

ELECTRONIC STRUCTURES OF $RN(PX_2)_2$ ($R=CH_3$ OR C_6H_5 ; $X=Cl, OCH_3$ OR OC_6H_5) LIGANDS: AN ULTRAVIOLET PHOTOELECTRON SPECTROSCOPIC STUDY*

T. PRADEEP and M.S. HEGDE

*Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012
(India)*

M.S. BALAKRISHNA and S.S. KRISHNAMURTHY

*Inorganic and Physical Chemistry Department, Indian Institute of Science, Bangalore 560 012
(India)*

(First received 5 January 1990; in final form 19 April 1990)

ABSTRACT

Vapour phase HeI photoelectron spectra of the diphosphazane ligands $RN(PX_2)_2$ ($R=CH_3$ or C_6H_5 , $X=Cl, OCH_3$ or OC_6H_5) are presented along with the assignments of bands on the basis of molecular orbital calculations. The spectra are in accordance with the structural studies which indicate multiple bonding in the P-N-P segment. The phosphorus lone pair ionization energy appears to follow the σ donor ability of the ligands.

INTRODUCTION

Ultraviolet photoelectron spectroscopy (UVPES) has emerged as a powerful tool for investigating the electronic structures of molecules in the gas phase [1,2]. The photoelectron spectra of a number of phosphine ligands and their complexes have been reported recently [3-6]. The primary motivation for these studies is to determine the σ and π donor properties of the ligands. Although the conformational and synthetic aspects [7] of the ligands of the type $RN(PX_2)_2$ have received considerable attention, their electronic structures have not been investigated in detail. In this report, we shall present the UVPES of some of the phosphine ligands of the type $RN(PX_2)_2$ where $X=Cl, OCH_3$ or OC_6H_5 and $R=CH_3$ or C_6H_5 , and interpret the results on the basis of molecular orbital (MO) calculations. Attempts have been made to study the changes in the electronic structures of the ligands on complexation.

*Contribution No. 661 from the Solid State and Structural Chemistry Unit.

EXPERIMENTAL

The methods of preparation of the compounds are fully described elsewhere [8]. The UVPE spectra were recorded using a home-built instrument described in detail previously [9]. All the compounds are liquids at room temperature. They were placed in a glass ampoule which was sealed at one end, and the ampoule was directly connected to the spectrometer via a needle valve. The vapours were admitted into the spectrometer at room temperature except for *N*-phenyl compounds where slight heating was necessary to obtain a sufficiently intense photoelectron count rate. Heating up to 200°C was necessary for complexes to obtain sufficient vapour pressure; however, at this temperature significant decomposition occurred and hence attempts to record the spectra of the complexes were unsuccessful. All the spectra were reproducible; in each case the spectrum was recorded at least five times to establish the peak positions. The spectrometer resolution was typically 60 meV at a 15.9 eV ionization energy (IE) and the spectra were calibrated with air.

COMPUTATIONAL DETAILS

Molecular orbital calculations with MNDO and ab initio methods were carried out on $\text{CH}_3\text{N}(\text{PCl}_2)_2$. Only MNDO calculations were performed on $\text{CH}_3\text{N}[\text{P}(\text{OCH}_3)_2]_2$. It has been established, based on electron diffraction, X-ray diffraction and NMR spectral studies, that there could be three possible structures for these kind of molecules with C_s , C_{2v} and $C_{2v'}$ symmetries as defined in ref. 10. Whereas for smaller R and X groups the C_{2v} conformer is the most stable, the C_s conformer predominates for larger R groups. The $C_{2v'}$ structure is not observed experimentally. In order to decide on the most probable structure, we carried out MO calculations in the HF/STO-3G level with full geometry optimization on the model compound $\text{HN}(\text{PCl}_2)_2$. We have assumed the HNP_2 skeleton to be planar since all the experimental observations point towards this conclusion [11,12]. The difference in the total energies of C_s and C_{2v} optimized structures was 2.7×10^{-7} kcal mol⁻¹ with the C_{2v} structure predicted to be more stable. On the basis of the above result, we have considered only the C_{2v} structures in our calculations on $\text{RN}(\text{PX}_2)_2$ molecules. It may be noted that this definition of symmetry is with respect to the P-N-P segment, the atom attached to nitrogen and the phosphorus lone pairs. When a group such as CH_3 is attached to the nitrogen atom, the overall symmetry will be C_s even for this conformer and the spectroscopic assignments have been made on the basis of this overall C_s symmetry. All the structural parameters were fully optimized, the only constraint being the symmetry. Published parameters [13] were used for MNDO calculations. Ab initio calculations were carried out using the STO-3G basis set and the GAUSSIAN-86 program [14].

