Conformational Structure of Chloromethyldichlorophosphines

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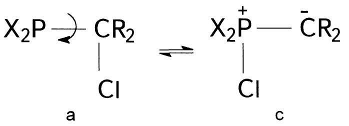
The ^{35}Cl nuclear quadrupole resonances (77 K) and ab initio calculations of trichloromethyldichlorophosphine (**I**) show that it exists in the chess conformation form. The barrier to internal rotation about the P-C bond in **I** at the RHF/6-31^{++} G(d,p) level equals to 38.1 kJ mol^{-1}. In chloromethyldichlorophosphine (**II**) the extension of the basis set up to the RHF/6-311^{++}G(df, pd) level does not improve the description of the most preferable gauche-conformation; only if electron correlation (at the MP2 level) is taken into account the results are in a good agreement with experimental data.

Key words: Chloromethyl- and Trichloromethyldichlorophosphine; Conformations;
^{35} Cl NQR Frequencies; *ab initio* and MNDO-PM3 Calculations.

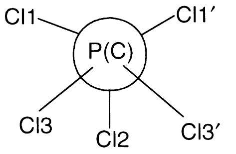
Introduction

α-Chloroalkylphosphines (along with the isomeric P-chloroylides) are potential chlorotropic systems for the study the reversible transfer of a chlorine atom from the carbon centre to the phosphorus site and, on the other hand, α-chloroalkylphosphines possess an additional degree of freedom for rotation about the P-C bond stipulating the conformation mobility of the compounds.

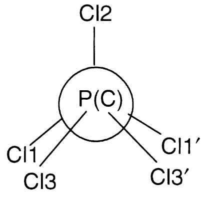


Formerly, the study of chlorotropy in large dialkylaminochlorophosphines [1, 2] (which contain up to 50 atoms) on the MNDO-PM3 level offered a clear view on the structure, thermodynamic parameters and probable chlorotropy mechanisms of the species. It was stated that as a rule the transformation runs with formation of ionic pairs, the structure and activation energy of the rearrangement being determined by the nature of the ligand at the phosphorus atom. So the sigmatropic mechanism of the chlorotropy in bis(diethylamino)derivatives is governed mainly by the easiness of ionic pair formation due to cation stabilization *versus* energy of P-C bond cleavage. However, for the cation of sterically hindered bis(diisopropylamine)-derivatives, the planes of the PR_2 and CX_2 fragments are typically at the right angles, and the P-C bond is considerably weakened [2]. The latter effect is responsible for bridging the gap between dissociation energies of P-Cl and P-C ylide bonds, thus activating the parallel channel for ylide bond rupture.

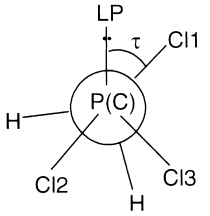
The present communication presents the results on conformation isomerism, structure and properties of the species in other phosphine-type systems: trichloromethyl- (**Ia**) and chloromethyldichlorophosphines (**IIa**), which are supposed to be prone for chlorotropy transformations in trichlorophosphoniumdichloromethylide (**Ic**) and trichlorophosphoniummethylide (**IIc**), respectively. As the species **Ia**, **c** and **IIa**,**c** are relatively small, this allows to study their structures by *ab initio* RHF/6-31^{++}G (d, p) [3] and RHF/6-311^{++}G(df, pd) [4] methods. The electron correlation was taken into account on the MP2 level of theory [5]. The structural and electronic character-



chess conformation **Ia**



eclipsed conformation **Ib**



gauche-conformation **IIa**

istics and thermodynamic properties computed by the techniques mentioned are then used for comparison with available structural data and with experimental results on the ^{35}Cl nuclear quadrupole resonance (NQR). The role of the lone pair (LP) at the phosphorus atom on the conformational structure of the phosphines **Ia** and **IIa** is also discussed.

