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

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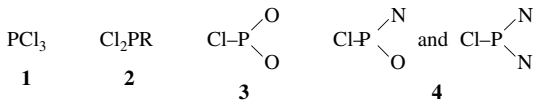
The molecular structure of gaseous 2-fluoro-3,5-di-*tert*-butyl-1,3,2-oxazaphospholene has been determined by electron diffraction and *ab initio* calculations. The structural analysis has shown that the diheterophospholene ring possesses a P-envelope conformation with axial orientation of the P–F bond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

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



1 **2** **3** **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 bon ds 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 bon d lengths and C(Me)–C –C(M e) 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 ∠(XNC), ∠(XPF) were constrained to the *ab initio* values (see Table 1). The bond length differences were applied to the *r* 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*		O–P–N	92.7(11)	91.2
P–F	1.641(11)[a]	1.638	1.610	P–N–C (4)	107.5(12)	108.7
P–O	1.645(9)	1.644	1.628	C=C–N	112.4(16)	112.9
P–N	1.706	1.705	1.689	C=C–O [d]	113.0(18)	111.2
d(PX)[c]	–0. 061(20)		–0 .061	P–O–C [d]	112.1(20)	112.8
C–O [d]	1.365(9)	1.362	1.387	P–N–C (7)	125.1(19)	127.1
C=C	1.344(ass.)	1.342	1.318	C–N– C	119.9	121.9
N–C (4)	1.435(9)	1.431	1.414	∠(XNC)[g]	5.2	5.2
N–C (7)	1.494	1.490	1.473	O–P–F	102.5(20)	98.8
d(NC)[e]	–0. 059		–0.059	N–P–F	105.1	101.4
C–C (Me)	1.542(3)	1.535	1.535[b]	∠(XPF)[h]	–2 .6(11)	–2 .6
C(5)–C (8)	1.513	1.506	1.506	C=C–C	131.4(42)	132.9
d(CC)[f]	–0. 029		–0.029	N(C5)–C –C(M e)	110.6(11)	109.5[b]
C–H	1.095(4)	1.079	1.085	=C–C– C(Me)	110.6	109.5[b]
				C(Me)–C (7,8)–C(Me)[d]	108.4(11)	109.5[b]
R-factor: 3.44						
				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]∠(XNC) = ∠[P–N– C(7)] – ∠(C–N– C). [h]∠(XPF) = ∠(O–P–F) – ∠(N–P– F).

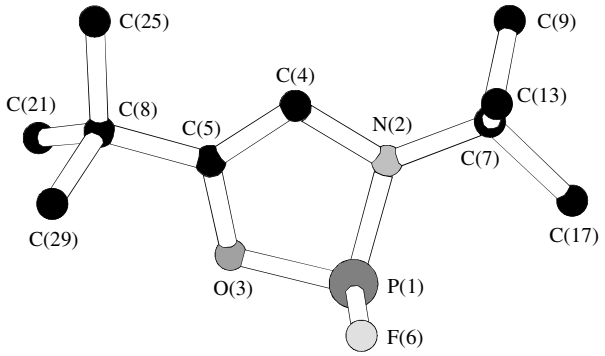


Figure 1 Atomic numbering of 2-fluoro-3,5-di-*tert*-butyl-1,3,2-oxazaphospholene.

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_2PX, *e.g.* F_2PBu^t [1.589(4) Å],[5] F_2PNH_2 [1.587(4) Å][6] and F_2POCH_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_2POMe [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_2PNH_2 [r(P–N) = 1.650(4) Å]. In cyclic compounds such as 2-chloro-3-methyl-1,3,2-oxazaphospholane 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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