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QUANTUM-CHEMICAL STUDY OF THE COORDINATION ISOMERISM OF P(V)-P(IV) IN CHLOROPHOSPHORIC HETEROCYCLIC COMPOUNDS

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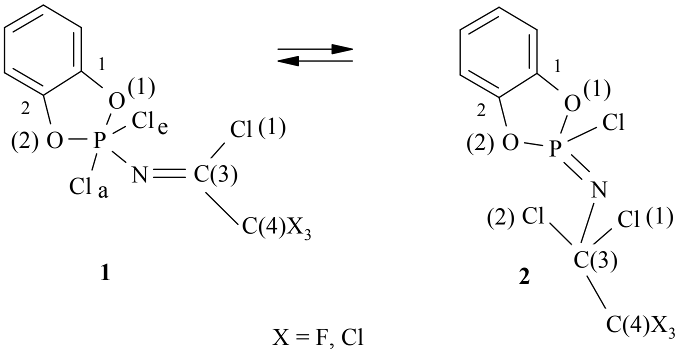
Using the RHF/6-31G method calculations have been carried out on the isomeric chlorophosphoric heterocyclic molecules $C_6H_4O_2PCl_2N{=}CClX_3$ and $C_6H_4O_2PCl{=}NCCl_2CX_3$ (X = F and Cl) with full optimization of their geometries. Conclusions are drawn regarding the chlorotropic conversion of these isomers which contain phosphorus with coordination numbers V and IV. The relative stabilization energies of the isomeric compounds have been determined for variation of X.*

Keywords: chlorophosphoric heterocyclic compounds, non-empirical quantum-chemical calculations, isomeric form structure, chlorotropic conversion.

Using ^{31}P NMR in solutions of the chlorophosphoric heterocyclic benzodioxaphosphole series **1** and **2** with X = F or Cl it was found that they exist in chlorotropic tautomerism thus leading to a change in the coordination number of the phosphorus atom from P(V) to P(IV) [1].



The isomeric conversion with migration of the Cl atom between the P and C atoms in the PNC triad was also shown in the crystalline state by ^{35}Cl NQR for X = Cl [2].

The aim of our work was to study the geometric features of isomers **1** and **2**, determination of the nature of their chlorotropic conversion, and also to establish the relative stability of the isomeric forms **1** and **2** for the isolated molecules by comparing the stability of the compound in solution and in the solid phase. For this we have used the non empirical quantum-chemical calculations of such molecules within the Hartree-Fock RHF/6-31G* method using the

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GAUSSIAN 94W program [3] with full optimization of their geometry (Tables 1-3). The calculated phosphorane structure for isomer **1** agrees with the experimental data [1]. From the calculations it was found that, for the pentacoordinate P atom, the axial P–O(1) and P–Cl_a bonds are longer than the corresponding equatorial P–O(2) and P–Cl_e bonds (see Tables 1-3). The negative charges on the axial atoms O(1) (-0.786 e) and Cl_a (-0.319 e) are markedly larger in absolute value than those of the analogous equatorial atoms O(2) (-0.699 e) and Cl_e (-0.114 e) (the values of the charges of these atoms and the bond lengths involving them in isomer **1** where X = F and Cl coincide). For X = Cl the ratio of the P–Cl_a and P–Cl_e bond lengths and also the charges on the axial and equatorial chlorine atoms in isomer **1** are in line with the ratio of their ^{35}NQR frequencies of 25.804 and 30.590 MHz at 77°K [1, 2] and which agree with the basic idea regarding the relationship between the ^{35}NQR frequency and the ionicity of the chemical bond in which the chlorine atom participates (see, e.g. [4]).

As the calculation results show (Tables 1-3) the characteristic trigonal bipyramidal phosphorane coordinate structure of phosphorus in the isomer **1** is achieved quite well: the angles between the axial and equatorial bonds being close to linear and all of the equatorial atoms lying strictly in one plane with the P atom (sum of the three angles between the equatorial phosphorus atom bonds being 360.0°).

The N=C(3)Cl(1)C(4) fragment in isomer **1** is planar (the sum of the angles between the C(3) atom bonds also being 360.0°). Judged by the small value of the torsional angles Cl_ePN=C(3) and PN=C(3)Cl(1) and also the near to 180° torsional angle PN=C(3)C(4) this fragment is found virtually in a single plane with equatorial P atom bonds. These structural features in isomer **1** apparently play a deciding role in the migration of the chlorine atom in the chlorotropic conversion of isomers **1** and **2**.

