

## Ab initio study of the structure of poly[di(phenoxy)thionylphosphazene]

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Received 17 October 1994; accepted 24 November 1994

### Abstract

The stable structure of poly[(diphenoxy)thionylphosphazene] single chains was modeled with a small molecular compound consisting of one repeat unit of the polymer. The geometrical parameters of the nonplanar “trans–cis” conformations of these molecular models were obtained using the ab initio molecular orbital theory. The 3-21G\* basis set was used in the computation. It was found that the phenoxy groups are positioned approximately parallel to the backbone and the groups located on adjacent phosphorus atoms point in opposite directions. The bonding of the short chain segment exhibits a “single–double” alternating pattern along the backbone. The charge distribution along the backbone is highly polarized. The total dipole moment is oriented parallel to the backbone and is equal to 6.75 debye. The molecular diameter of this compound is estimated to be 13 Å.

### 1. Introduction

Poly[(diphenoxy)thionylphosphazene] [(NSOCl)-(NP(OPh)<sub>2</sub>)<sub>n</sub>] (where Ph denotes a phenyl group) is an inorganic polymer [1] that belongs to the class of polymers referred to as poly[(aryloxy)thionylphosphazene]s. These polymers have many potential uses as elastomers which, due to the presence of the hydrophobic aryloxy side groups, are stable to moisture [2,3]. The first step in the synthesis of a poly[(diphenoxy)thionylphosphazene] involves a thermal ring opening of a cyclic thionylphosphazene [(NSOCl)(NPCl<sub>2</sub>)<sub>n</sub>]. The resultant polymerization produces a chlorinated poly(thionylphosphazene) [(NSOCl)(NPCl<sub>2</sub>)<sub>n</sub>]

[1–3]. A subsequent reaction of [(NSOCl)(NPCl<sub>2</sub>)<sub>n</sub>] with sodium phenoxide yields a poly[(diphenoxy)thionylphosphazene]. In this reaction only the chlorine atoms on phosphorus atoms are replaced by phenoxy groups; the sulfur–chlorine bonds are retained. Poly[(diphenoxy)thionylphosphazene]s, in contrast to poly[(dichloro)thionylphosphazene]s, form hydrolytically stable elastomers. They are characterized by a glass transition temperature ( $T_g$ ) of 10°C which is 56° higher than  $T_g$  for chlorine substituted poly(thionylphosphazene)s (PTPs) and 16°C higher than  $T_g$  for the classical poly[(diphenoxy)phosphazene]s.

In this work we investigate the structure and bonding of poly[(diphenoxy)thionylphosphazene] with the use of a model compound. The model compound consists of one repeat unit. The

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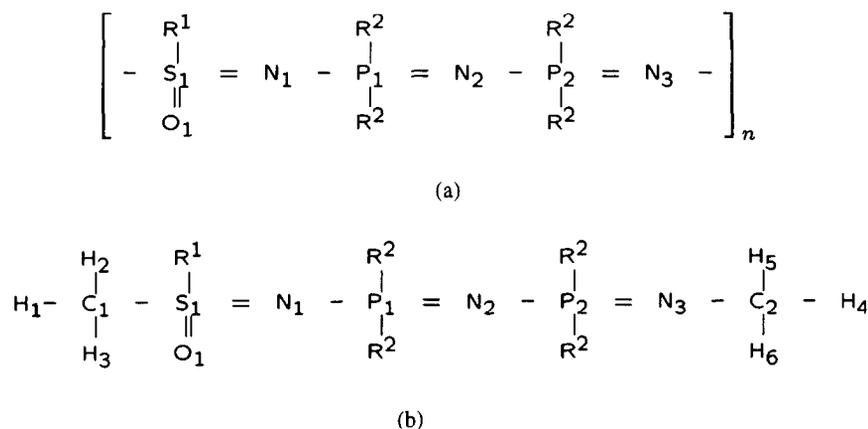


Fig. 1. (a) The monomer unit of a poly[(thionyl)phosphazene] chain. (b) The structure of the model compound ( $\text{R}^1$  is Cl and  $\text{R}^2$  is OPh).

relationship between the polymer and the model compound studied is illustrated in Fig. 1. The structure of the model compound was obtained using the ab initio molecular orbital method [4,5]. The results of an ab initio investigation for hydrogen, chlorine and methyl substituted PTP model compounds have recently been presented [6,7]. Two basis sets were used in these fully geometry optimized computations: 3-21G\* and 6-31G\*. We have found that the 3-21G\* and 6-31G\* basis set calculations produced comparable results [6,7]. However, in the case of chlorinated PTP, the calculations have shown large discrepancies in the SNP and PNP bond angles. The crystallographic data obtained from X-ray scattering experiments on chlorinated polyphosphazenes [8,9] tend to support the smaller SNP and PNP bond angles (in the range 129–146°) produced by the 6-31G\* basis set computation. It should be noted that the same crystallographic experiments performed on the poly(aryloxyphosphazene)s show that the PNP bond can also be quite large (138–142°) [9]. For bulky substituents such as a phenoxy group, use of the 6-31G\* basis set would result in a very lengthy computation (the 3-21G\* basis set computation took of the order of 3–4 months of CPU time on RISK workstations), and thus our initial calculations were performed with the 3-21G\* basis set only.

