Molecular structure of 2-chloro-3,5-di-*tert*-butyl-1,3,2-oxazaphospholene as determined by electron diffraction and *ab initio* calculations

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The diheterophospholene ring of the title compound possesses a P-envelope conformation with the axial orientation of the P–Cl bond, which is very long [r_a = 2.177(6) Å].

The molecular structure of unsaturated 1,3,2-diheterophospholenes is scantily known. Only 2-chloro-5-methyl-1,3,2-oxathiaphospholene **1**,[1] 2-chloro-1,3,2-dioxaphospholene **2**[2] and 2-fluoro-3,5-di-*tert*-butyl-1,3,2-oxazaphospholehe **3**[3] have been studied by electron diffraction. These studies have demonstrated that the P–Hal bond length depends on the nature of substituents at phosphorus. In compounds **1**–**3** the P–Hal bond lengths are 2.08(2), 2.101(6) and 1.641(11) Å, respectively. In this work, we investigated the stucture of 2-chloro-3,5-di-*tert*-butyl-1,3,2-oxazaphospholene in the gas phase using electron diffraction and *ab initio* calculations.

The diffraction patterns were recorded at 60 °C on Kazan EMR-100M ED-instruments using two camera distances. The long and short camera distances covered the *s*-ranges 4.00–14.75 and 12.00–27 .25 Å^{-1} , respectively. The refinements of the structure were performed by applying a least-squares procedure based on the molecular intensities. The molecular structure optimization by means of *ab initio* calculations was carried out at the HF/6-31G**, MP2/6-31G** and b3pw91/6-31G** levels.[4,5]

The vibrational amplitudes l_{ij} and perpendicular corrections K_{ij} were derived from the theoretical force field provided by the basis set HF/6-31G** and used in the structural analysis. For describing the geometry of the five-membered ring, the P–O, P-N, C=C and N–C(4) bond lengths, the O-P-N, P-N-C(4) and N-C =C bond angles and the O–P-N -C(4) torsional angle were chosen as independent parameters (Figure 1). The N-C =C-O moiety was assumed to be planar. This assumption is justified by *ab initio* calculations, which predicted this dihedral angle to be 0.4° (MP2/6-31G**), 0.7° (b3w91/6-31G**) or 0.2° (HF/6-31G**). The structure of the exo-groups and their orientations were described by the P-Cl, N-C (7), C(5)-C(8), C–C_{Me} and C-H bond lengths, the O–P-Cl, N–P-Cl, P-N -C(7) , C(4)-N– C(7), C=C–C(8), N–C(7)-C_{Me} and C(5)-C(8) -C_{Me} bond angles and the P–N-C(7)–C(9) and C=C–C–C(21) torsional angles. Because of large correlations between some of the geometric parameters, the following assumptions were made during the structural refinement: (i) C_{3v} symmetry was assumed for the methyl and *tert*-butyl groups, and all C-C bond lengths and C_{Me}-C-C_{Me} bond angles in the two *tert*-butyl groups were set equal. These assumptions are justified by *ab initio* calculations, which predicted deviations to be less than 0.005 Å and 0.9°; (ii) the differences between bond lengths d(NC) = r[N-C(4)] – r[N–C(7)], d(CC) = r[C(8)-C_{Me}] – r[C(5)-C(8)] w ere adopted from the MP2/6-31G** and b3pw91/6-31G** results, averaged and introduced as separate parameters. The bond length differences were applied to the r structure. The refined bond lengths were converted to r_a distances.

According to preliminary experimental results, the diheterophospholene ring possesses a P-envelope conformation with the axial orientation of the P-Cl bond. These results have also shown that the sum of the angles at the N atom is 360°, which is in a good agreement with the *ab initio* results 357.3 (MP2/6-31G**),

Table 1 Geometric parameters for 2-chloro-3,5-di-*tert*-butyl-1,3,2-oxazaphospholene as found by the electron diffraction analysis and *ab initio* calculations.[a]