RESULTS AND DISCUSSION

We shall first consider the photoelectron spectrum of $\text{RN}(\text{PCl}_2)_2$ (Fig. 1). Most of the bands are narrow, with no vibrational fine structure suggesting lone pair ionizations. The first band at 9.7 eV can be immediately assigned to the phosphorus lone pair ionization. This ionization occurs at 10.52 eV in PCl_3 [15] and at 10.95 eV in $\text{CH}_3\text{N}(\text{PF}_2)_2$ [3]. The phosphorus lone pair ionization is expected to be lower than that of PCl_3 and $\text{CH}_3\text{N}(\text{PF}_2)_2$. Further support for this assignment comes from the molecular orbital calculations. An MNDO calculation on $\text{CH}_3\text{N}(\text{PCl}_2)_2$ gives the highest occupied molecular orbital (HOMO) as the nitrogen lone pair. However, the ab initio calculation, although at minimum basis set level, predicts the HOMO to be a phosphorus lone pair. This change in the ordering of the orbitals with two different methods is not altogether unexpected. In these compounds the two phosphorus lone pairs are expected to interact, giving rise to two bands in the photoelectron spectrum. The spectrum of $\text{CH}_3\text{N}(\text{PCl}_2)_2$ reveals the first two bands at 9.71 and 10.33 eV with an approximate intensity ratio of 3:1. This would mean that the two lone pairs reside in the same band. In the case of $\text{CH}_3\text{N}(\text{PF}_2)_2$ also the two phosphorus lone pairs show up only as a single band [3].

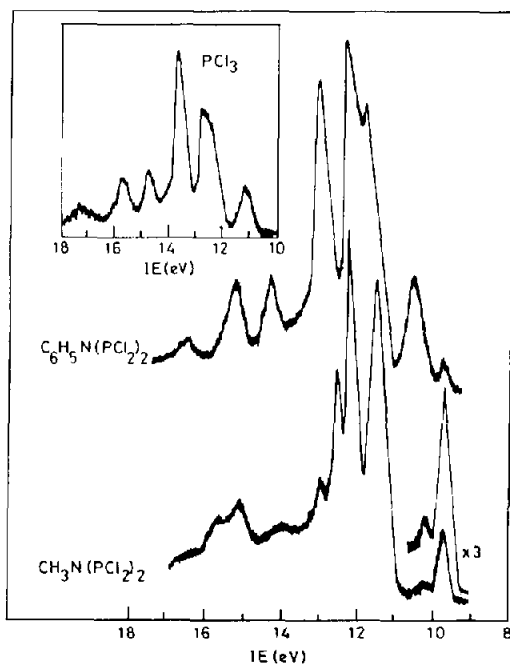


Fig. 1. UV PES of $\text{CH}_3\text{N}(\text{PCl}_2)_2$ and $\text{C}_6\text{H}_5\text{N}(\text{PCl}_2)_2$. The spectrum of PCl_3 is shown in the inset.

The band at 10.33 eV for $\text{CH}_3\text{N}(\text{PCl}_2)_2$ and the band at 10.51 eV for $\text{C}_6\text{H}_5\text{N}(\text{PCl}_2)_2$ are assigned to the nitrogen lone pair ionization. This n_{N} ionization occurs at 11.45 eV for $\text{CH}_3\text{N}(\text{PF}_2)_2$; the shift to higher IEs is due to the higher electronegativity of the $-\text{PF}_2$ group. The STO-3G calculation gives an eigenvalue of 10.07 eV for this orbital. The n_{N} band of $\text{C}_6\text{H}_5\text{N}(\text{PCl}_2)_2$ is broader and has a higher intensity compared with that of $\text{CH}_3\text{N}(\text{PCl}_2)_2$. Presumably this band has contributions from the π orbital ionizations of the phenyl ring. In aniline [2] these ionizations occur at 8.00 and 9.21 eV. As the two hydrogens are replaced by $-\text{PCl}_2$ groups to form $\text{C}_6\text{H}_5\text{N}(\text{PCl}_2)_2$, the ionization energy is expected to increase owing to an inductive effect. We have not been able to identify other phenyl ionizations of $\text{C}_6\text{H}_5\text{N}(\text{PCl}_2)_2$.