Based on our previous investigations [6,7] and the X-ray studies performed on the closely related polymers, polyphosphazenes [1] (which showed

that the nearly planar trans–cis structure is most stable for these polymers), we expect that the final fully geometry-optimized structure will be a non-planar trans–cis conformation. In addition, our initial rigid rotor calculations for the model compounds [10] clearly show a global minimum to be a nonplanar trans–cis conformation, in agreement with the experimental observations. Thus in order to minimize our computation time, the starting geometry of the phenoxy substituted model compound was taken to be trans–cis conformation. The deviations from planarity in the optimized structure are discussed below.

In Section 3 the structure, bonding and charge distribution in the model compound and their implications in terms of material properties are discussed.

## 2. Method of calculation

Some initial calculations were performed on the HP 755 workstation at the Department of Chemistry, University of Toronto, using the ab initio molecular orbital program GAUSSIAN 90 [4]. Most of the computations were performed on the Crimson SGI workstation at the Department of Physics, Memorial University of Newfoundland, using the GAUSSIAN 92 [5] version of the program. The geometry optimization was performed at the closed-shell, restricted Hartree–Fock SCF level of theory, using the 3-21G\* basis set. The 3-21G\*

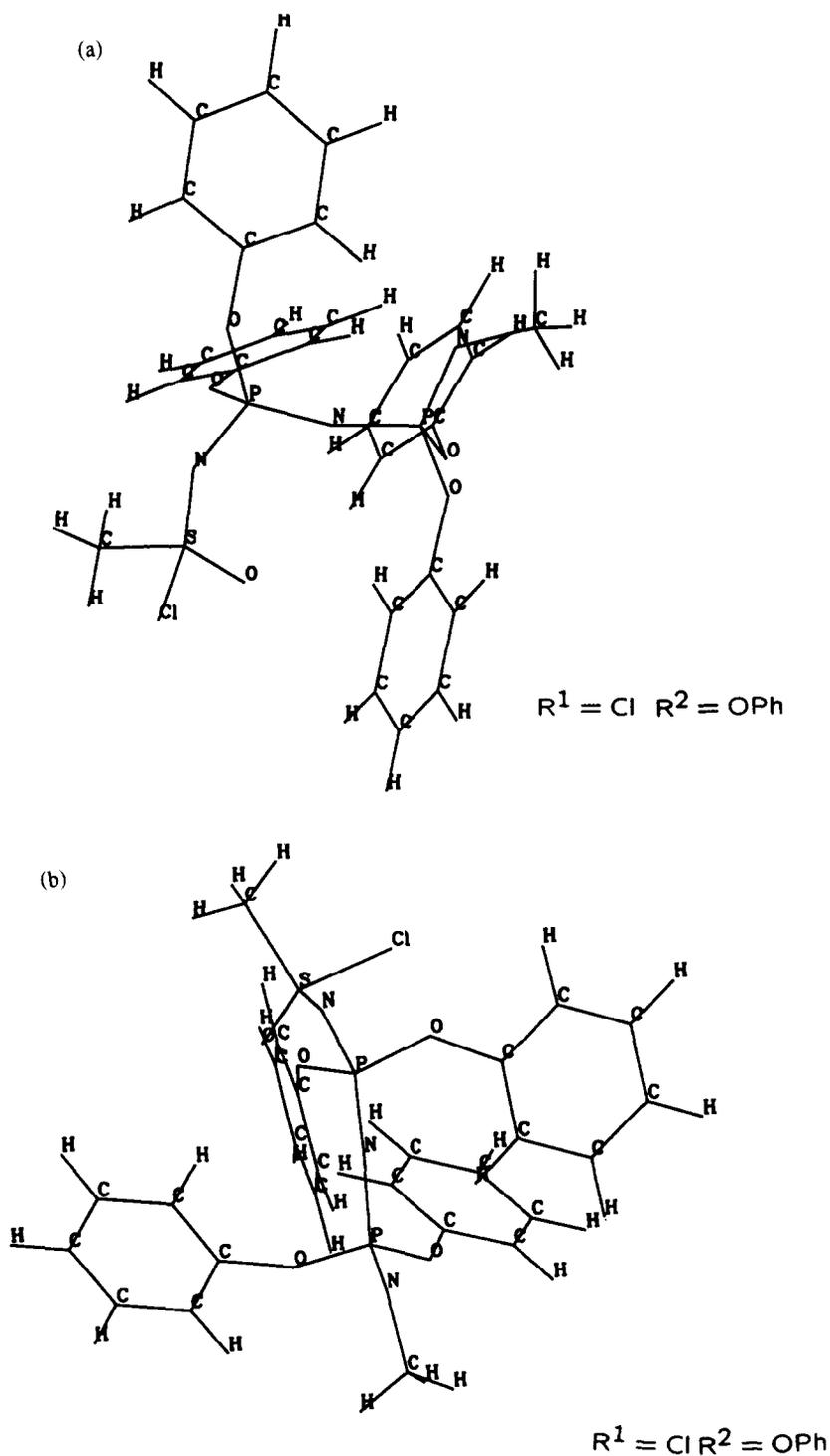


Fig. 2. (a) Stick figure of the model compound ( $R^1$  is Cl and  $R^2$  is OPh) with the plane formed by P–N–P atoms parallel to the paper and (b) with the P–N–P plane perpendicular to the paper. The geometries plotted correspond to the results obtained using the 3-21G\* basis set.

Table 1

Bond lengths, bond angles and dihedral angles for the model compound, obtained using the 3-21G\* basis set in the restricted Hartree-Fock computation [4,5]