	Experiment		Calculation		
Bond length/Å	r_a	r	HF/6-31G**	MP2/6-31G**	b3pw91/6-31G**
P-Cl	2.177(6)	2.167	2.169	2.196	2.225
P–O	1.657(10)	1.653	1.623	1.664	1.657
P–N	1.698(15)	1.694	1.676	1.700	1.700
C-O [b]	1.392(27)	1.389	1.386	1.401	1.391
C=C	1.348(16)	1.344	1.319	1.350	1.342
N-C (4)	1.398(13)	1.396	1.413	1.409	1.404
N-C (7)	1.474	1.468	1.478	1.479	1.481
d(NC)	0.072(39)		0.054	0.070	0.077
C-C_{Me}	1.557(5)	1.542	[1.537]	[1.530]	[1.537]
C(5)-C (8)	1.510	1.506	1.506	1.493	1.502
d(CC)	[0.036]		0.031	0.037	0.035
C-H	1.091(5)	1.055	[1.084]	[1.089]	[1.095]
Bond angle/°					
O-P-N	94.5(12)		91.4	90.8	90.7
P-N-C (4)	108.7(19)		109.1	110.0	110.1
C-N -C [b]	121.7(21)		122.1	121.5	122.4
C=C-N	112.2(28)		112.7	112.3	112.7
C=C-O [b]	115.0(23)		111.0	111.5	111.2
P-O-C [b]	108.8(15)		112.9	112.0	113.0
O-P-C 1	99.1(10)		99.0	99.1	99.6
N-P-C 1	101.1(8)		103.4	103.5	103.8
P-N-C (7)	129.6(11)		127.7	125.8	126.0
C=C-C	134.6(24)		133.1	132.9	132.6
N-C –C_{Me} C-C -C_{Me}	109.3(8)		[109.4]	[109.0]	[109.2]
C_{Me}–C-C_{Me} [b]	109.6(8)		[109.9]	[109.9]	[108.7]
Torsion angle/°					
O-P-N -C(4)	8.4(16)		15.0	16.6	16.7
C(9)-C (7)–N-P	139.9(30)		133.9	138.8	134.8
C(21)-C (8)-C= C	120.3(131)		120.4	120.1	121.0
R(sMs)$_{long}$		4.20			
R(sMs)$_{short}$		7.45			
R(sMs)$_{average}$		5.67			
R[f(r)]		3.31			

[a]Experimental uncertainties 3σ are given in parentheses. Average values are given in square brackets. [b]Dependent parameters.

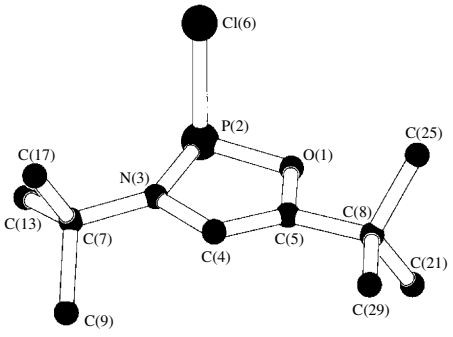

Figure 1 Molecular structure of 2-chloro-3,5-di-*tert*-butyl-1,3,2-oxazaphospholene.

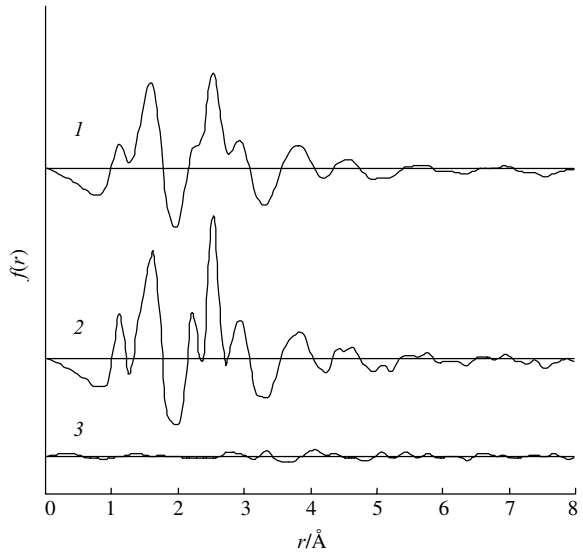

Figure 2 Experimental radial distribution function with (*1*) $b = 0.0031$, (*2*) $b = 0.000001$ and (*3*) difference curve $f(r)_{exp} - f(r)_{theor}$, 3 .