The spectra of $\text{RN}(\text{PCl}_2)_2$ have many maxima in the 11–16 eV region. The bands in the 11.4–13 eV region could be due to chlorine lone pair ionizations. An STO-3G calculation shows that there are six chlorine lone pair orbitals in this energy region. The bands at 14.2 and 15.14 eV for the phenyl compound can be assigned to σ_{PCl} by a comparison with the spectrum of PCl_3 . This entire energy region of 11–15 eV has a close similarity to the PCl_3 spectrum (see Fig. 1) suggesting similar ionizations. The broad band in the energy range 15–16 eV for $\text{CH}_3\text{N}(\text{PCl}_2)_2$ and 16–17 eV for $\text{C}_6\text{H}_5\text{N}(\text{PCl}_2)_2$ contains contributions from σ_{NP} , σ_{CN} and σ_{CH_3} ionizations. All the assignments discussed above are listed in Table 1.

We shall now discuss the UVPES of $\text{RN}[\text{P}(\text{OCH}_3)_2]_2$ and $\text{RN}[\text{P}(\text{OC}_6\text{H}_5)_2]_2$ compounds (Fig. 2). The low IE region shows a similarity to the $\text{RN}(\text{PCl}_2)_2$ spectra. This region is particularly interesting for $\text{CH}_3\text{N}[\text{P}(\text{OCH}_3)_2]_2$ because it contains three sharp bands. This is the region where the lone pairs of phosphorus, nitrogen and oxygen are expected to ionize. The first band at 8.39 eV has been assigned to phosphorus lone pair ionization shifted to lower IE by 1.37 eV compared with $\text{CH}_3\text{N}(\text{PCl}_2)_2$. Here also the two phosphorus lone pairs reside in the same band. As the chlorines are replaced by $-\text{OCH}_3$ groups the $-\text{PX}_2$ group becomes less electronegative. This is also very clear from MNDO calculations; the phosphorus lone pair eigenvalues for $\text{CH}_3\text{N}(\text{PCl}_2)_2$ and $\text{CH}_3\text{N}[\text{P}(\text{OCH}_3)_2]_2$ are 12.17 and 10.62 eV, respectively.

The second band at 9.82 eV is assigned to the nitrogen lone pair. This ionization is observed at 9.64 eV for methylamine [2]. The slight increase in the ionization energy can be explained on the basis of the electronegativity of the atoms surrounding nitrogen and the sum of the bond angles around it [4]. The next band has a maximum at 10.96 eV and a shoulder at 11.25 eV. Our MNDO calculation shows that possible ionizations in this region are from n_{O} orbitals. We have assigned the features at 10.96 and 11.25 eV to these orbital ionizations.

The complexity of the energy region (up to 11.25 eV) discussed above for $\text{CH}_3\text{N}[\text{P}(\text{OCH}_3)_2]_2$ increases as we move to $\text{RN}[\text{P}(\text{OC}_6\text{H}_5)_2]_2$ compounds. The phosphorus lone pair ionization for $\text{CH}_3\text{N}[\text{P}(\text{OC}_6\text{H}_5)_2]_2$ is observed at 8.68 eV, shifted to a higher IE than $\text{CH}_3\text{N}[\text{P}(\text{OCH}_3)_2]_2$. This band could also

TABLE 1

MNDO and ab initio computed MOs for $\text{CH}_3\text{N}(\text{PCl}_2)_2$ and the UVPES IEs for $\text{CH}_3\text{N}(\text{PCl}_2)_2$ and $\text{C}_6\text{H}_5\text{N}(\text{PCl}_2)_2$

