The determination of the molecular structure of 2-fluoro-3,5-di-*tert*-butyl-1,3,2-oxazaphospholene by means of electron diffraction and *ab initio* calculations

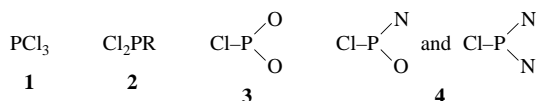**Victor A. Naumov,**[*a] **Marwan Dakkuori,**[*b] **Rida N. Ziatdinova**[a] **and Heinz Oberhammer**[*c]

[a] *A. E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, 420088 Kazan, Russian Federation.*
E-mail: naumov@glass.ksu.ras.ru
[b] *Abteilung für Elektrochemie, University of Ulm, 89069 Ulm, Germany. Fax: +49 731 502 5409;*
e-mail: marwan.dakkuori@chemie.uni-ulm.de
[c] *Institut für Physikalische und Theoretische Chemie, University of Tuebingen, 72076 Tuebingen, Germany. Fax: +49 7071 29 6910;*
e-mail: heinz.oberhammer@uni-tuebingen.de

The molecular structure of gaseous 2-fluoro-3,5-di-*tert*-butyl-1,3,2-oxazaphospholene has been determined by electron diffraction and *ab initio* calculations. The structural analysis has shown that the diheterophospholene ring possesses a P-envelope conformation with axial orientation of the P–F bond which is very long, 1.641(11) Å.

It is well known[1] that the P–Cl bond length depends strongly on the nature of the substituents at phosphorus. In compounds of the type **1**–**4**:

$$PCl_3 \quad Cl_2PR \quad Cl-P\begin{smallmatrix}O\\O\end{smallmatrix} \quad Cl-P\begin{smallmatrix}N\\O\end{smallmatrix} \quad and \quad Cl-P\begin{smallmatrix}N\\N\end{smallmatrix}$$

$$\mathbf{1} \qquad \mathbf{2} \qquad\quad \mathbf{3} \qquad\qquad \mathbf{4}$$

the P–Cl bond length changes from 2.04 Å (type **1**) to 2.18 Å (type **4**). It is interesting to note that P–Cl bonds in compounds of type **4** are considerably longer than the sum of the covalent radii of P and Cl (2.09 Å). One can expect that similar changes in P–F bond lengths occur in fluorine-containing compounds of phosphorus. With this aim we studied the structure of 2-fluoro-3,5-di-*tert*-butyl-1,3,2-oxazaphospholene in the gas phase by electron diffraction.

Diffraction photographs were recorded at 40 °C on Kazan EMR-100M ED-instruments at three camera distances which cover the *s*-ranges $3.00 < s < 10.50$, $4.00 < s < 15.25$ and $11.00 < s < 27.50$ Å^{-1}. Refinements of the structure were carried out by a least-squares method based on molecular intensities. The geometric structures were also optimized by *ab initio* calculations at the HF/6-31G** level.[2] Vibrational amplitudes l_{ij} and perpendicular amplitudes K_{ij} were derived from the theoretical force field (HF/3-21G*)[2] and used in the experimental analysis.

For describing the geometry of the five-membered ring, the bond lengths P–O, P–N, C=C and N–C(4), the bond angles O–P–N, C=C–N, and P–N–C(4), and the torsional angle C(4)–N–P–O were chosen as independent parameters (Figure 1). Planarity was assumed for the N–C=C–O moiety. This assumption is justified by the *ab initio* calculation which predicts this dihedral angle to be 0.4°. The substituents and their orientation were described by the P–F, N–C(7), C(5)–C(8), C–C(Me) and C–H bond lengths, the O–P–F, N–P–F, 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 by the C(9)–C(7)–N–P and C(21)–C–C=C dihedral angles. Because of large correlations between some of the geometric parameters the following assumptions were made during the structure refinement: (1) 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 groups were set as equal. These assumptions are justified by the *ab initio* calculations which predict deviations to be less than 0.007 Å and 0.8°. (2) The differences between bond lengths, $d(PX)$, $d(NC)$, $d(CC)$, and between bond angles $\angle(XNC)$, $\angle(XPF)$ were constrained to the *ab initio* values (see Table 1). The bond length differences were applied to the r_{α} structure. The refined bond lengths were converted to r_{a} distances.

Table 1 Geometric parameters for 2-fluoro-3,5-di-*tert*-butyl-1,3,2-oxazaphospholene as obtained from electron diffraction analysis and *ab initio* calculations.

