JOURNAL OF MATERIALS SCIENCE **39** (2004) 3201–3202

XPS determination of the binding energies of phosphorus and nitrogen in phosphazenes

P. VASSILEVA*, V. KRASTEV, L. LAKOV, O. PESHEV
Bulgarian Academy of Sciences, Institute of General and Inorganic Chemistry, Acad. G. Bonchev Str., Block 11, Sofia 1113, Bulgaria
E-mail: adsor@svr.igic.bas.bg

Phosphazenes are compounds in which repeating units -N = P(L_1, L_2)— are arranged in cyclic or linear structures including polymeric ones. Representatives are numerous due to the possibility of varying the ligands L_1 and L_2. This determines the wide spectrum of useful properties of the phosphazenes such as elasticity, thermal stability, biological compatibility etc. and, a consequence there is enhanced interest in these compounds [1–3]. Although the literature on phosphazenes is impressive [4–6], it seems that the nitrogen-phosphorus bond and the effect of substituents on this bond are not yet sufficiently investigated [7].

Dake *et al.* [8] have used XPS and Raman spectroscopy to investigate the effect of electron-accepting substituents on the distribution of the electron charge in the nitrogen-phosphorus chains, comparing cyclic trimers and linear polymers when substitution is homogeneous ($L_1 = L_2$). The results of these authors confirm the assumptions based on theoretical considerations, according to which the N—P bond is strongly polarized, this effect being more pronounced with polymers rather than with cyclic trimers. As to the influence of substituents on the binding energies of nitrogen and phosphorus, it is found to depend not only on the electromeric effect of the substituent but also on the conformation of the phosphazene molecule.

The present paper is aimed at determining the binding energies of nitrogen and phosphorus in some cyclic phosphazene molecules in the cases of identical ($L_1 = L_2$) or different ($L_1 \neq L_2$) substituents as well as in linear polymers having electron-donating or electron-accepting ligands.

The following 7 phosphazenes were investigated: Cyclic trimers (No1 hexachlorocyclotriphosphazene $(NPCl_2)_3$, No2 cis-bis-(dimethylamino)-tetrachlorocyclotriphosphazene $N_3P_3[N(CH_3)_2]Cl_4$, No3 bis-(dimethylamino)-bis-(trifluorethoxy)-dichlorocyclotriphosphazene and $N_3P_3[N(CH_3)_2]_2(OCH_2CF_3)_2Cl_2)$, Cyclic tetramert (No4 octabutylaminocyclotetraphosphazene $N_4P_4[NH(C_4H_9)]_8)$, Cyclomatrix polymer (No5 phospham $[(NPNH)_3]_n$) and Linear polymers (No6 poly-bis-(butylamino)phosphazene $\{NP[NH(C_4H_9)]_2\}_n$, No7 poly-bis-(trifluoroethoxy)-phosphazene $[NP(OCH_2CF_3)_2]_n$).

The compounds were prepared according to usual methods [9, 10]. Elemental analysis, IR and ^{31}P-NMR spectra, X-ray phase analysis and measurement of the melting temperatures of the above phosphazenes were used for their characterization [11].

All XPS spectra were obtained using a Perkin Elmer Physical Electronics Model 560 Auger/XPS equipped with a double-pass cylindrical mirror analyzer. A Mg K_α anode (1253.6 eV) was applied. The spectrophotometer was calibrated with the Cu $2p_{3/2}$ line with an energy $E = 932.67 \pm 0.05$ eV. The indicator used for measuring the sample charge was the C 1s line of the hydrocarbons at 284.6 eV.

The phosphazenes (excepting phospham) were introduced to the holder as diluted solutions, which were subjected to evaporation. In order to minimize decomposition caused by heat coming from the X-ray source, in the case of volatile samples the holder was cooled with liquid nitrogen.

The XPS measurements were used for determining the composition of the sample surfaces and the electron binding energies of phosphorus and nitrogen. The latter give information on the N—P bond and the effect of the substituents.

The compositions of results are given in Table I. It is evident that the stoichiometry of the surface is close to that in the bulk except for a small C, O and Cl excess in some cases probably due to synthesis processes. The P:N ratio is in all cases close to its theoretical value.

The binding energies obtained from the P_{2p} and N_{1s} photolines of the corresponding phosphazene compound and the effective charges of P and N atoms are presented in Table II.

It is known [12, 13] that electron density distribution in the P—N bonds is strongly polarized and the charge of the atoms themselves correlates with electronegativity of the substituents at the P atom. With inhomogeneous substitution (as it is for cyclophosphazenes No2 and No3), specific segments of the molecule can differ in their total electron charge because bond lengths and angles in them can be essentially different.