$\text{CH}_3\text{N}(\text{PCl}_2)_2$						
Experimental IE	Calculated MOs					
	MNDO			Ab initio		
	$-\epsilon$	MO	Character	$-\epsilon$	MO	Character
9.71	12.03	14a'	n_{N}	9.76	25a'	n_{P}
	12.17	11a''	n_{P}	9.78	32a'	n_{P}
10.33	12.26	13a'	n_{P}	10.01	31a'	n_{N}
11.47	13.19	10a''	n_{Cl}	10.91	24a''	n_{Cl}
	13.20	12a'	n_{Cl}	10.94	30a'	n_{Cl}
12.27	13.40	9a''	n_{Cl}	11.11	23a''	n_{Cl}
12.61	13.54	11a'	n_{Cl}	11.42	29a'	n_{Cl}
	13.58	8a''	n_{Cl}	11.47	22a''	n_{Cl}
12.96	13.89	10a'	n_{Cl}	11.79	28a'	n_{Cl}
	14.39	7a''	π_{CH_2}	12.66	21a''	σ_{PCl}
14.00	14.86	9a'	σ_{PCl}	12.74	27a'	σ_{PCl}
	15.13	6a''	π_{CH_2}	13.39	20a''	σ_{PCl}
	15.48	8a'	π_{CH_3}	13.85	19a''	σ_{CN}
15.06	16.66	5a''	σ_{PCl}	15.99	25a'	σ_{NP}
	17.96	4a''	σ_{PCl}	16.67	18a''	σ_{NP}
$\text{C}_6\text{H}_5\text{N}(\text{PCl}_2)_2$						
Experimental IE	Assignment					
9.76	n_{P}					
10.51	$n_{\text{N}} + \pi_{\text{phenyl}}$					
11.71	n_{Cl}					
12.19	n_{Cl}					
12.97	n_{Cl}					
14.23	σ_{PCl}					
15.14	σ_{PCl}					
16.67	$\sigma_{\text{CN}}, \sigma_{\text{NP}}, \sigma_{\text{CC}}$					

contain contributions from π_{phenyl} orbitals since this is the region where these orbitals are expected to ionize. The next band with a maximum of 9.59 eV is due to n_{N} orbital ionization. As we move to $\text{C}_6\text{H}_5\text{N}[\text{P}(\text{OC}_6\text{H}_5)_2]_2$, this region becomes more complex. We assign the first band to the π_{phenyl} orbital ionization. The shoulder at the higher IE side at 8.60 eV has been assigned to the n_{P} orbital ionization. The next band has two well-resolved maxima at 9.25 and 9.65 eV which may be assigned to n_{N} and n_{O} ionizations, respectively. An MNDO calculation shows that the next higher energy orbitals are σ_{PO} and π_{CH_3} . We

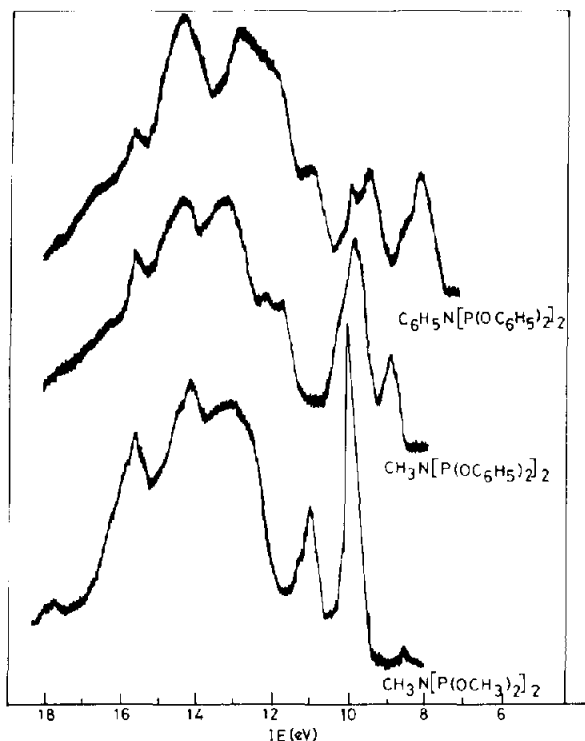


Fig. 2. UV PES of $\text{CH}_3\text{N}[\text{P}(\text{OCH}_3)_2]_2$, $\text{CH}_3\text{N}[\text{P}(\text{OC}_6\text{H}_5)_2]_2$ and $\text{C}_6\text{H}_5\text{N}[\text{P}(\text{OC}_6\text{H}_5)_2]_2$.

assign the next feature at 12.90 eV in the $\text{CH}_3\text{N}[\text{P}(\text{OCH}_3)_2]_2$ spectrum to these orbital ionizations.

The MNDO calculation shows that the orbitals expected to ionize in the next higher energy region are σ_{CO} , σ_{CH_3} and σ_{CN} . Even though the spectra show remarkable similarity, precise assignments are not possible as the features are very complex. All the assignments discussed above are listed in Table 2.

