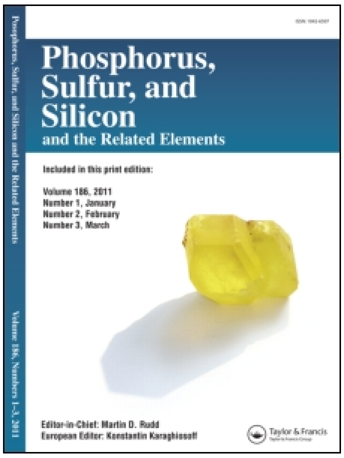

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THE PHOSPHOROTRITHIOUS ACID $(HS)_3P$ IS STABLE IN THE DILUTE GAS PHASE

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Using the technique of neutralization-reionization mass spectrometry (NRMS) it could be shown that the elusive phosphorotrithious acid $(HS)_3P$ is a stable molecule in the rarefied gas phase. A triple propene elimination from the molecular ions of the dipropyl ester of propylphosphonotrithioic acid, $PrP(S)(SPr)_2$, (70 eV EI) yields m/z 130 radical cations of composition "$[H_3PS_3]^{\cdot+}$". Analysis of their collisional activation (CA) mass spectrum using thermochemical data shows that these "$[H_3PS_3]^{\cdot+}$" ions have the structure $[(HS)_3P]^{\cdot+}$ rather than that of the tautomer $[(HS)_2P({=}S)H]^{\cdot+}$. Subjected to a NRMS experiment, these ions retain their structure and are cleanly reduced to $(HS)_3P$. The results are entirely compatible with *ab initio* MO-calculations executed at the HF/3-21G* and HF/6-31G** levels of theory (GAUSSIAN 92 system of programs). The calculations predict that $[(HS)_3P]^{\cdot+}$ and $[(HS)_2P({=}S)H]^{\cdot+}$ and their respective neutral counterparts are local minima which are separated by high potential energy barriers. Neutral $(HS)_3P$ is calculated to be lower in energy than its tautomer $(HS)_2P({=}S)H$ but upon ionization this order of stability is reversed.

Key words: $(HS)_3P/(HS)_2P(S)H$, mass spectrometry, neutralization-reionization, *ab initio* MO-calculations.

INTRODUCTION

Phosphonous acid, H_3PO_3, is well-known but knowledge about its thioanalogue H_3PS_3 **1** is almost exclusively limited to its instability in the condensed phase.[1] However, various stable salts of composition MPS_3 exist (M is Ni, Mn or Fe).[2] So far, attempts to synthesize the free thioacid e.g. by hydrolysis of the stable salt $K_2[PHS_3]$ have failed, because even at low temperatures the acid decomposes by formation of H_2S.[3] According to a theoretical study dealing with a minima search in the conformational space of the thiophosphane "$(HS)_3P$" the neutral molecule possesses five conformations: two of C_3 symmetry, two of C_S symmetry and one of C_1 symmetry.[4] Recently we successfully used the technique of neutralization-reionization mass spectrometry (NRMS)[5] to generate related "HPS" compounds, viz. "H_3PS"[6] and "H_3PS_2,"[7] and the simple analogues "HPS" and "HSP".[8] This prompted us to investigate the use of the NRMS technique for the generation of the elusive H_3PS_3 neutral. Moreover it was of special interest to us to establish the structure of **1** which may well exist in two tautomeric forms, viz. the phosphorotrithious acid (**1a**) and the phosphonotrithioic acid, (**1b**).

$$\underset{\mathbf{1a}}{(HS)_3P} \quad \underset{\mathbf{1b}}{(HS)_2P(S)H}$$

We report on investigations on the structure of $\mathbf{1}^{\cdot+}$ using collisional activation (CA) mass spectrometry,[9] and on the results of the reduction of $\mathbf{1}^{\cdot+}$ in a NRMS experiment. The experimental findings are analysed using thermochemical data and the results of *ab initio* MO-calculations for both the radical cation $\mathbf{1}^{\cdot+}$ and its neutral counterpart **1**. The total energies and optimized geometries of calculated minima and transition states on the potential energy surfaces of $\mathbf{1}^{\cdot+}$ and **1** are also presented.

RESULTS AND DISCUSSION

Radical cations of composition $[H_3PS_3]^{\cdot+}$ (m/z 130), $\mathbf{1}^{\cdot+}$, are generated by consecutive loss of three C_3H_6 molecules after ionization (70 eV electron impact) of propylphosphonotrithioic acid dipropylester, $PrP(S)(SPr)_2$.