Bond	(Å)	Bond angle	(deg.)	Dihedral angle	(deg.)
S <sub>1</sub> -O <sub>1</sub>	1.436	N <sub>1</sub> S <sub>1</sub> O <sub>1</sub>	122.230	P <sub>1</sub> N <sub>1</sub> -S <sub>1</sub> O <sub>1</sub>	-36.716
N <sub>1</sub> -S <sub>1</sub>	1.463	P <sub>1</sub> N <sub>1</sub> S <sub>1</sub>	148.463	N <sub>2</sub> P <sub>1</sub> -N <sub>1</sub> S <sub>1</sub>	7.155
P <sub>1</sub> -N <sub>1</sub>	1.615	N <sub>2</sub> P <sub>1</sub> N <sub>1</sub>	114.945	P <sub>2</sub> N <sub>2</sub> -P <sub>1</sub> N <sub>1</sub>	150.663
N <sub>2</sub> -P <sub>1</sub>	1.505	P <sub>2</sub> N <sub>2</sub> P <sub>1</sub>	166.253	N <sub>3</sub> P <sub>2</sub> -N <sub>2</sub> P <sub>1</sub>	20.289
P <sub>2</sub> -N <sub>2</sub>	1.575	N <sub>3</sub> P <sub>2</sub> N <sub>2</sub>	113.636	ClS <sub>1</sub> -N <sub>1</sub> O <sub>1</sub>	124.753
N <sub>3</sub> -P <sub>2</sub>	1.523	ClS <sub>1</sub> N <sub>1</sub>	108.864	C <sub>1</sub> S <sub>1</sub> -N <sub>1</sub> Cl	107.109
Cl-S <sub>1</sub>	2.033	C <sub>1</sub> S <sub>1</sub> N <sub>1</sub>	107.281	O <sub>2</sub> P <sub>1</sub> -N <sub>1</sub> N <sub>2</sub>	125.967
C <sub>1</sub> -S <sub>1</sub>	1.751	O <sub>2</sub> P <sub>1</sub> N <sub>1</sub>	100.973	O <sub>3</sub> P <sub>1</sub> -N <sub>1</sub> O <sub>2</sub>	107.956
O <sub>2</sub> -P <sub>1</sub>	1.572	O <sub>3</sub> P <sub>1</sub> N <sub>1</sub>	103.752	O <sub>4</sub> P <sub>2</sub> -N <sub>2</sub> N <sub>3</sub>	126.421
O <sub>3</sub> -P <sub>1</sub>	1.572	O <sub>4</sub> P <sub>2</sub> N <sub>2</sub>	108.810	O <sub>5</sub> P <sub>2</sub> -N <sub>2</sub> O <sub>4</sub>	104.641
O <sub>4</sub> -P <sub>2</sub>	1.592	O <sub>5</sub> P <sub>2</sub> N <sub>2</sub>	105.001	H <sub>1</sub> C <sub>1</sub> -S <sub>1</sub> O <sub>1</sub>	50.738
O <sub>5</sub> -P <sub>2</sub>	1.614	H <sub>2</sub> C <sub>1</sub> S <sub>1</sub>	109.576	H <sub>2</sub> C <sub>1</sub> -S <sub>1</sub> H <sub>1</sub>	-119.295
H <sub>1</sub> -C <sub>1</sub>	1.080	H <sub>3</sub> C <sub>1</sub> S <sub>1</sub>	106.905	H <sub>3</sub> C <sub>1</sub> -S <sub>1</sub> H <sub>1</sub>	122.062
H <sub>2</sub> -C <sub>1</sub>	1.083	H <sub>3</sub> C <sub>1</sub> S <sub>1</sub>	109.383	C <sub>2</sub> N <sub>3</sub> -P <sub>2</sub> N <sub>2</sub>	170.003
H <sub>3</sub> -C <sub>1</sub>	1.079	C <sub>2</sub> N <sub>3</sub> P <sub>2</sub>	129.817	H <sub>4</sub> C <sub>2</sub> -N <sub>3</sub> P <sub>2</sub>	-49.364