The data in Table II seem to agree with this picture. The electronegativity of the substituents decreases in the sequence:

$$Cl > OCH_2CF_3 \gg N(CH_3)_2 > NHC_4H_9.$$

Thus, replacement of the electron-accepting substituent Cl by the electron-donating $N(CH_3)_2$ decreases the binding energy of the 2p electrons in the corresponding

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*Author to whom all correspondence should be addressed.

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TABLE I Surface composition of the samples (at.%)

No		P	N	O	C	Cl	F
1	Theor.	26.7	12.1	–	–	61.2	–
	Exper.	20.2	8.7	26.3	–	45.6	–
2	Theor.	25.5	19.2	–	13.1	38.9	–
	Exper.	18.6	12.8	–	37.4	31.2	–
3	Theor.	18.8	19.6	6.5	20.2	14.9	23.1
	Exper.	9.8	10.3	26.2	30.1	6.6	16.9
4	Theor.	16.4	22.2	–	50.8	–	–
	Exper.	10.1	18.6	–	63.0	4.8	–
5	Theor.	51.7	46.7	–	–	–	–
	Exper.	58.1	36.0	–	–	5.3	–
6	Theor.	16.4	22.2	–	50.8	–	–
	Exper.	8.2	14.3	20.0	45.1	–	–
7	Theor.	12.8	5.8	13.1	19.8	–	46.9
	Exper.	16.4	6.2	10.6	25.6	–	41.9

TABLE II Binding energies and effective charges of phosphorus and nitrogen in phosphazenes

No	E_B (P_{2p})(eV)	q_P (a.u.)	E_B (N_{1s})(eV)	q_N (a.u.)
1	134.6	+1.80	398.5	−0.41
2	134.2	+1.56	398.5	−0.41
	132.8	+0.72	400.2	−0.17
3	134.0	+1.44	398.3	−0.44
	133.0	+0.84	399.3	−0.30
4	132.0	+0.24	397.8	−0.51
			398.9	−0.36
5	132.4	+0.48	399.6	−0.26
			400.3	−0.16
6	132.0	+0.24	398.2	−0.46
			399.8	−0.23
7	135.0	+2.04	399.0	−0.34

phosphorus atom. This is the effect of the lone electron pair in the dimethylamino group (the so called +M effect). With the samples of inhomogeneous substitution (No2 and No3), two values are registered which correspond to the two different P atoms: one with two identical chlorine or fluorethoxy substituents, and the other, with one chlorine and one dimethylamine substituent (sample No2 is nongeminal isomer). The decrease in binding energy is most pronounced when the replacement of the chlorine ligands by amino groups is complete (sample No4). The small difference in the cases PCl_2 and $P(OCH_2CF_3)_2$ should indicate that the substituents Cl and OCH_2CF_3 do not differ much in electronegativity.

All samples having in their structure both endo- (i.e., from the phosphazene chain) and exo-(i.e., from the substituents) nitrogen atoms display two binding energy values for the 1s electrons of the nitrogen atoms; these are samples No2 through to No6. And this is not the case with samples No1 and No7 which have but endo-nitrogen atoms. Taking into account that an increase in the electron density leads to a decrease in the binding energy, one could assume that of the two values mentioned the lower one corresponds to the endo-nitrogen atoms while the higher one belongs to exo-nitrogen atoms (those of the amino groups). This assumption is in agreement with an experimentally established fact, which is well known: when amino groups are present as substituents at the P atoms, the N atoms on the phosphazene chain are the sites of protonation. The shift of the electron density towards the endo-nitrogen atoms is an induction effect of the substituents.

The data for the polymer samples (No6 and No7) exhibit the same trends as those with the cyclic ones: replacement of the electron-donating group (sample No6) by an electron-accepting-group (sample No7) increases the binding energy of the electrons in both phosphorus and endo-nitrogen atoms. The values for the cyclomatrix polymer (No5) are close to those for the linear polyaminophosphazene (No6).

Table II shows the effective charges of the P and N atoms as calculated using the empirical equations [14]:

$$E_B(P) = 1.67q_P + 131.6$$

$$E_B(N) = 7q_N + 401.4$$

where E_B is the binding energy in eV and q (a.u.) stands for the effective atomic charge in atomic units.

As known, this type of calculations have a comparative rather than absolute meaning with respect to the effective charges. The values presented confirm that the N—P bond in phosphazenes has, to a large extent, an ionic character.

Acknowledgment

We wish to thank Dr. P. Stefanov for helpful discussion of the XPS spectra.

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Received 11 August
and accepted 24 November 2003