For $\mathbf{1}^{\cdot+}$ two structures seem to be chemically significant: the radical cations of the phosphorotrithious acid $\mathbf{1a}^{\cdot+}$ and that of its tautomer, phosphonotrithioic acid $\mathbf{1b}^{\cdot+}$:

$$\underset{\mathbf{1a}^{\cdot+}}{[(HS)_3P]^{\cdot+}} \quad \underset{\mathbf{1b}^{\cdot+}}{[(HS)_2P(S)H]^{\cdot+}}$$

Mass selection of m/z 130 and subsequent collision-induced dissociation with O_2 afforded the collisional activation (CA) mass spectrum of $\mathbf{1}^{\cdot+}$ (Figure 1a).

The spectrum shows a group of intense peaks at m/z 97 ($[H_2PS_2]^+$), m/z 96 ($[HPS_2]^{\cdot+}$) and m/z 95 (PS_2^+), an abundant peak at m/z 63 (PS^+) and a less intense cluster of peaks at m/z 31 (P^+), m/z 32 ($S^{\cdot+}$) and m/z 33 (SH^+). The peak at m/z 65 results from a charge stripping process according to:

$$130^{\cdot+} + O_2 \rightarrow 130^{++} + O_2 + e^-$$

Thus $[H_3PS_3]^{\cdot+}$ decomposes by loss of an SH radical yielding m/z 97 ions, which in turn readily lose H_2 or H_2S to generate the ions at m/z 95 and m/z 63 respectively. In addition $\mathbf{1}^{\cdot+}$ decomposes by loss of H_2S yielding m/z 96 radical cations which serve as a second precursor of the abundant PS ions at m/z 63. These observations are compatible with the exclusive generation of ions of structure $\mathbf{1a}^{\cdot+}$. Had the tautomer $\mathbf{1b}^{\cdot+}$ been cogenerated, then loss of an H radical from cleavage of its P—H bond should have been observed. Also, a substantial loss of S, yielding ions of m/z 98 ($[H_3PS_2]^{\cdot+}$) should occur, which is clearly not the case; calculations with the semiempirical PM3 method support this conclusion. According to these calculations, see Table I, loss of $SH^{\cdot}$ from $\mathbf{1b}^{\cdot+}$ is energetically favoured over loss of sulfur but the difference (34.7 kJ/mol) is so small that both fragmentations should be observed, if $\mathbf{1b}^{\cdot+}$ had been generated (Table I).

The CA experiment and the calculations show that the radical cations $[H_3PS_3]^{\cdot+}$ generated in this way exclusively have structure $\mathbf{1a}^{\cdot+}$, in accordance with earlier