	Bond lengths/Å				Bond angles/°	
Parameters	Experimental		*ab initio*	Parameters	Experimental	*ab initio*
	r_a	r_α				
P–F	1.641(11)[a]	1.638	1.610	O–P–N	92.7(11)	91.2
P–O	1.645(9)	1.644	1.628	P–N–C(4)	107.5(12)	108.7
P–N	1.706	1.705	1.689	C=C–N	112.4(16)	112.9
$d(PX)$[c]	–0.061(20)		–0.061	C=C–O[d]	113.0(18)	111.2
C–O[d]	1.365(9)	1.362	1.387	P–O–C[d]	112.1(20)	112.8
C=C	1.344(ass.)	1.342	1.318	P–N–C(7)	125.1(19)	127.1
N–C(4)	1.435(9)	1.431	1.414	C–N–C	119.9	121.9
N–C(7)	1.494	1.490	1.473	$\angle(XNC)$[g]	5.2	5.2
$d(NC)$[e]	–0.059		–0.059	O–P–F	102.5(20)	98.8
C–C(Me)	1.542(3)	1.535	1.535[b]	N–P–F	105.1	101.4
C(5)–C(8)	1.513	1.506	1.506	$\angle(XPF)$[h]	–2.6(11)	–2.6
$d(CC)$[f]	–0.029		–0.029	C=C–C	131.4(42)	132.9
C–H	1.095(4)	1.079	1.085	N(C5)–C–C(Me)	110.6(11)	109.5[b]
				=C–C–C(Me)	110.6	109.5[b]
R-factor: 3.44				C(Me)–C(7,8)–C(Me)[d]	108.4(11)	109.5[b]

	Torsional angles/°	
C(4)–N–P–O	13.2(54)	15.5
C(9)–C(7)–N–P	144.7(60)	139.5
C(Me)–C–C=C	126.1(98)	120.0

[a]Uncertainty values in parentheses are 3σ values. [b]Mean values for similar parameters. [c]$d(PX) = r(P–O) – r(P–N)$. [d]Dependent parameter. [e]$d(NC) = r[N–C(4)] – r[N–C(7)]$. [f]$d(CC) = r[C(5)–C(8)] – r[C–C(Me)]$. [g]$\angle(XNC) = \angle[P–N–C(7)] – \angle(C–N–C)$. [h]$\angle(XPF) = \angle(O–P–F) – \angle(N–P–F)$.
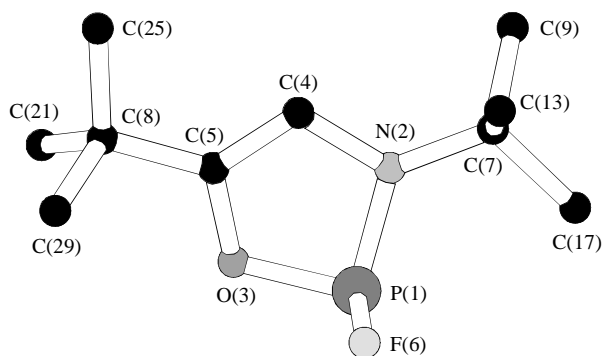
Figure 1 Atomic numbering of 2-fluoro-3,5-di-*tert*-butyl-1,3,2-oxaza-phospholene.

With these assumptions the least-squares refinement resulted in a C=C bond [1.344(29) Å] and a C–O bond [1.366(24) Å] with very large error limits. The C=C bond length correlates strongly with other ring bonds and angles. This value is in good agreement with the experimental C=C bond length in methyl vinyl ether, 1.343(6) Å.[3] On the other hand, HF/6-31G** values for C=C double bond lengths are known to be too short. On the basis of the experimental C=C bond length in methyl vinyl ether and HF/6-31G** values for this compound (1.320 Å) and for the phospholene (1.318 Å), an r_a value of 1.341 Å is estimated in the oxazaphospholene. Therefore the C=C distance was constrained to 1.344 Å (Table 1).

The structure analysis showed that the diheterophospholene ring possesses a P-envelope conformation with axial orientation of the P–F bond. The *tert*-butyl group bonded to N is pseudoequatorial. The sum of angles at the N atom is 354.2(15)° in good agreement with the *ab initio* result of 357.7°. As expected from trends in P–Cl bond lengths, the P–F bond in oxazaphospholene [1.641(12) Å] is very long. It is about 0.08 Å longer than that in PF$_3$ [1.565(1) Å].[4] Intermediate values have been reported for compounds of the type F$_2$PX, *e.g.* F$_2$PBu^t [1.589(4) Å],[5] F$_2$PNH$_2$ [1.587(4) Å][6] and F$_2$POCH$_3$ [1.591(10) Å].[7] A very long P–F bond has been observed in FPBu$^t_2$ 1.619(7) Å.[5] The variations in the P–F bond lengths, however, are considerably smaller than those for the P–Cl bond lengths.

The C–O and C–N bonds in the ring are shorter than normal single bonds and this indicates conjugation in the O–C=C–N part of the ring. The P–O and P–N bonds in the ring, however, are longer than or equal to those in non-cyclic compounds such as P(OCMe)$_3$ [r(P–O) = 1.620(2) Å],[1] F$_2$POMe [r(P–O) = = 1.56(2) Å], P(NMe$_2$)$_3$ [r(P–N) = 1.70(1) Å],[1] ClP(NMe$_2$)$_2$ [r(P–N) = 1.730(5) Å][1] and F$_2$PNH$_2$ [r(P–N) = 1.650(4) Å]. In cyclic compounds such as 2-chloro-3-methyl-1,3,2-oxaza-phospholane or in 1,3,4,2-oxadiazaphospholene P–O and P–N bonds are 1.62–1.63 and 1.70 Å respectively.[1]

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