In both isomers the five membered C(1)O(1)PO(2)C(2) heterocycle is virtually planar (the sum of the internal angles being close to 540°). The nature of the small deviation from planarity is seen in the Table from the dihedral angles in the ring (the deviation in isomer **2** being a little larger than in **1**). It should be noted that in isomer **2** the lengths of the two P–O bonds become the same, as do the C–O bonds. A significant transformation of the molecular structure occurs on changing from isomer **1** to isomer **2** associated with the change in coordination number of the phosphorus atom and the spatial arrangement of the nitrogen containing PNC(3)

TABLE 1. Basic Bond Lengths (*d*) for the Isomeric Molcules of Compounds **1** and **2**[**] Calculated by the RHF/6-31G* Method

Bond	*d*, Å			
	X = F		X = Cl	
	1	**2**	**1**	**2**
C(1)–C(2)	1.374	1.378	1.374	1.378
C(1)–O(1)	1.351	1.379	1.350	1.379
C(2)–O(2)	1.378	1.380	1.378	1.379
P–O(1)	1.687	1.603	1.688	1.603
P–O(2)	1.607	1.603	1.608	1.603
P–Cl_a	2.116	—	2.116	—
P–Cl_e	2.028	—	2.028	—
P–Cl	—	1.985	—	1.985
P–N	1.669	1.504	1.665	1.502
N–C(3)	1.225	1.379	1.223	1.376
C(3)–Cl(1)	1.733	1.803	1.737	1.807
C(3)–Cl(2)	—	1.798	—	1.801
C(3)–C(4)	1.528	1.545	1.546	1.581

[**] The atomic numbering in Tables 1-3 corresponds with that given in the Scheme.

TABLE 2. Valence Angles (ω) for the Isomeric Molcules of Compounds **1** and **2** Calculated by the RHF/6-31G* Method

Angle	α, deg			
	X = F		X = Cl	
	1	**2**	**1**	**2**
O(1)C(1)C(2)	111.0	111.3	111.0	111.4
O(2)C(2)C(1)	110.7	111.3	110.7	111.3
C(1)O(1)P	112.8	110.4	112.8	110.4
C(2)O(2)P	114.5	110.3	114.5	110.3
O(1)PO(2)	90.8	95.9	90.8	95.9
O(1)PCl$_e$	91.2	—	91.2	—
O(1)PN	88.3	119.9	88.4	119.9
O(1)PCl	—	104.8	—	104.7
Cl$_a$PO(2)	88.1	—	88.1	—
Cl$_a$PCl$_e$	92.7	—	92.7	—
Cl$_a$PN	89.0	—	89.0	—
O(2)PCl$_e$	117.0	—	116.8	—
O(2)PN	120.5	120.1	120.4	120.1
O(2)PCl	—	105.4	—	105.3
Cl$_e$PN	122.5	—	122.8	—
ClPN	—	108.8	—	108.9
PNC(3)	138.8	137.3	140.0	138.4
NC(3)C(4)	120.1	108.2	120.8	108.6
NC(3)Cl(1)	126.9	113.5	124.9	112.7
C(4)C(3)Cl(1)	113.0	107.3	114.3	108.7
NC(3)Cl(2)	—	112.3	—	111.4
C(4)C(3)Cl(2)	—	107.5	—	108.9
Cl(1)C(3)Cl(2)	—	107.7	—	106.5

fragment. Hence in isomers **1** and **2** the dihedral angles Cl$_e$PNC(3) and Cl$_a$PNC(3) and also the interatomic bonds of the PNC(3)C(4) fragment (Tables 1-3) are fundamentally different causing a shift of the Cl atom from the P atom to the C(3) atom with change in hybridization of the latter in these isomers.