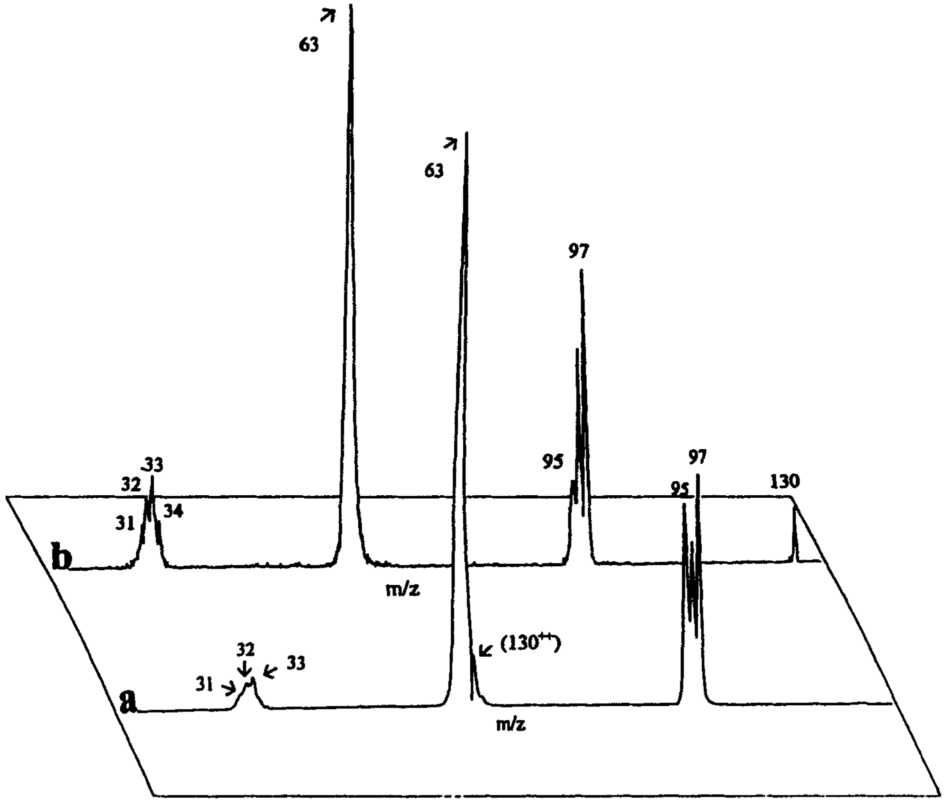


FIGURE 1 a) Partial CA mass spectrum of $[H_3PS_3]^{\cdot +}$ m/z 130. b) NR mass spectrum of $[H_3PS_3]^{\cdot +}$ m/z 130.

TABLE I

Minimum energy requirements for the structure diagnostic fragmentations of $[H_3PS_3]^{\cdot +}$. Standard heats of formation ΔH° in kJ/mol, calculated with PM3.

Structure $1a^{\cdot +}$, $[(HS)_3P]^{\cdot +}$

	m/z	ion	ΔH°	fragment	ΔH°	ΣΔH°
$1a^{\cdot +}$ →	97	$[HS\text{-}P\text{-}SH]^+$	825.6	+ HS˙	159.9	985.5
$1a^{\cdot +}$ →	96	$[HS\text{-}P\text{-}S]^{\cdot +}$	882.6	+ H_2S	-3.8	878.8

Structure $1b^{\cdot +}$, $[(HS)_2P(S)H]^{\cdot +}$

	m/z	ion	ΔH°	fragment	ΔH°	ΣΔH°
$1b^{\cdot +}$ →	98	$[(HS)_2PH]^{\cdot +}$	764.4	+ S	278	1042.4
$1b^{\cdot +}$ →	97	$[HS\text{-}P(S)H]^+$	847.8	+ HS˙	159.9	1007.7
$1b^{\cdot +}$ →	96	$[HS\text{-}P\text{-}S]^{\cdot +}$	882.6	+ H_2S	-3.8	878.8

observations that ternary HPS radical cations favour structures with SH moieties over those with a PH moiety.[6,18,19]

A neutralization-reionization experiment on $\mathbf{1}^{\cdot+}$ was carried out using N,N-dimethylaniline for neutralization of $\mathbf{1}^{\cdot+}$, followed by reionization with O_2 after 1 μs (see Figure 1b). The NR spectrum shows an enhanced relative intensity of the m/z 96 peak in the m/z 95–97 cluster which indicates that the neutral molecules generated in the neutralization step partly dissociate by loss of H_2S. Note also that the NR spectrum contains m/z 34 $H_2S^{\cdot+}$ ions. These experimental findings correspond excellently with an *ab initio* study at the HF/3-21G* and HF/6-31G** levels of theory, dealing with **1a**, **1b**, their radical cations $\mathbf{1a}^{\cdot+}$ and $\mathbf{1b}^{\cdot+}$, and the transition states **TS** and $\mathbf{TS}^{\cdot+}$ for the unimolecular rearrangements between these tautomeric structures. According to these calculations both species $\mathbf{1a}^{\cdot+}$ and $\mathbf{1b}^{\cdot+}$ are minima on the potential hypersurface of $[H_3PS_3]^{\cdot+}$. $\mathbf{1b}^{\cdot+}$ is found to be the more stable structure at both levels of theory and the tautomers are separated by such a high potential energy barrier, see Figure 2, that isomerization prior to collisional activation is highly unlikely; Figure 3 displays the optimized geometries of $\mathbf{1a}^{\cdot+}$, $\mathbf{1b}^{\cdot+}$ and the transition state $\mathbf{TS}^{\cdot+}$ connecting the two ions as well as their total energies. A Mulliken population analysis of the observed radical cation $\mathbf{1a}^{\cdot+}$ indicates that

