries	
Molecule	Symmetry	Bond length, Å	Bond angle, degree
AsH_3	C_{3v}	1.528	93.64
	D_{3h}	1.467	120
SeH_3^+	C_{3v}	1.465	95.65
	D_{3h}	1.444	120

	Basis Sets	
	As	Se
1s	32.278	33.255
2s	12.064	12.448
3s	6.198	6.466
2p	14.537	15.033
3p	5.950	6.235
3d	5.797	6.159
4s	2.326 (C_{3v}), 2.405 (D_{3h})	2.569 (C_{3v}), 2.589 (D_{3h})
4p	2.054 (C_{3v}), 1.977 (D_{3h})	2.280 (C_{3v}), 2.221 (D_{3h})
H1s	1.06 (C_{3v}), 1.10 (D_{3h})	1.15 (C_{3v}), 1.18 (D_{3h})

to ±0.02 Å and ±1.5°. Each large basis set calculation (61 orbitals) required 35 min of CPU time on an IBM 360/91.

Since previous work on NH_3[3] and PH_3[5a] suggests that these barriers may also be obtained from minimum basis set calculations, we have obtained optimized valence shell exponents, geometries, and barrier heights for these molecules at this level of approximation. Exponents of the inner shell orbitals were again taken from best atom results,[11] and the 3d orbital was also treated as an inner shell after preliminary optimizations indicated that this exponent did not change from the free atom value. Each minimum basis set calculation required 0.67 min of CPU time.

It is generally assumed that inversion barriers for simple molecules can be calculated accurately at the Hartree–Fock level without corrections for correlation effects. This result is in agreement with the prediction of Freed[12] and has been critically tested by ab initio SCF-CI calculations using large basis sets on NH_3,[3] PH_3,[5] CH_3^-,[13] and SH_3^+.[14] Although accurate theoretical values for the inversion barriers of these molecules are known, only semiempirical estimates for the barrier in AsH_3 have previously been made. For instance, CNDO calculations on AsH_3 yield a barrier of 54.5 kcal/mol.[15] Our new large basis set values for AsH_3 (46.4 kcal/mol, Table II) and SeH_3^+ (29.8 kcal/mol) should be accurate to within a maximum of 10%.[16] The barrier in AsH_3, as was found for PH_3, is slightly larger than the barriers for substituted AsR_3 molecules where R is a hydrocarbon. The Koopmans' theorem ionization potential for AsH_3 is 10.27 eV, compared with the experimental value of 10.03 eV.[17]

In Figures 1 and 2, we illustrate electron density contour maps for the highest occupied molecular orbital of the pyramidal and planar forms of AsH_3. Of particular interest is the substantial amount of electron density found at the hydrogen atom in the pyramidal form. A recent discussion[18] of inversion barriers in AH_3 molecules has stressed the importance of stabilization of the "lone pair" in the pyramidal form, and these maps suggest that such stabilization may be physically associated with delocalization from the central atom to the hydrogens. However, a detailed, quantitative explanation of these inversion barrier trends must await analysis of accurate ab initio wavefunctions and calculation of barriers in other molecules in this series. Finally, in Figure 3 we present a difference density map between the "lone-pair" orbitals of AsH_3 and SeH_3^+ in the planar forms. This map illustrates the relative diffuseness of the AsH_3 density.

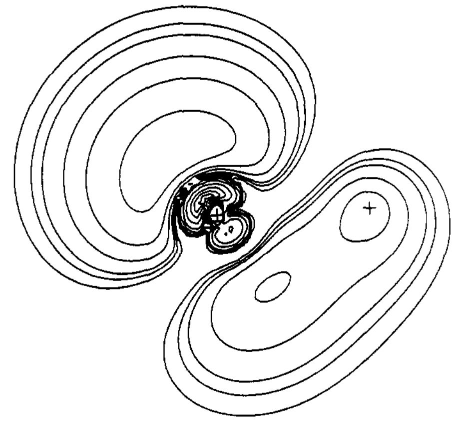

Figure 1. Total electron density of the highest occupied molecular orbital of pyramidal AsH_3. The plane is defined by the coordinates of As, H_1 (denoted by +) and the average coordinates of H_2 and H_3 (not shown). Contour levels are 0.3, 0.25, 0.20, 0.15, 0.10, 0.05, 0.02, 0.01, 0.005, 0.0035, and 0.002 e/au.[3]

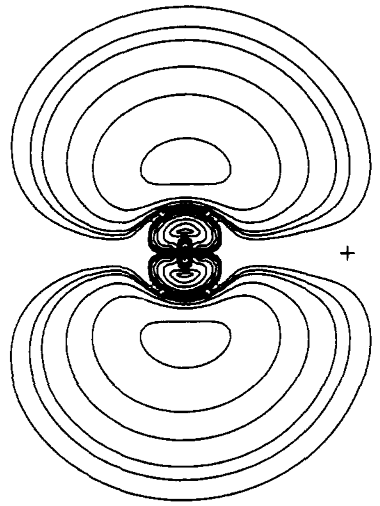

Figure 2. Total electron density of the highest occupied molecular orbital of planar AsH_3. The plane is perpendicular to the plane of the molecule. Contour levels are identical with those of Figure 1.