C <sub>2</sub> -N <sub>3</sub>	1.467	H <sub>4</sub> C <sub>2</sub> N <sub>3</sub>	112.494	H <sub>5</sub> C <sub>2</sub> -N <sub>3</sub> H <sub>4</sub>	121.480
H <sub>4</sub> -C <sub>2</sub>	1.087	H <sub>5</sub> C <sub>2</sub> N <sub>3</sub>	112.720	H <sub>6</sub> C <sub>2</sub> -N <sub>3</sub> H <sub>4</sub>	-119.488
H <sub>5</sub> -C <sub>2</sub>	1.089	H <sub>6</sub> C <sub>2</sub> N <sub>3</sub>	108.917	C <sub>3</sub> O <sub>2</sub> -P <sub>1</sub> N <sub>1</sub>	168.465
H <sub>6</sub> -C <sub>2</sub>	1.082	C <sub>3</sub> O <sub>2</sub> P <sub>1</sub>	132.428	C <sub>4</sub> C <sub>3</sub> -O <sub>2</sub> P <sub>1</sub>	45.537
C <sub>3</sub> -O <sub>2</sub>	1.410	C <sub>9</sub> O <sub>3</sub> P <sub>1</sub>	136.712	C <sub>9</sub> O <sub>3</sub> -P <sub>1</sub> N <sub>1</sub>	145.836
C <sub>9</sub> -O <sub>3</sub>	1.404	C <sub>15</sub> O <sub>4</sub> P <sub>2</sub>	135.012	C <sub>10</sub> C <sub>9</sub> -O <sub>3</sub> P <sub>1</sub>	15.672
C <sub>15</sub> -O <sub>4</sub>	1.378	C <sub>21</sub> O <sub>5</sub> P <sub>2</sub>	126.298	C <sub>15</sub> O <sub>4</sub> -P <sub>2</sub> N <sub>2</sub>	47.691
C <sub>21</sub> -C <sub>5</sub>	1.396	C <sub>4</sub> C <sub>3</sub> O <sub>2</sub>	121.791	C <sub>16</sub> C <sub>15</sub> -O <sub>4</sub> P <sub>2</sub>	194.921
		C <sub>5</sub> C <sub>3</sub> O <sub>2</sub>	116.270	C <sub>21</sub> O <sub>5</sub> -P <sub>2</sub> N <sub>2</sub>	63.251
		C <sub>10</sub> C <sub>9</sub> O <sub>3</sub>	123.141	C <sub>22</sub> C <sub>21</sub> -O <sub>5</sub> P <sub>2</sub>	72.393
		C <sub>11</sub> C <sub>9</sub> O <sub>3</sub>	115.306		
		C <sub>16</sub> C <sub>15</sub> O <sub>4</sub>	116.267		
		C <sub>17</sub> C <sub>15</sub> O <sub>4</sub>	123.073		
		C <sub>22</sub> C <sub>21</sub> O <sub>5</sub>	120.198		
		C <sub>23</sub> C <sub>21</sub> O <sub>5</sub>	118.884		

basis set is the smallest one which includes *d* atomic orbitals, but only for the second row elements. The program used employs a gradient method for the geometry optimization.

### 3. Results and discussion

In this section we discuss the results of the fully geometry-optimized computation for the model compound with substituents R<sup>1</sup> is Cl and R<sup>2</sup> is OPh (Fig. 1). The geometrical parameters (that is the bond lengths, bond angles and dihedral angles) for the model compound (Fig. 2) are given in Table 1. (The software package BIOSYM [11] was used to generate Fig. 2.) The net charges

on the atoms in the molecule and the total dipole moment are given in Tables 2 and 3.