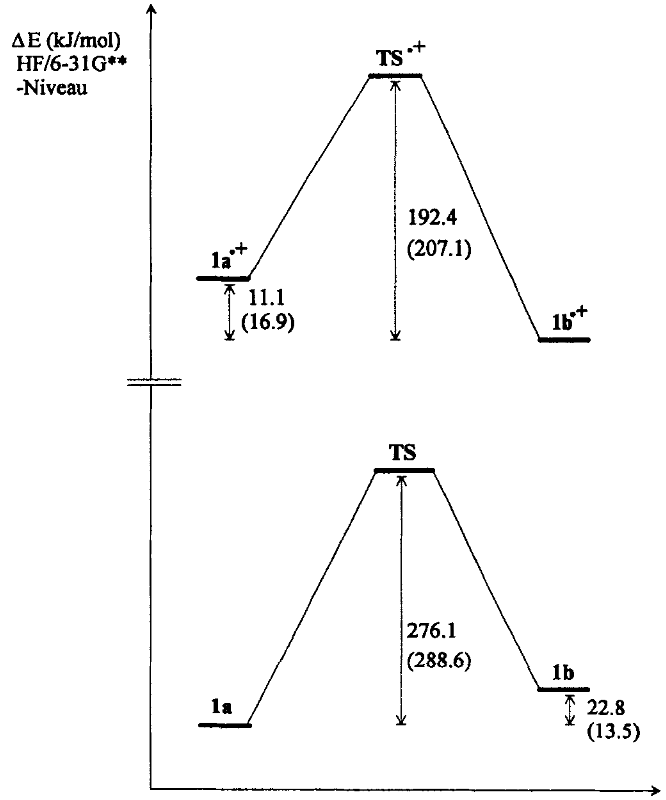
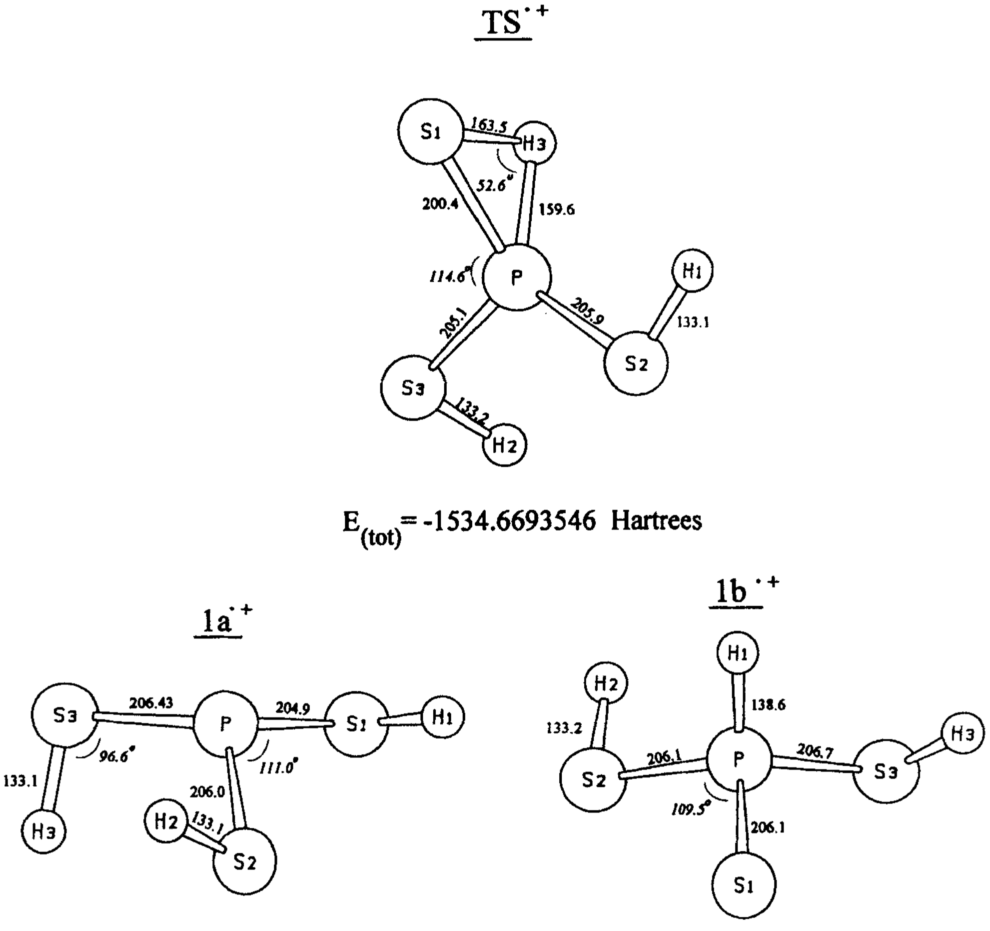


FIGURE 2 Schematic energy profile in the systems $[H_3PS_3]^{\cdot+}$ and H_3PS_3 at the HF/6-31G** level (in brackets HF/3-21G* niveau).