The barriers calculated using minimum basis sets are 43.8 kcal/mol for AsH_3 and 35.3 kcal/mol for SeH_3^+ (Table II), in reasonably good agreement with the large basis set results.[19] The optimized exponents and geometries are presented in Table III. Significant differences in the valence exponents are found for the pyramidal and planar structures of both molecules. The central atom 4s and hydrogen 1s orbitals both contract when going from pyramidal to planar, while the 4p orbitals expand.

These new and accurate predictions of the barrier heights for AsH_3 and SeH_3^+ will be useful in understanding the nature of these barriers and also for parameterization of semiempirical methods such as CNDO. In Table IV we summarize the known barriers for AH_3 and AH_3^+ molecules, and we note that these two isoelectronic series do not even display the same trends of

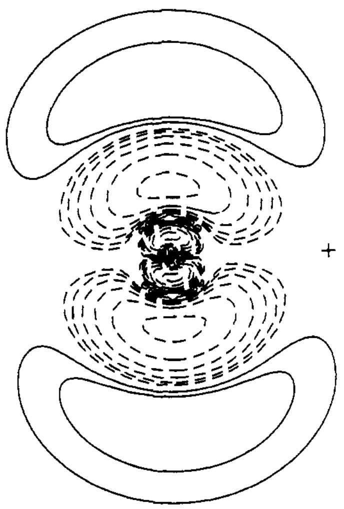

Figure 3. Electron density difference map of the highest occupied molecular orbitals of AsH_3-SeH_3^+ in the planar form. The plane is perpendicular to the plane of the molecules. The contour levels are 0.032, 0.016, 0.008, 0.004, 0.002, 0.001, −0.001, −0.002, −0.004, −0.008, −0.016, −0.032, −0.064, −0.128, and −0.256.

Table IV. Inversion Barriers for AH_3 and AH_3^+ Molecules

Molecule	Barrier[a]	Molecule	Barrier[a]
NH_3	6[b]	H_3O^+	1-2[c,d]
PH_3	36[e]	H_3S^+	32[f]
AsH_3	46[g]	H_3Se^+	30[g]

[a] Kilocalories/mole. [b] References 2 and 3. [c] S. Novick, R. M. Stevens, and W. Klemperer, unpublished results. [d] R. Ahlrichs, F. Driessler, H. Lischka, V. Staemmler, and W. Kutzelnigg, *J. Chem. Phys.*, **62**, 1235 (1975). [e] Reference 5. [f] References 1 and 8. [g] This work.

relative barrier heights. Further work on other molecules in this series is anticipated to elucidate these trends more clearly.