Results and Discussion

According to the results of our calculations, the phosphines **Ia**, **IIa** and their chlorotropic isomers **Ic, IIc** are thermodynamically stable compounds; the former isomers are thermodynamically more stable on both the semi- and non-empirical levels. Though the phosphines **Ia**, **IIa** are known as individual species, the ylides **Ic**, **IIc** are not yet described. The results on the ylides **Ic, IIc** are consistent with the classical ylidic structure with *transoid* positioning of the PCl_2^{tr} and CR_2 fragments (*trans*-bent conformation [6, 7]), where the carbon atom has a slightly pyramidal structure (ΣC_i 356.6° **Ic**, 358.1° **IIc**); this effect is noticeable only if the d-polarisation functions on carbon are included into the basis sets. The comparison of the $CPCl^{non\text{-}tr}$ (123.9 - 124.6°) and $CPCl^{tr}$ (110.7 - 112.0°) bond angles could give rise to the assumption that $PCl^{non\text{-}tr}$ should be stronger, as the role of *s*-AOs in bonding is larger in the former group. However, the *non-transoid* P-Cl bond length (2.057 - 2.070 Å) is greater (and the bond is weaker) than that of the *transoid* bonds (1.992 - 2.007 Å). The final lengthening of the coplanar P-Cl bond may be interpreted only by the effect of donation of the LP at the carbon atom to the $P\text{-}Cl^{non\text{-}tr}$ σ^*-antibonding MO. Simultaneously, the latter effect makes the P-C ylide bond in trichlorophosphoniummethylide **IIc** stronger (1.625 Å) as compared to triphenylphosphoniummethylide (1.692 Å) [8].

In the experimental ^{35}Cl NQR spectrum of the phosphine Cl_2PCCl_3 (**Ia**), recorded at 77 K, there are three lines, the intensities of which indicate twofold spectral degeneracy for two of them (see Table 1). The form of the spectrum and the ratio of the signal intensities correspond well with the molecular symmetry of the two conformers. At the RHF/6-31^{++}G(d, p) level computations we recognize that the ground state (conformation) of **I** has the *chess* conformation **Ia**, and the *eclipsed* conformation **Ib** is actually a transition state with $\nu_{im} = 59i$ cm^{-1}, while the results at the MNDO-PM3 level erroneously corresponds to the reverse assignment of the structures. The activation barrier to trichloromethyl group reorientation about the P-C bond in phosphine **Ia** at the RHF/6-31^{++}G(d, p) level equals 38.1 kJ mol^{-1} (cf. 45.2 kJ mol^{-1}) in hexachloroethane, evaluated from the ED results [9]). The two-fold degenerated signals at 27.306 and 38.851 MHz should be assigned to chlorine atoms at the equivalent P-Cl3(Cl3′) and C-Cl1(Cl1′) bonds, respectively. It is important to stress that in phosphine **Ia,** as compared with phosphine **IIa**, the shortening of the C-Cl bonds is accompanied by a definite weakening of the P-C bond. The bond length of the P-C bond mentioned equals 1.911 Å, a value that exceeds the sum of the covalence radii of phosphorus and carbon atoms (1.87 Å). Hence, in our opinion, it may be responsible for the exceptional predisposition to dissociation of the P-C bond in phosphine **Ia**.

The results on the phosphine **IIa** structure at the RHF/6-31^{++}G (d, p) level corresponds to the *gauche* conformer, and the torsion angle between the C-Cl bond and the phosphorus LP $\tau_{Cl1CP(LP)}$ equals 51.5°, the LP being placed in the bisector plane of the Cl2PCl3 angle. The extension of the basis set up to the RHF/6-311^{++}G(df, pd) level does not improve the description of the most preferable *gauche*-conformation. The results obtained at the MP2//6-31^{++}G(d, p) level enlarge this value up to 54.0°, which is practically the same as measured by electron diffraction (ED) (55.0°) [10].