#### 3.1. Structure of the model compound

Many structural features of the model compound can be attributed to its underlying asymmetry which is a result of both the presence of sulfur at one end of the model compound and the fact that the substituents on the sulfur atom are different from each other and from those attached to the phosphorus atoms. As in previous studies [6,7], the alternating "single-double" bond-length pattern is observed along the chain backbone. The lengths of the N<sub>1</sub>-S<sub>1</sub>, P<sub>1</sub>-N<sub>1</sub>, N<sub>2</sub>-P<sub>1</sub>, P<sub>2</sub>-N<sub>2</sub> and N<sub>3</sub>-P<sub>2</sub> bonds are 1.46, 1.62, 1.51, 1.58 and 1.52 Å,

respectively. In general, it has been found that, in computations with 6-31G\* basis set, the bond lengths are longer than those obtained in 3-21G\* basis set computations [6,7]. We would expect that for the model compound investigated in this work the 6-31G\* basis set computation would result in an increase in the above bond distances of approximately 0.02 Å.

The difference between the “single” and “double” N–P bonds are larger between bonds located closer to sulfur than between the corresponding bonds located farther away. We suspect that this decreasing trend is due to end effects and would possibly disappear if the end methyl group connected to N<sub>3</sub> was replaced by another sulfur atom and its corresponding side groups. However, it is highly unlikely that the alternating pattern would vanish. The unequal (alternating) bond lengths clearly indicate that the valence charge is at least partially localized along the backbone in the model compound. However, the “single” and “double” bonds are typically shorter than the corresponding values in smaller molecules, suggesting that charge delocalization is also present (see refs. 8, 9 and 13). For example the single P–N bonds found in compounds like NaH<sub>3</sub>NPO<sub>3</sub> and (NH<sub>2</sub>)<sub>3</sub>PBH<sub>3</sub> [9] are 1.76 and 1.65 Å, respectively (there is a significant amount

Table 2

Comparison of net charges obtained from the Mulliken population analysis [12] for the repeat unit using the 3-21G\* basis set (R<sup>1</sup> is Cl and R<sup>2</sup> is OPh)

Element or group	Net atomic charge
O <sub>1</sub>	–0.54
S <sub>1</sub>	+1.31
N <sub>1</sub>	–0.89
P <sub>1</sub>	+1.77
N <sub>2</sub>	–1.02
P <sub>2</sub>	+1.75
N <sub>3</sub>	–0.83
Cl <sub>1</sub>	–0.16
O <sub>2</sub> Ph <sub>1</sub>	–0.36
O <sub>3</sub> Ph <sub>2</sub>	–0.35
O <sub>4</sub> Ph <sub>3</sub>	–0.42
O <sub>5</sub> Ph <sub>4</sub>	–0.42
Methyl <sub>1</sub>	–0.01
Methyl <sub>2</sub>	+0.17

Table 3

x, y and z components (see text for description) and the total magnitude of the dipole moment for the model compound (R<sup>1</sup> is Cl and R<sup>2</sup> is OPh)

Component	Dipole (debye)
x	–0.3427
y	+1.1735
z	+6.6346
total	6.7462

of variation in the P–N bond lengths, even in the small compounds).

The O–P bond lengths are not all equal. In fact, the O<sub>2</sub>–P<sub>1</sub> and O<sub>3</sub>–P<sub>1</sub> bonds are substantially shorter (both 1.572 Å) than O<sub>4</sub>–P<sub>2</sub> (1.592 Å) and O<sub>5</sub>–P<sub>2</sub> (1.614 Å). It should be noted that the single O–P bond distance is 1.61 Å [14], indicating that the delocalization of the skeletal electrons extends beyond the backbone into the side groups (especially for the first two oxygen atoms). The other bonds of interest are the C–O bonds. These are all within ±0.02 Å of 1.40 Å with the C–O bond lengths closer to the sulfur atom being longer than 1.4 Å and those farther away being shorter than 1.4 Å. This is in contrast to what has been observed for the O–P bond lengths. The remaining bond lengths belong to the phenyl groups and are of the C–C and C–H types. They have the expected values for substituted benzene rings obtained with the 3-21G\* basis set [12].