The apparent low intensity of the n_{N} band in the $\text{RN}(\text{PCl}_2)_2$ compounds discussed above may arise as a result of a bonding interaction between this orbital and the vacant d orbitals of phosphorus. Structural data on diphosphazanes and their complexes indicate a considerable degree of multiple bonding in the P–N–P segments [16]. The nature of this multiple bonding has been controversial. However, planarity of nitrogen and the short P–N bond lengths found from the X-ray crystallographic investigations are best accounted for in terms of a three-centre π -island model [17]. We have made a theoretical examination of this aspect of multiple bonding in the P–N–P segment. Computations have been carried out on a model compound $\text{HN}(\text{PH}_2)_2$ with full geometry optimization on the C_s symmetry at four different basis set levels, namely STO-3G, 3-21G, 3-21G* and 3-21G** in the Hartree-Fock approxi-

TABLE 2

MNDO computed MOs for $\text{CH}_3\text{N}[\text{P}(\text{OCH}_3)_2]_2$ and the UVPES data for $\text{CH}_3\text{N}[\text{P}(\text{OCH}_3)_2]_2$, $\text{CH}_3\text{N}[\text{P}(\text{OC}_6\text{H}_5)_2]_2$ and $\text{C}_6\text{H}_5\text{N}[\text{P}(\text{OC}_6\text{H}_5)_2]_2$

$\text{CH}_3\text{N}[\text{P}(\text{OCH}_3)_2]_2$		
Experimental IE	MNDO computed MOs	
	$-\epsilon$ MO Character	
8.39	10.30 $20a'$ n_{N}	
9.82	{ 10.62 $17a''$ n_{P}	
		10.72 $19a'$ n_{P}
10.96	{ 11.42 $16a''$ n_{O}	
		11.55 $15a''$ n_{O}
11.25	{ 11.56 $18a'$ n_{O}	
		11.79 $17a'$ n_{O}
12.90	{ 12.66 $14a''$ σ_{PO}	
		12.81 $16a'$ π_{CH_3}
		12.81 $13a''$ π_{CH_3}
13.97	{ 13.75 $15a'$ σ_{CO}	
		14.08 $12a''$ σ_{CH_3}
		14.35 $14a'$ σ_{CN}
15.53	{ 15.24 $11a''$ σ_{CO}	
		15.48 $13a'$ σ_{CO}
		15.50 $10a''$ σ_{CH_3}
		15.51 $12a'$ σ_{CH_3}

$\text{CH}_3\text{N}[\text{P}(\text{OC}_6\text{H}_5)_2]_2$	Assignment
Experimental IE	
8.68	$n_{\text{P}} + \pi_{\text{phenyl}}$
9.59	n_{N}
11.53	n_{O}
12.05	n_{O}

$\text{C}_6\text{H}_5\text{N}[\text{P}(\text{OC}_6\text{H}_5)_2]_2$	Assignment
Experimental IE	
8.00	π_{phenyl}
8.60	n_{P}
9.25	n_{N}
9.65	n_{O}
10.85	n_{O}

mation. The relevant results are summarized in Table 3. The most probable structure in all these cases turns out to be one in which the sum of bond angles around nitrogen is 360° . This result implies considerable π interaction between the nitrogen lone pair and the d_π orbitals of phosphorus. In fact, as we move from 3-21G to 3-21G* (i.e. adding one d function on phosphorus atoms),

TABLE 3

Computed parameters of $\text{HN}(\text{PH}_2)_2$

Parameter	STO-3G	3-21G	3-21G*	3-21G**
Total energy (Hartree)	-730.45944	-735.00406	-735.23530	-735.25785
Sum of bond angles around nitrogen ($^\circ$)	359.99	360.00	360.00	360.00
$r_{\text{N-P}}$ (Å)	1.72	1.75	1.70	1.70
$\angle \text{P-N-P}$ ($^\circ$)	123.99	122.99	122.62	122.81
Charge on nitrogen (e)	-0.66	-1.20	-0.99	-0.89
Charge on phosphorus (e)	+0.52	+0.58	+0.40	+0.48
Phosphorus lone pair ionization energy (eV)	7.67	10.07	10.01	10.00

the negative charge on nitrogen decreases by 0.20e while the positive charge on phosphorus atoms decreases by 0.18e. This is evident in the phosphorus lone pair eigenvalues – a gradual decrease from 10.07 (3-21G) to 10.01 (3-21G*) to 10.00 (3-21G**) – even though the magnitude is small. Structurally this effect, namely the involvement of phosphorus *d* orbitals in bonding, results in a decrease in the N–P bond lengths and P–N–P angle as one goes from 3-21G to 3-21G*.

