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QUANTUM-CHEMICAL STUDY OF THE STRUCTURE OF 1,2,2,3,4,4-HEXACHLORO-1,3-DIPHOSPHETANE ISOMERS

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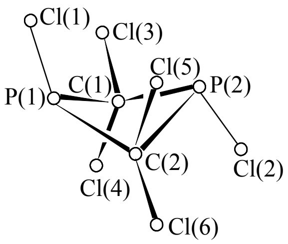
We have used the RHF/6-31G method to optimize the geometric parameters of three isomers of the $(ClP\text{–}CCl_2)_2$ molecule. We have established that the trans isomer is the most stable, and that it is energetically more favorable than the two cis isomers by 7.8 and 14.2 kJ/mole respectively.*

Keywords: 1,2,2,3,4,4-hexachloro-1,3-diphosphetane, *cis* and *trans* isomers, the RHF/6-31G* method, nonempirical calculations, molecular structure.

The structural features of molecules with four-membered phosphorus-carbon heterocycles have attracted the attention of researchers for a rather long time; see, for example, [1]. In [2], X-ray diffraction was used to study the molecular structure of crystalline 1,2,2,3,4,4-hexachloro-1,3-diphosphetane $(ClP\text{–}CCl_2)_2$, as a result of which it was established that its molecules in the solid state exist as the *trans* isomer, contrary to the opinion that the *cis* isomer is preferred (see the discussion in [2]). So it seemed to be of interest to use quantum-chemical calculations to determine which of the isomers of the given diphosphetane is energetically more favorable, and also the structural features of its possible isomers.



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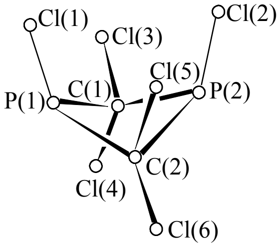

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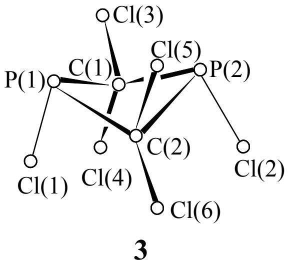

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With this objective, we carried out a nonempirical quantum-chemical calculation for the indicated molecule with full optimization of its geometry by the restricted Hartree–Fock method (RHF) in the split-valence basis 6-31G* using the program Gaussian 94W [3], and we established that the four-membered heterocycle PCPC is nonplanar with a bend along the C···C line (the same nonplanarity of the ring was observed by X-ray diffraction in [2]). Consequently, the existence of three isomers is possible: one *trans* isomer (**1**) and two *cis* isomers (**2** and **3**).

In the *trans* isomer **1**, the P–Cl bonds are on different sides of the nonplanar P_2C_2 ring, while in the other two isomers these bonds are located either on the concave side of the ring (*cis* isomer **2**) or on the convex side of the ring (*cis* isomer **3**). According to the calculation, the bending angle of the P_2C_2 ring along the C(1)···C(2) line in the *trans* form **1** is equal to 21.2°, while in the *cis* forms **2** and **3** it is 8.6° and 27.8° respectively. For comparison, we note that in the *trans* isomer, in the crystal this bending angle is as large as 29.9° [2].

As we see from the calculated energies of the *E*-isomers (see Table 1), for the free molecule the *trans* isomer is the most stable, i.e., just as was experimentally established in the case of the crystal for the studied compound in [2]. In this case, the differences between the total energies of the isomeric forms suggest that the *trans* isomer **1** is more stable than the *cis* isomers **2** and **3** by 7.8 and 14.2 kJ/mole respectively. These data are consistent with the conclusion in [2] that as a result of dimerization of the phosphaalkene $Cl_2C{=}PCl$, the *trans* isomer **1** is mainly formed. They allow us to also hypothesize that the other dimerization product, the yield of which is ~2% [4], may be the *cis* isomer **2**.

Comparison of the calculated bond lengths and bond angles with those found by X-ray diffraction (see Tables 1-3) indicates that their agreement is satisfactory, considering that the calculation was carried out for the free molecule while the experimental structure refers to the crystal.

Note the appreciable difference between the lengths of the two P–Cl bonds in the *trans* isomer: the P(1)–Cl(1) bond is longer than the P(2)–Cl(2) bond. This difference is also shown in the experiment, with a somewhat different value. We see differences between the calculated and experimental P–C bond lengths of the other two portions of the dimer ring for the *trans* isomer that are also qualitatively the same. Such a pattern is also observed for the ClPC and CPC angles in different halves of the given isomer (see Table 1). All these structural features of the *trans* isomer are due to the different directions of the two P–Cl bonds in the molecule relative to the line of bend for the ring of the four-membered P_2C_2, which leads to nonequivalence of not only the P–Cl bonds themselves but also bond angles at the two phosphorus atoms.

TABLE 1. Bond Lengths (*d*) of *trans*-(**1**) and *cis* (**2** and **3**) Isomers of the $(ClP{-}CCl_2)_2$ Molecule, Calculated by the RHF/6-31G* Method, and Bond Lengths of the *trans* Isomer According to X-ray Diffraction Data [2], and the Molecular Energies (-*E*)*

Bond	*d*, Å			
	X-ray diffraction (**1**)	**1**	**2**	**3**
P(1)–Cl(1)	2.032	2.048	2.042	2.027
P(2)–Cl(2)	2.013	2.033	2.042	2.027
P(1)–C(1), P(1)–C(2)	1.911, 1.890	1.915	1.912	1.906
P(2)–C(1), P(2)–C(2)	1.876, 1.879	1.889	1.912	1.906
C(1)–Cl(3), C(2)–Cl(5)	~1.761	1.767	1.755	1.779
C(1)–Cl(4), C(2)–Cl(6)	~1.770	1.774	1.790	1.761

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* Molecular energy, -*E*, au: 3514.03628 (**1**); 3514.029672 (**2**); 3514.027235 (**3**).