The two important bond angles, P<sub>1</sub>N<sub>1</sub>S<sub>1</sub> and P<sub>2</sub>N<sub>2</sub>P<sub>1</sub>, which are closely related to the chain flexibility in these materials, have values of 148° and 166°, respectively. These values are larger than would be expected from X-ray diffraction experiments performed on the closely related poly-[(diphenoxy)phosphazene] short chain, OP(OPh)<sub>2</sub>–NP(OPh)<sub>3</sub> [8], in which the PNP bond angle was determined to be 134°. The 3-21G\* and 6-31G\* basis set calculations [7] have shown that the biggest discrepancies (of the order of 30–40°) occur in the values of the NSP and PNP bond angles in the chlorinated model compounds. Thus we would expect that the bond angles P<sub>1</sub>N<sub>1</sub>S<sub>1</sub> and P<sub>2</sub>N<sub>2</sub>P<sub>1</sub> in the phenoxy substituted model compound would most likely be smaller (to compensate

for the possible bond extensions discussed above) in 6-31G\* basis set computations (and thus be in better agreement with the “experimental” values). In particular, we would expect that the  $P_1N_1S_1$  bond angle would be closer to  $130^\circ$  and the  $P_2N_2P_1$  bond angle would be in the range  $120$ – $130^\circ$ .

Other angles of interest are the OPN angles, which vary from  $101^\circ$  to  $109^\circ$ . Similar values for OPN angles have been obtained for the poly-[(diphenoxy)phosphazene]s [8,9]. More interestingly, we note that bond angles for the COP type are all close to  $130^\circ$ . For example, the  $C_3O_2P_1$  and  $C_9O_3P_1$  angles are  $132.4^\circ$  and  $136.7^\circ$ , respectively, and  $C_{15}O_4P_2$  and  $C_{21}O_5P_2$  are  $135.0^\circ$  and  $126.3^\circ$ , respectively. These COP bond angles are, on average, a few degrees larger than the same angles in poly[(diphenoxy)phosphazene]s [8,9]. These results point to the fact that the planar phenyl groups are more parallel than perpendicular to the chain backbone. We will see in the discussion of dihedral angles below that phenyl groups point in the opposite directions (see Fig. 2). These positions and orientations are determined primarily by the repulsive steric interactions between these bulky groups. The bond angles related to the structure of the phenyl groups have the expected values to within a few degrees, and they will not be discussed in detail here (with the exception of the CCO type bond angles, see Table 2). The CCO bond angles indicate that there are deviations of the order of  $4^\circ$  from the “expected” value of  $120^\circ$ , indicating that the phenyl groups are not centered exactly on the C–O bonds.

The dihedral angles determine the conformation of the molecule. The dihedral angle  $N_2P_1-N_1S_1$  of  $7.2^\circ$  indicates that there is a small deviation from the planar cis structure near the sulfur atom. However, larger deviations from the planar trans–cis structure occur at the subsequent trans and cis arrangements that are described by the two dihedral angles  $P_2N_2-P_1N_1$  and  $N_3P_2-N_2P_1$ . The first of these angles,  $P_2N_2-P_1N_1$  is  $150^\circ$ , i.e. there is a  $30^\circ$  distortion from the trans conformation. The second angle,  $P_2N_2-P_1N_1$ , compensates for this deviation and the chain twists in the opposite direction,  $20^\circ$  away from the planar cis

conformation. In the chlorine and hydrogen substituted model compounds (with chlorine on the sulfur atom) the magnitudes of the dihedral angle  $N_2P_1-N_1S_1$  are  $-11.586^\circ$  and  $-46.977^\circ$ , respectively [6,7] (3-21G\* basis set computation) which is considerably larger than the value ( $7.155^\circ$ ) in the phenoxy substituted model compound. The values obtained with the 6-31G\* basis set are  $-41.554^\circ$  and  $-29.607^\circ$  in the chlorinated and hydrogenated model compounds, respectively. The fact that this dihedral angle is not zero in these model compounds is the primary reason why they do not have a planar trans–cis structure (i.e. the major distortion occurs at the sulfur atom) with either of the basis sets used. This is not the case for the phenoxy substituted model compound, which exhibits distortions throughout the backbone and not just at a particular atom (see Fig. 2(b)).

Other dihedral angles of interest are the  $O_2P_1-N_1N_2$  and  $O_4P_2-N_2N_3$  angles, which give the orientation of the oxygen atoms with respect to the model compound backbone. Both these dihedral angles are close to  $126^\circ$ , which means that the chain backbone and the two oxygen atoms on each phosphorus atom have an approximately three-fold symmetry. The dihedral angles that determine the orientation of the phenyl groups with respect to each other and the chain backbone are very important. As the phenyl groups are predominately planar the orientation of the carbon atoms that are attached to the oxygen atoms determines the directions along which the phenyl groups will point. The values of the dihedral angles of the type CO–PN (see Fig. 2) indicate that the phenyl groups on the phosphorus atoms point in opposite directions. That is, the values of the dihedral angles  $C_3O_2-P_1N_1$  and  $C_9O_3-P_1N_1$  on  $P_1$  are  $168.5^\circ$  and  $145.8^\circ$ , respectively, indicating that these phenyl groups on  $P_1$  point away from the sulfur atom. Conversely, the values of the dihedral angles  $C_{15}O_4-P_2N_2$  and  $C_{21}O_5-P_2N_2$  on  $P_2$  are  $47.7^\circ$  and  $63.3^\circ$ , respectively, indicating that these phenyl groups on  $P_2$  are pointing toward the sulfur atom. In order to specify the orientations of the phenyl groups more completely, we also need to know the positions of their planes relative to the