Table 1. The experimental ^{35}Cl NQR frequencies (ν^{exp}), signal-to-noise ratio (s/n), and Mulliken charges on atoms (q^{calc})[a], structural parameters (ℓ and ω) of trichloromethyl- (**Ia**) and chloromethyldichlorophosphine (**IIa**).

ν^{exp} (s/n)[b] MHz	q^{calc} e	ℓ, Å calc.[c]	exp.[d]	ω(ClPC), deg. calc.[c]	exp.[d]	Assignment
Cl_2PCCl_3 (**Ia**):						
27.306(8)	–0.161	2.046		100.3		P-Cl3
		2.046		100.3		P-Cl3'
38.851(10)	–0.020	1.776		105.8[e]		C-Cl1
		1.776		105.8[e]		C-Cl1'
39.471(5)	0.059	1.753		116.2[e]		C-Cl2
		1.911				P-C
Cl_2PCH_2Cl (**IIa**):						
26.275	–0.168	2.068	2.051±0.003	96.1	98.9±1.7	P-Cl2
	(–0.168)	(2.071)		(95.4)		
27.025	–0.164	2.057	2.051±0.003	99.5	98.9±1.7	P-Cl3
	(–0.162)	(2.060)		(98.8)		
36.09	–0.052	1.782	1.765±0.018	110.4[e]	106.4±2.0	C-Cl1
	(–0.050)	(1.777)		(110.1)		
		1.855	1.860±0.027			P-C
		(1.855)				

[a] computed at the RHF/6-31^{++}G(d,p) level. [b] Frequencies for **IIa** from [11]. [c] Structural parameters and the charges at the MP2/RHF/6-31^{++}G(d, p) level are given in brackets. [d] Electron diffraction data [10]. [e] The ClCP bond angle.

The data on bond lengths, computed on the MP2//6-31++(d,p) level, may also be used to revise the equivalence of the P-Cl bonds stated by exploring the ED data [10]. The results presented in Table 1 show that the difference in the P-Cl2 and P-Cl3 bond lengths equals 0.011 Å, well out of the experimental ED error limits (0.003 Å). It also should be stressed that this non-equivalence clearly manifests itself in the ^{35}Cl NQR spectrum of phosphine **IIa** [11]. These data testify, at first, that the structure of the *gauche* conformer **IIa** is kept undistorted in the crystalline state as compared with the gas phase (cf. [12]) and, secondly, that the low-frequency signal of 26.275 MHz must be attributed to the chlorine atom of the PCl2 bond as more ionic. Indeed, the results of the computations show near-to-coplanar positioning of the CCl1 and PCl2 bonds, *trans*- to each other (see the Scheme). The *trans*-effect leads to greater negative charge on the Cl2 atom (–0.168 e), thus increasing the ionic character of the PCl2 bond and, therefore, in line with Townes-Dailey equation

$$U_p \approx 1 - i,$$

where i is the ionicity of the X-Cl bond, diminishing of NQR chlorine atom frequency in the PCl2 bond. It also should be mentioned that increasing the ionic character of the {P-Cl} bond might lead to some bond lengthening.

Experimental

Phosphine **Ia** was obtained by the method [13]. The ^{35}Cl NQR spectrum was recorded on a pulse spertrometer ISSH 1-13M at 77 K.

Conclusion

The ^{35}Cl nuclear quadrupole resonances (77 K) and *ab initio* calculations of trichloromethyldichlorophosphine (**I**) show that it exists in the chess conformation form. The barrier to internal rotation about the P-C bond in **I** at the RHF/6-31^{++}G(d,p) level equals to 38.1 kJ mol^{-1}. In chloromethyldichlorophosphine (**II**) the extension of the basis set up to the RHF/6-311^{++}G(df, pd) level does not improve the description of the most preferable gauche-conformation; only if electron correlation (at the MP2 level) is taken into account, the results agree well with the experimental data.

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