It has been shown that the lone pair orbital ionization energy is inversely proportional to the σ -donor ability [5]. From data presented in Tables 1 and 2, it is clear that the σ -donor ability would be in the order $\text{C}_6\text{H}_5\text{N}[\text{P}(\text{OC}_6\text{H}_5)_2]_2 \sim \text{CH}_3\text{N}[\text{P}(\text{OCH}_3)_2]_2 > \text{CH}_3\text{N}[\text{P}(\text{OC}_6\text{H}_5)_2]_2 > \text{C}_6\text{H}_5\text{N}(\text{PCl}_2)_2 \sim \text{CH}_3\text{N}(\text{PCl}_2)_2$.

ACKNOWLEDGEMENTS

We thank the Department of Science and Technology, Government of India, New Delhi, for supporting this research. One of the authors (T.P.) is grateful to the Council of Scientific and Industrial Research, New Delhi, for a research fellowship.

REFERENCES

- 1 C.N.R. Rao, P.K. Basu and M.S. Hegde, *Appl. Spectrom. Rev.*, 15 (1979) 193.
- 2 K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki and S. Iwata, *Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules*, Halsted Press, New York, 1981.
- 3 M.V. Andreocci, C. Cauletti, C. Furlani and R. Bruce King, *Inorg. Chem.*, 18 (1979) 954.
- 4 A.H. Cowley, M. Lattman, P.M. Stricklen and J.G. Verkade, *Inorg. Chem.*, 21 (1982) 543.
- 5 A.H. Cowley, R.A. Kemp, M. Lattman and M.L. McKee, *Inorg. Chem.*, 21 (1982) 85.

- 6 P.C. Knuppel, G. Pawelke, H. Sommer, O. Stelzer, H. Oberhammer, M.F. Lappert, R.J. Suffolk and J.D. Watts, *J. Organomet. Chem.*, 355 (1988) 55.
- 7 M.L. Thompson, A. Tarassoli, R.C. Haltiwanger and A.D. Norman, *J. Am. Chem. Soc.*, 103 (1981) 6770.
- 8 M.S. Balakrishna, Ph.D. Thesis, Indian Institute of Science, Bangalore, India, 1989.
- 9 V. Jayaram and M.S. Hegde, *Proc. Indian Acad. Sci. (Chem. Sci.)*, 97 (1986) 617.
- 10 H.-J. Chen, J.M. Barendt, R.C. Haltiwanger, T.G. Hill and A.D. Norman, *Phosphorus and Sulfur*, 26 (1986) 155.
- 11 R. Keat, L.M. Muir and D.S. Rycroft, *J. Chem. Soc. Dalton Trans.*, (1981) 2192.
- 12 A. Tarassoli, R.C. Haltiwanger, T.G. Hill and A.D. Norman, *Inorg. Chem.*, 21 (1982) 2684.
- 13 M.J.S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 99 (1977) 4907.
M.J.S. Dewar and M.L. McKee, *J. Am. Chem. Soc.*, 99 (1977) 5231.
- 14 M. Frisch, J.S. Binkley, H.B. Schlegel, K. Raghavachari, C.F. Melius, R.L. Martin, J.J.P. Stewart, F.W. Bobrowitz, C.M. Rohlfing, L.R. Khan, D.J. Defrees, R. Seeger, R.A. Whiteside, D.J. Fox, E.M. Fleuder and J.A. Pople, *GAUSSIAN-86*, Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA, 1984.
- 15 A.W. Potts and W.C. Price, *Proc. R. Soc. London Ser. A*, 326 (1972) 181.
- 16 E. Hedberg, L. Hedberg and K. Hedberg, *J. Am. Chem. Soc.*, 96 (1974) 4417.
- 17 H.G. Heal, *The Inorganic Heterocyclic Chemistry of Sulfur, Nitrogen and Phosphorus*, Academic Press, London, 1980, pp. 186 and 243.