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References and Notes

(1) For a review see L. C. Allen, A. Rauk, and K. Mislow, *Angew. Chem.*, **9**, 400 (1970).
(2) J. D. Swalen and J. A. Ibers, *J. Chem. Phys.*, **36**, 1914 (1962).
(3) R. M. Stevens, *J. Chem. Phys.*, **55**, 1725 (1971); **61**, 2086 (1974), and references therein.
(4) R. D. Baechler, J. P. Casey, R. J. Cook, G. H. Senkler, Jr., and K. Mislow, *J. Am. Chem. Soc.*, **94**, 2859 (1972).
(5) (a) D. S. Marynick and D. A. Dixon, *Discuss. Faraday Soc.*, **62**, 47 (1977); (b) D. S. Marynick and D. A. Dixon, unpublished work; (c) J. M. Lehn and B. Munsch, *Mol. Phys.*, **23**, 91 (1972); (d) R. Ahlrichs, F. Keil, H. Lischka, W. Kutzelnigg, and V. Staemmler, *J. Chem. Phys.*, **63**, 455 (1975).
(6) C. Roetti and E. Clementi, *J. Chem. Phys.*, **60**, 4725 (1974).
(7) The 4d exponent was calculated as $\zeta(4d) = 0.79(\zeta(4p') - \zeta(4p)) + \zeta(4p)$.
(8) Double zeta 1s and 2s hydrogen exponents were optimized for PH_3 and SH_3^+. The exponents of the 2p polarization functions were taken as the weighted average of the $2p_\sigma$ and $2p_\pi$ exponents on P-H and S-H as calculated by P. E. Cade and W. M. Huo, *J. Chem. Phys.*, **47**, 649 (1967). These values were used without change of AsH_3 and SeH_3^+, respectively.
(9) A wide variety of geometries are summarized in G. W. Keoppl, D. S. Sagatys, G. S. Krishnamurthy, and S. I. Miller, *J. Am. Chem. Soc.*, **89**, 3396 (1967).
(10) Minimum basis set calculations for these molecules give M-H bond lengths that are somewhat too long and H-M-H bond angles that are somewhat too large.
(11) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).
(12) K. F. Freed, *Chem. Phys. Lett.*, **2**, 255 (1968).
(13) D. S. Marynick and D. A. Dixon, *Proc. Natl. Acad. Sci. U.S.A.*, **74**, 410 (1977).
(14) D. A. Dixon and D. S. Marynick, unpublished work.
(15) J. D. Andose, A. Rauk, and K. Mislow, *J. Am. Chem. Soc.*, **96**, 6904 (1974).
(16) Alrichs et al.[5d] have shown that the effect of additional polarization functions beyond the polarized double zeta level on the inversion barrier in PH_3 is likely to be <1 kcal/mol within the SCF approximation. They further estimate that correlation energy *lowers* the computed barrier from 38 kcal/mol (SCF) to 35 kcal/mol (including correlation); however, we have recently obtained a value of 35.7 kcal/mol for PH_3 using a very large Slater orbital basis set *without* correlation corrections.[5b]
(17) J. L. Franklin and J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions", NSRDS-NBS 36, U.S. Government Printing Office, Washington, D.C., 1969.
(18) W. Cherry and N. Epiotis, *J. Am. Chem. Soc.*, **98**, 1135 (1976).
(19) We note that the minimum basis set barrier for SH_3^+ is ~10 kcal/mol too low and the agreement is not so good as expected.

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Nature of the Iron–Oxygen Bond in Oxyhemoglobin

Sir:

The nature of the iron-oxygen bond in oxyhemoglobin has been a controversial problem for decades. Although x-ray data from model compounds[1]-support the bent Fe-O(1)-O(2) geometry proposed by Pauling,[2] questions concerned with the details of the bonding, including the charge on the oxygen (O_2 or O_2^-),[2-4] have not been resolved. In this communication we present the results of two quantum mechanical calculations which support a *neutral* oxygen model and show that it is consistent with Mossbauer and vibrational spectra data that have been interpreted as favoring a Fe^{+3}-O_2^- unit. Analysis of the electronic structure shows that it can be considered to arise from the interaction of an iron porphine moiety and an O_2 molecule with both species in either $S = 0$ or $S = 1$ valence states; the latter corresponds to ozone-like bonding, an analogy mentioned by Pauling[2] and emphasized recently by Goddard and Olafson.[4]

The system treated consists of a planar iron porphine with an imidazole group and an oxygen molecule as axial ligands. The geometry is that given by Collman et al.;[1] the porphine is in the xy plane with the x and y axes bisecting the N-Fe-N angles and both the imidazole and the FeO_2 unit are in the yz plane. The first calculation is of the extended SCF-CI Pariser-Parr-Pople (PPP) type.[5] It includes the iron 3d, 4s, and 4p orbitals, the oxygen 2s and 2p orbitals, the nitrogen lone-pair σ orbitals, and the π orbitals of the porphine and imidazole. The iron, porphine, and imidazole parameters were taken from ref 5 and those for oxygen from a PPP study of ozone.[6] The second calculation employs the Xα multiple scattering method,[7] which has been shown to yield excellent results for copper porphine.[8]

The charge distribution obtained in the PPP calculation corresponds to a neutral oxygen (O(1), +0.14; O(2), −0.08), an iron atom with net charge +0.44, and an imidazole group with a charge of +0.31. For the Xα wave function, a simple decomposition into atomic charges has been found not to be meaningful.[8] However, the charge distributions obtained from other calculations do correlate with the Xα atomic potentials. These indicate that in the O_2 unit the atoms are very similar to each other and to a free oxygen atom, with O(1) slightly positive. The Fe potential is that appropriate for a positive iron (+0.1).

To test the charge distributions, we consider first the electric field gradient tensor (EFG) at the iron nucleus evaluated from the Mössbauer spectrum. Since the EFG depends upon the individual orbital populations, we compare four different FeO_2