The most likely case for chlorotropic conversion of isomer **1** to isomer **2** involves migration of the axial chlorine atom. This proposal is confirmed by the fact that the axial P–Cl$_a$ bond is longer and thus weaker than the equatorial. In addition the axial chlorine atom has a greater negative charge than the equatorial (see before) and it is situated closer to the positive charge (+ 0.224 e) on the C(3) atom than the equatorial. The calculated distances are Cl$_a$…C(3) 3.445 and Cl$_e$…C(3) 3.813 Å. As a result, the interaction of the axial chlorine atom with atom C(3) proves much stronger than the equatorial and this leads to bonding of atoms Cl$_a$ and C(3). The molecular configuration of isomer **2** made as a result of this confirms the deduction made regarding the chlorotropic conversion. Hence a marked approach of atoms O(2) and C(3) occurs in the molecule, the distance between them decreasing from 4.048 (in isomer **1**) to 3.512 Å (in isomer **2**) with a simultaneous decrease of the O(2)PNC(3) dihedral angle from about 180 to 54° (See Tables 1-3). These changes in molecular geometry on changing from isomer **1** to isomer **2** are a result of the contact between the Cl$_a$ and C(3) atoms with formation of a second C(3)–Cl bond (see Scheme). Moreover, in the structure of isomer **2** the C(3)–Cl(1) and C(3)–Cl(2) bonds are found on different sides of the PNC(3) plane since the dihedral angles PNC(3)Cl(1) and PNC(3)Cl(2) have opposite signs (Tables 1-3).

A separate and interesting question concerns the relative stabilities of isomers **1** and **2**. According to ^{31}P spectroscopic data these isomers (both for X= F and for X = Cl) are found in solution in equilibrium thanks to migration of the chlorine atom in the PNC triad, however the fraction of one or the other depends on the solvent

TABLE 3. Torsional Angles (τ) and Total Energies (*E*)** for the Isomeric Molcules of Compounds 1 and 2 Calculated by the RHF/6-31G* Method

Angle	τ, deg			
	X = F		X =Cl	
	1	**2**	**1**	**2**
O(1)C(1)C(2)O(2)	-0.4	0.0	-0.4	0.0
PO(1)C(1)C(2)	3.5	-5.6	3.4	-5.4
PO(2)C(2)C(1)	-3.0	5.6	-2.9	5.4
O(1)PNC(3)	-88.4	-64.6	-88.3	-65.4
O(2)PNC(3)	-178.3	53.5	-178.2	54.3
Cl_aPNC(3)	94.6	—	94.6	—
Cl_ePNC(3)	2.0	—	2.1	—
ClPNC(3)	—	174.9	—	174.1
PNC(3)C(4)	178.6	169.0	178.6	167.0
PNC(3)Cl(1)	-1.7	50.0	-1.8	46.5
PNC(3)Cl(2)	—	-72.4	—	-73.1

** -*E*, a.u.: 2526.947982 (**1**, X = F), 2526.961084 (**2**, X = F), 3607.033835 (**1**, X = Cl), and 3607.041064 (**2**, X = Cl).

[1]. Hence the amounts of isomers **1** and **2** (where X = Cl) are 75 and 25% in CH_2Cl_2 but 28 and 72% in the less polar CCl_4 solvent, i.e. the ratio is reversed. In compounds **1** and **2** (where X = F) the equilibrium position is shifted strongly to an increase of the isomer **2** (84 in CH_2Cl_2 and 97% in CCl_4 [1]). Overall, a greater tendency to the more stable phosphazo compound structure in isomer **2** can be seen.

According to ^{35}Cl NQR the crystal of the compound with X = F exists only in the isomer **2** form whereas with X = Cl this form becomes metastable. For the compound with X = Cl in the sold state the phosphorane structure **1** is preferred [2]. It evidently appears here that the condensed phase of the material determining stabilization of the isomeric form may be its aggregate state, the role of which has been noted in, for example, the effect on the conformational stability of certain compounds [5-7].

The stability of the isomeric forms of the isolated molecules were determined in our work by the values of the total energies obtained from non-empirical quantum-chemical calculations. As a result of the latter it was found that the isomeric phosphazo compound forms **2** are more stable in the compounds investigated with X = F and X = Cl. The structure of the isomers in form **2** was found in the free molecule state to be energetically more favored when compared with form **1** by 34.4 and 19.0 kJ/mol for X = F and X = Cl respectively (see Tables 1-3). The presence in the molcule with X = F of a markedly larger difference in energy for the two isomers explains why, in these molcules, form **2** is observed in the crystal as the sole [2] and in solution as the predominant species independently of the solvent polarity [1].

Hence a quantum-chemical study of the chlorotropic reaction in the discussed chlorophosphoric compounds has allowed us to determine the nature of the chlorine atom migration in the molcule and the stability of its isomers with change in the coordination number of the phosphorus atom.

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