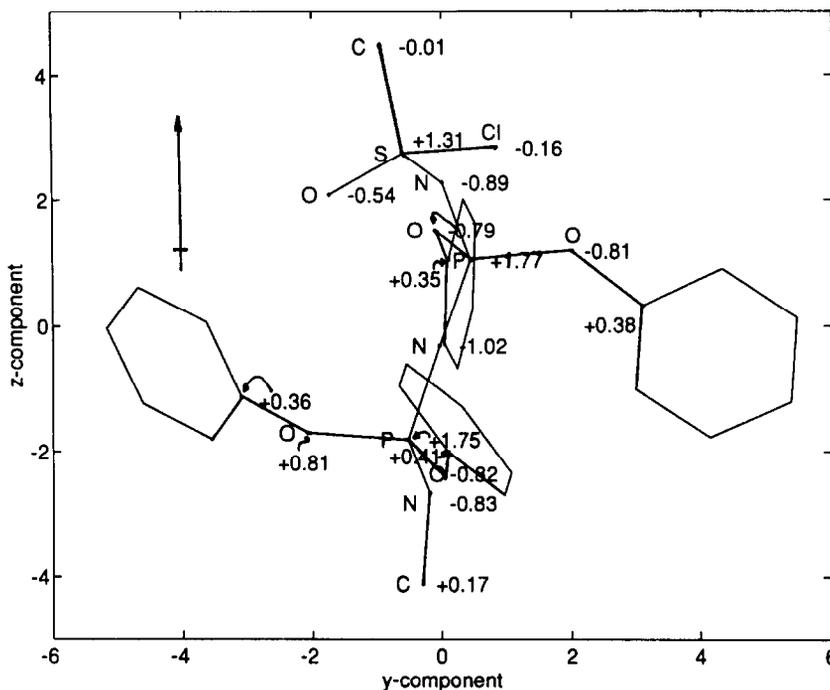


Fig. 3. The  $y$ - $z$  cross-section of the model compound ( $R^1$  is Cl and  $R^2$  is OPh) showing the net charges (obtained using the 3-21G\* basis set) and the orientation of the main component of the total dipole moment. In the phenoxy groups, only the charge on the carbon atoms connected to oxygen atoms are displayed (the charges on the remaining carbon atoms are very close to zero and are not shown). In addition, for clarity, hydrogen atoms in the phenoxy and methyl groups are not displayed.

back-bone and to each other. The dihedral angles  $C_4C_3-O_2P_1$ ,  $C_{10}C_9-O_3P_1$ ,  $C_{16}C_{15}-O_4P_2$  and  $C_{22}C_{21}-O_5P_2$  determine the orientation of the phenyl group planes relative to the backbone. From the values given in Table 1, we note that the planes of the phenyl groups on the same phosphorus atoms are facing each other, with the plane containing the central P1N2P2 atoms located between them (see Fig. 2).

We note that this feature of the phenoxy groups located on  $P_1$  and  $P_2$  pointing in opposite directions may not necessarily be present in the classical polyphosphazenes where the phenoxy groups are most likely oriented in one direction relative to the backbone [8,9]. The presence of sulfur with different substituents breaks this symmetry and thus introduces more randomness into the system. This may be one of the reasons why these materials, in contrast to poly[(diphenoxy)phosphazenes], do not form crystals. The remaining dihedral angles are related

to the structure of the phenyl groups and have the expected values to within  $1-2^\circ$ .