We note that in the *trans* isomer **1** the dihedral angle Cl(1)P(1)P(2)Cl(2) according to X-ray diffraction is -179.85° [2], while the calculation gives -179.97° (in the *cis* isomers **2** and **3**, this angle is equal to 0° after full optimization of their geometry). In this case, in the *trans* isomer **1**, according to the calculation the P_2C_2 ring (and the entire molecule along with it in the free state) has a symmetry plane passing through the Cl(1), P(1), P(2), Cl(2) atoms. As we see from X-ray diffraction data in [2], such symmetry (C_s) is absent in the crystal. The crystal effects lead to distortion of the P_2C_2 ring, as a result of which the pairwise equality of the P–C bond lengths and ClPC angles in each half of the dimer structure **1** breaks down (Tables 1 and 2).

While there is a clear difference between the lengths of the two P–Cl bonds in the *trans* isomer and this causes nonequivalence of the two halves of the four-membered ring, in the *cis* isomers we observe that the two parts of the dimer are completely identical. The latter means that the molecule has C_{2v} symmetry, i.e., in addition to the symmetry plane characteristic of the free *trans* isomer, the *cis* isomer has another symmetry plane and a two-fold symmetry axis of rotation.

TABLE 2. Bond Angles (α) of *trans* (**1**) and *cis* (**2** and **3**) Isomers of the $(ClP–CCl_2)_2$ Molecule, Calculated by the RHF/6-31G* Method, and Bond Angles of the *trans* Isomer **1** According to X-ray Diffraction Data [2]

Angle	α, deg.			
	X-ray diffraction (**1**)	**1**	**2**	**3**
Cl(1)P(1)C(1)	100.1	102.2	102.7	106.8
Cl(1)P(1)C(2)	100.6	102.2	102.7	106.8
Cl(2)P(2)C(1)	105.3	107.4	102.7	106.9
Cl(2)P(2)C(2)	105.5	107.4	102.7	106.9
Cl(3)C(1)P(1)		117.2	117.8	111.1
Cl(3)C(1)P(2)		112.1	117.8	111.1
Cl(4)C(1)P(1)		107.0	106.7	116.9
Cl(4)C(1)P(2)		117.5	106.7	116.9
Cl(3)C(1)Cl(4)		109.2	109.2	109.4
Cl(5)C(2)P(1)		117.2	117.8	111.1
Cl(5)C(2)P(2)		112.1	117.8	111.1
Cl(6)C(2)P(1)		107.0	106.7	116.9
Cl(6)C(2)P(2)		117.5	106.7	116.9
Cl(5)C(2)Cl(6)		109.2	109.2	109.4
C(1)P(1)C(2)	81.3	82.0	81.9	82.7
C(1)P(2)C(2)	82.5	83.4	81.9	82.7
P(1)C(1)P(2)	93.4	93.3	97.5	90.3
P(1)C(2)P(2)	94.0	93.3	97.5	90.3

TABLE 3. Charges on the Atoms (q) of *trans* (**1**) and *cis* (**2** and **3**) Isomers of the $(ClP–CCl_2)_2$ Molecule, Calculated by the RHF/6-31G* Method

Atom	q, e		
	1	**2**	**3**
P(1)	+0.760	+0.777	+0.742
P(2)	+0.763	+0.777	+0.742
Cl(1)	-0.226	-0.224	-0.199
Cl(2)	-0.213	-0.224	-0.199
C(1), C(2)	-0.658	-0.664	-0.653
Cl(3), Cl(5)	+0.055	+0.075	+0.033
Cl(4), Cl(6)	+0.061	+0.037	+0.077

The charges q on the atoms are distributed accordingly: in the *trans* isomer, the charges on the chlorine atoms of the two P–Cl are different (as on the phosphorus atoms, although to a significantly lesser degree), while in each of the *cis* isomers these charges are identical (Table 3). Of course, in both the *trans* and the *cis* isomers, the C–Cl bonds located on different sides of the nonplanar P_2C_2 ring remain nonequivalent, which is apparent in the differences between their lengths and the charges on the corresponding chlorine atoms (Tables 1 and 3). As we see, the ratios of the charges on the chlorine atoms of the C–Cl bonds and the lengths of the latter bonds on different sides of the ring in *cis* isomers **2** and **3** depend on the position of the P–Cl bonds relative to the bend of the P_2C_2 ring: the shorter C–Cl bonds are located on the same side of the ring as the P–Cl bonds. In the *trans* isomer, the differences between the C–Cl bond lengths are significantly smaller.

On the whole, as a result of the quantum chemical study of the conformations of the free $(ClP{-}CCl_2)_2$ molecule, we have established that its *trans* isomer has the highest stability, which according to the data in [2] is also apparent in the solid state. The secondary product of dimerization of the phosphaalkene $Cl_2C{=}PCl$ [4] is probably the *cis* isomer **2**.

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