$E_{(tot)}$ = -1534.6693546 Hartrees

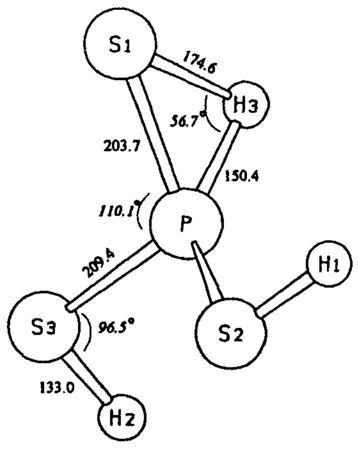
$E_{(tot)}$ = -1534.7384088 Hartrees

$E_{(tot)}$ = - 1534.7426537 Hartrees

FIGURE 3 Total energies and optimized geometries in the system $[H_3PS_3]^{\cdot+}$ calculated at the HF/6-31G** level. Bond lengths are given in picometres and bond angles in degrees.

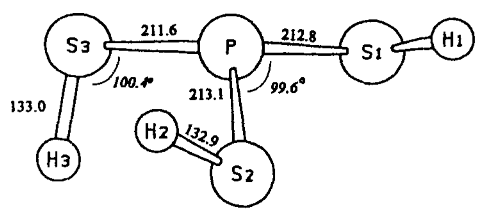
the positive charge is mainly localized on the P atom (P, +0.40, S1, +0.22, S2, +0.19 and S3 +0.19, at the HF/6-31G** level of theory). Concerning the neutral counterparts **1a** and **1b**, we note that again both structures are minima on the hypersurface of **1**. In contrast to the radical cations, the phosphorotrithious acid **1a** is the energetically favoured tautomer, with a high barrier for interconversion. The total energies and optimized geometries are given in Figure 4. The prediction from theory that the neutral and the ionized tautomers both exhibit high isomerization barriers, explicitly confirms that it is feasible to generate the less stable, elusive phosphorotrithious acid $(HS)_3P$ by neutralization of the more stable radical cation $[(HS)_3P]^{\cdot+}$. In the same vein, it should be possible to generate the elusive phosphonotrithioic acid **1b** by the same procedure provided a suitable precursor is available for the generation of the radical cation $\mathbf{1b}^{\cdot+}$

TS

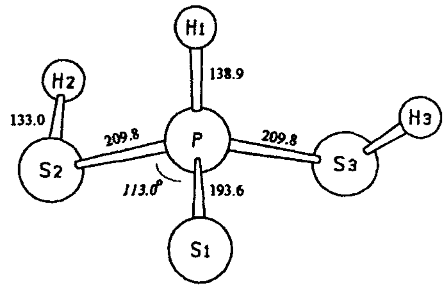


$E_{(tot)}$ = -1534.9274443 Hartrees

1a



1b



$E_{(tot)}$ = -1935.0326208 Hartrees

$E_{(tot)}$ = - 1935.0239165 Hartrees

FIGURE 4 Total energies and optimized geometries in the system H_3PS_3 calculated at the HF/6-31G** level. Bond lengths are given in picometres and bond angles in degrees.

EXPERIMENTAL

The mass spectrometric experiments were carried out with the VG Analytical ZAB-R mass spectrometer, a three sector BE_1E_2-type instrument whose design is based on the standard, nonextended geometry of the ZAB-2f.[10a] The spectrometer is equipped with three collision gas chambers for NR experiments in the second field free region (2ffr) between B and E_1, and it has an additional collision gas chamber in front of E_2 for double collision experiments (MS/MS/MS) in the third ffr.[10b] The NR mass spectra were obtained using N,N-dimethylaniline for neutralization and oxygen for reionization. Oxygen was also used as the collision gas in the collisional activation (CA) experiments. The spectra were recorded with a small PC-based data system developed by Mommers Technologies Inc. (Ottawa). The compound $PrP(S)(SPr)_2$ was synthesized by standard procedures.[11] The PM3[12] calculations were performed with the VAMP Erlangen Vectorized Molecular Orbital Package Version 4.40. The *ab initio* MO-calculations reported in this work were performed using the Gaussian 92[13] system of programs on a Convex C210 supercomputer. To optimize the geometries of stationary points, the analytical gradient technique (Berny optimization)[14] was used for minima, and the eigenvector following (EF)[15] technique was used for saddle points. The following levels of theory were used:

(a) UHF/3-21G* and UHF/6-31G**, the unrestricted Hartree-Fock (UHF) formalism with two different bases for the radical cations.[16]

(b) RHF/3-21G* and RHF/6-31G** the restricted Hartree-Fock (RHF) formalism with the same bases for the neutrals.[17] In order to characterize all stationary points considered as minimum or saddle point the harmonic vibrational frequencies were determined at the HF/3-21G* level.

REFERENCES

1. F. Seel and G. Zindler, *Z. Anorg. Allg. Chem.*, **470,** 167 (1980).
2. R. Brec, D. M. Schleich, G. Ouvrard, A. Louisy and J. Rouxel, *Inorg. Chem.*, **18,** 1814 (1979).
3. U. Ahrens and H. Falius, *Z. Anorg. Allg. Chem.*, **480,** 95 (1981).
4. M. Korn, H. Oberhammer and R. Minkwitz, *J. Mol. Structure*, **300,** 61 (1993).
5. For a recent review see: N. Goldberg and H. Schwarz, *Acc. Chem. Res.*, **27,** 347 (1994).
6. H. Keck, W. Kuchen, H. Renneberg and J. K. Terlouw, *Phosphorus Sulfur Relat. Elem.*, **40,** 227 (1988).
7. H. Keck, W. Kuchen, H. Renneberg, J. K. Terlouw and H. C. Visser, *Z. Anorg. Allg. Chem.*, **580,** 181 (1990).
8. T. Wong, J. K. Terlouw, H. Keck, W. Kuchen and P. Tommes, *J. Am. Chem. Soc.*, **114,** 8208 (1992).
9. Reviews: (a) K. Levsen and H. Schwarz, *Angew. Chem.*, **88,** 589 (1976); *Angew. Chem. Int. Ed. Engl.*, **15,** 509 (1976); (b) K. Levsen and H. Schwarz, *Mass. Spectrom. Rev.*, **2,** 77 (1983); (c) J. L. Holmes, *Org. Mass Spectrom.*, **20,** 169 (1985).
10. (a) R. P. Morgan, J. H. Beynon, R. H. Bateman and B. N. Green, *Int. J. Mass Spectrom. Ion Phys.*, **28,** 171 (1978); (b) H. F. van Garderen, P. J. A. Ruttink, P. C. Burgers, G. A. McGibbon and J. K. Terlouw, *Int. J. Mass. Spectrom. Ion Processes*, **121,** 159 (1992).
11. K. Sasse, in "Methoden der Org. Chemie," Houben Weyl, ed. by E. Müller, Vol. 12/1, G. Thieme Verlag, Stuttgart, 1963.
12. J. J. Stewart, *J. Comput. Chem.*, **10,** 209 (1989).
13. M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Reploge, R. Gomberts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzales, R. L. Martin, D. J. Fox, D. J. DeFrees, J. Baker, J. J. P. Stewart and J. A. Pople, Gaussian, Inc., Pittsburgh PA (1992).
14. H. B. Schlegel, *J. Comput. Chem.*, **3,** 214 (1982).
15. (a) C. J. Cerjan and W. H. Miller, *J. Chem. Phys.*, **75,** 2800 (1981); (b) J. Simons, P. Jørgensen, H. Taylor and J. Ozment, *J. Chem. Phys.*, **87,** 2745 (1983); (c) A. Bannerjee, N. Adams, J. Simons and J. R. Shepard, *J. Chem. Phys.*, **89,** 52 (1985).
16. M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro and W. J. Hehre, *J. Am. Chem. Soc.*, **104,** 1982 (1982).
17. C. C. J. Roothan, *Rev. Mod. Phys.*, **23,** 69 (1951).
18. H. Keck, W. Kuchen, H. Renneberg, J. K. Terlouw and H. C. Visser, *Angew. Chem.*, **103,** 331 (1991); *Angew. Chem. Int. Ed. Engl.*, **30,** 318 (1991).
19. H. Keck, W. Kuchen, W. Kückelhaus, S. Kühlborn and J. K. Terlouw, *Phosphorus Sulfur Relat. Elem.*, **34,** 169 (1987).