### 3.2. Total dipole moment

Our understanding of the bonding in the model compound can be enhanced by studying the magnitude and the direction of the electric dipole moment. The magnitude and the components of the total dipole moment are given in Table 3. Fig. 3 shows the coordinate system with respect to which the dipole moment components were computed and the corresponding  $y$ - $z$  cross-section of the model compounds (for the sake of clarity we have omitted the subscripts and superscripts from the elements, refer to Fig. 1 and Table 1 for these labels). Fig. 3 also shows the net charges on the atoms, as obtained in the 3-21G\* basis set computation. (Fig. 3, displaying the net charges, was drawn using the software package MATLAB [15]). The net charges were

obtained by subtracting the atomic numbers of individual nuclei from the atom populations obtained in a Mulliken population analysis [12]. The net atomic charges are listed in Table 2; the net charges of the constituent atoms of the phenoxy and methyl groups are not shown explicitly in Table 2, only the group net charges are given. The striking feature of the charge separations illustrated in Fig. 3 is their relatively large magnitudes and the fact that similar atomic centers or groups do not have equal net charges. We attribute this unequal charge separation to the "localization" effect of the  $\pi$  bonds.

The main component (the  $z$  component) of the dipole moment points away from  $N_3$  (negatively charged) and toward  $S_1$  (positively charged); the smaller  $y$  component points away from  $O_1$  and toward  $S_1$ ; and the even smaller  $x$  component points into the page in Fig. 3 (see Table 3 for the actual values). Note that the net charges on the phenoxy groups are considerably larger (range  $-0.35$  to  $-0.42$ ) than the net charges on the chlorine atoms (range  $-0.15$  to  $-0.26$ ) [7]. This clearly illustrates that the net effect of the phenoxy groups is to be more electron-withdrawing than chlorines. The greater electron-withdrawing property of the phenoxy groups results in larger charge separations along the chain backbone (see Fig. 3), which in turn produces a larger dipole moment in the phenoxy substituted model compound (6.7462 debye) than in the chlorine substituted model compound (6.4092 debye). We conclude that the phenoxy and chlorine substituted PTPs have comparable polarity. It should be noted that in ref. 12 it is indicated that the dipole moments for the hypervalent molecules, obtained using the 3-21G\* basis set, are too large by approximately 0.5–1.0 debye.

### 3.3. Some consequences for the material properties of the phenoxy substituted PTP

The chemical composition and the resultant structure and conformational stability of the chain backbone of inorganic polymers determine the overall properties of these materials, e.g. PTPs form amorphous glasses which are typically characterized by low  $T_g$  values and hydrolytical instability. Side groups enable scientists to fine

tune the physical and chemical properties of these materials. For example, the replacement of halogen atoms with organic groups (such as the one studied in this work) on phosphorus atoms often changes a hydrolytically unstable material into a hydrolytically stable one. At the same time,  $T_g$  is increased by a few tens of degrees celcius [2,3,16]. Thus another goal of this work was to relate the structural features of the model compound to the properties of the material produced from poly[(diphenoxy)thionylphosphazene]s.

As stated in Section 1, the phenoxy substituted PTP forms amorphous materials. These materials are characterized by a  $T_g$  of  $+10^\circ\text{C}$ , which is approximately  $60^\circ\text{C}$  higher than the corresponding temperature for chlorine substituted PTP. In addition, these materials exhibit greater stability to moisture than does chlorinated PTP. We can see from Fig. 2 that the phenoxy groups screen the chain backbone and thus tend to decrease interaction of the backbone with other chain molecules and/or small molecules (such as water) that may be present in the system. The fact that the phenyl groups are more or less parallel to the chain rather than pointing away from it makes the chain more cylindrical. The phenyl groups, which are hydrophobic, will tend to shield the hydrophilic backbone of the polymers, causing the material to become more hydrolytically stable.

Using the distance matrix obtained for the model compound, we can estimate that size of the corresponding polymers. In particular, the molecular diameter of the model compound is approximately 13 Å. This should be compared with the diameter for chlorine substituted model compounds which is close to 6 Å, indicating that the poly[(diphenoxy)thionylphosphazene]s are approximately twice as wide as the chlorinated PTPs. This larger size, combined with the fact that the phenoxy groups are rigid (in contrast, for example, to alkane chains which can also be used as substituents), will tend to reduce the chain flexibility and consequently raise  $T_g$ .

## 4. Conclusions

We can summarize our results as follows. With

regard to the structure of the model compound, we note that there is a “single–double” bond-length pattern along the backbone, there are significant distortions from the planar trans–cis conformation along the backbone, and there is a small deviation near the sulfur atom. Most interestingly, the phenoxy groups are positioned approximately parallel to the backbone and the groups located on neighboring phosphorus atoms point in opposite directions. We estimate the molecular diameter of this compound to be 13 Å. The model compound also exhibits a relatively large total dipole moment (6.7 debye) compared to other organic compounds. This total dipole moment is also slightly larger (by 0.3 debye) than the one observed in the chlorine substituted PTP model compound [7].

### Acknowledgments

The authors acknowledge the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Ontario Centre for Materials Research (OCMR) for financial support.

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