358.5 (b3pw91/6-31G**) and 358.9° (HF/6-31G**). Therefore, we include the P–N–C(7) and P–N–C (4) angles in the final refinement. The results of the final least-squares analysis of ED data and *ab initio* calculations are shown in Table 1. The following correlation coefficients have values higher than |0.6|: PN/PO –0 .82, PN/NC –0. 73, PO/NC 0.67, PN/CC 0.72, CC/NC 0.77, CC/OPN 0.65, PNC(7)/OPN –0. 74, NC=C/PNC(4) 0.91, ClPO/PNC(4) 0.69, CC=C/NC=C 0.68, $C_{Me}CN$/PNC(4) 0.77, $C_{Me}CN$/NC=C –0. 75. The experimental curve $f(r)$ is shown in Figure 2. The electron diffraction investigation of the structure of 2-chloro-3,5-di-*tert*-butyl-1,3,2-oxazaphospholene indicates that the P–Cl bon d of 2.177(6) Å is very long, as compared with other compounds.[6] For instance, this bond is about 0.13 Å longer than that in PCl_3 [2.042(2) Å[7]]. Note that the P–Cl bon d in oxazaphospholene is remarkably longer than the sum of the covalent radii of P and Cl (2.09 Å).

Table 2 Comparison between the geometrical parameters of 2-fluoro-3,5-di-*tert*-butyl-1,3,2-oxazaphospholene (F-OAP) and 2-chloro-di-*tert*-butyl-1,3,2-oxazaphospholene (Cl-OAP).

Bond length/Å	F-OAP	Cl-OAP
P–O	1.645(9)	1.657(10)
P–N	1.706(9)	1.698(15)
N–C (4)	1.435(9)	1.398(13)
C=C	1.344[a]	1.348(16)
N–C (7)	1.494(9)	1.474(13)
C–O [b]	1.365(9)	1.392(27)
Bond angle/°		
O–P–N	92.7(11)	94.5(12)
P–N–C (4)	107.5(12)	108.7(19)
C=C–N	112.4(16)	112.2(28)
C=C–O [b]	113.0(18)	115.0(23)
P–O–C [b]	112.1(20)	108.8(15)
C(4)–N– C(7)	119.9(9)	121.7(21)
Torsion angle/°		
O–P–N –C(4)	13.2(54)	8.4(16)
X–P–N –C(4)[b]	–90.4	–91.8
X–P–O –C(5)[b]	92.2	93.7

[a]Assumed value. [b]Dependent parameters.

On the other hand, the structural analysis shows that both C–O and C–N bonds within the ring are shorter than ordinary bonds. This indicates conjugative interaction within the O–C =C–N fragment of the ring. Note that the P–O and P–N bond lengths in the ring are comparable with those in non-cyclic compounds such as $P(OMe)_3$ [r(P–O) = 1.620(2) Å[6]], $P(NMe_2)_3$ [r(P–N) = = 1.70(1) Å[6]], $ClP(NMe_2)_2$ [r(P–N) = 1.730(5) Å[6]]. In cyclic compounds such as 2-chloro-3-methyl-1,3,2-oxazaphospholane or in 1,3,4,2-oxadiazaphospholene, the P–O and P–N bonds are 1.62–1. 63 and 1.70 Å, respectively.[6] In 2-chloro-1,3,2-dioxaphospholene,[2] the P–O bond length is 1.633(3) Å, and the P–Cl bond length is 2.101(3) Å. These values are considerably shorter than the corresponding bond lengths in 2-chloro-3,5-di-*tert*-butyl-1,3,2-oxazaphospholene.

For direct comparison of the influence of fluorine and chlorine substituents on the geometry of an oxazaphospholene ring, the most important parameters which have been obtained from the structural investigations of 2-fluoro- and 2-chloro-3,5-di-*tert*-butyl-1,3,2-oxazaphospholenes are summarised in Table 2. It is of particular importance to note that the oxazaphospholene ring has a P-envelope form. The sum of endocyclic angles is 537.7 or 539.2° for F and Cl derivatives, respectively. The dihedral angle between the O–P –N and O–C =C–N planes in chlorooxazaphospholene is 8.4 (1.6)°. In fluorooxazaphospholene, this angle is larger. A comparison the C–O and C–N terminal bonds within the X–P–N–C and X–P–O–C chains in fluoro- and chlorooxazaphospholenes shows that these differ by about 0.03 and 0.04 Å, respectively. We suppose that these differences are due to the different electronegativities of F and Cl atoms.

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