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Structure and Conformational Stability of 1,3-Dihalo-2,2,4,4-tetrachloro-1λ³,3λ³-diphosphetidines

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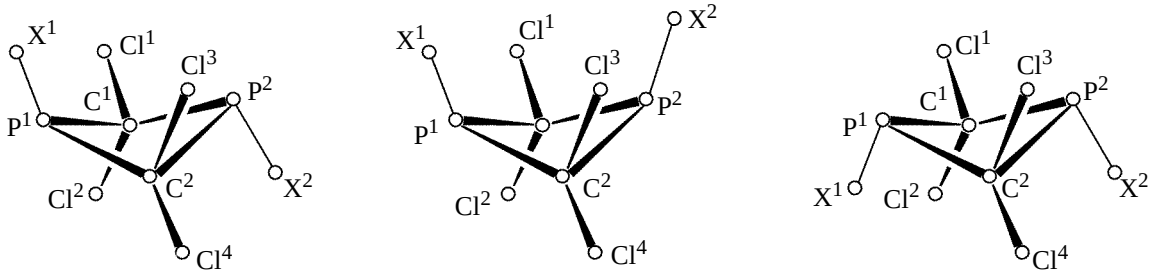
Abstract — The optimal geometry of isomeric molecules of $(XP–CCl_2)_2$ with X = F, Cl, Br was determined by RHF/6-31G(d) calculations. With X = F and Cl, the electronic correlation was considered on the MP2/6-31G(d) level. The P_2C_2 ring is nonplanar. With X = Cl and Br, the *trans* conformation is energetically preferable compared to the two possible *cis* conformations: by 7.8 and 14.2 kJ mol^{-1} for X = Cl and by 7.5 and 14.1 kJ mol^{-1} with X = Br. respectively. With X = F, the calculated energies of the *cis* and *trans* forms are very close.

The ^{31}P NMR spectra of 1,3-dihalo-2,2,4,4-tetrachloro-1λ³,3λ³-diphosphetanes $(XP–CCl_2)_2$, where X = F, Cl, and Br, allowed identification of these compounds as *cis* and *trans* isomers, with the former prevailing. For example, the *cis* isomer content in hexachlorodiphosphetidine $(ClP–CCl_2)$ is assumed to be as high as 98% [1]. However, X-ray diffraction studies have shown that, in the crystal, the compound exists in the *trans* form [2]. In this connection, it seemed appropriate to evaluate the structural parameters and conformational stability of these compounds by quantum-chemical calculations, which was the goal of this study. The calculations of all possible isomers of these molecules with the complete optimization of their geometry were carried out using the GAUSSIAN 94W program [3] by the RHF/6-31G(d) method, and in the case of X = F, Cl the electron correlation was also taken into account on the MP2/6-31G(d) level. These calculations revealed the stationary points on the potential energy surfaces of the molecules. In all the cases, the imaginary frequences of stretching vibrations were absent.



I **II** **III**

X = F (**a**), Cl (**b**), Br (**c**).

The nonplanarity of the phosphorus–carbon four-membered ring P_2C_2, established by calculations, suggests the existence of three geometric isomers, *trans* (**I**) and two *cis* (**I**, **III**). In the *trans* isomer **I**, the two P–X bonds are located on different sides of the nonplanar ring, whereas in the two other conformers (**II**, **III**) these bonds are located on the one side of the ring. In conformer **II** they are located on the "concave" side of the ring, and in conformer **III**, on the "convex" side. The dihedral angles $P^1C^2P^2C^1$ characterizing the folding of the rings along the $C^1\cdots C^2$ line as well as the other geometric parameters of molecules **I**–**III** with X = F, Cl, and Br are listed in Table 1. For all X, the dihedral angle $X^1P^1P^2X^2$ is

Table 1. Bond lengths (*d*), bons angles (ω), and dihedral angles $P^1C^2P^2C^1$ (τ) calculated by RHF/6-31G(d) and MP2/6-31G(d) methods for *trans* (**I**) and *cis* (**II, III**) isomers of diphosphetidines $(XP–CCl_2)_2$ with X = F, Cl, Br

Parameter	X = F				X = Cl						X = Br		
	I		**II**		**I**		**II**		**III**		**I**	**II**	**III**
	RHF	MP2	RHF	MP2	RHF	MP2	RHF	MP2	RHF	MP2	RHF	RHF	RHF
Bond	*d*, Å												
$P^1–X^1$	1.588	1.623	1.581	1.615	2.048	2.052	2.042	2.044	2.027	2.032	2.212	2.204	2.188
$P^2–X^2$	1.576	1.612	1.581	1.615	2.033	2.038	2.042	2.044	2.027	2.032	2.194	2.204	2.188
$P^1–C^1$	1.898	1.904	1.897	1.904	1.915	1.923	1.912	1.920	1.906	1.912	1.916	1.912	1.906
$P^2–C^1$	1.890	1.894	1.897	1.904	1.889	1.893	1.912	1.920	1.906	1.912	1.891	1.912	1.906
$C^1–Cl^1$	1.769	1.768	1.760	1.758	1.767	1.766	1.755	1.753	1.779	1.778	1.767	1.756	1.780
$C^1–Cl^2$	1.771	1.769	1.780	1.778	1.774	1.771	1.790	1.787	1.761	1.758	1.775	1.792	1.761
Angle	ω, τ, deg												
$C^1P^1C^2$	82.0	81.0	81.6	80.4	82.0	81.0	81.9	80.6	82.7	81.7	82.0	82.0	82.8
$C^1P^2C^2$	82.5	81.6	81.6	80.4	83.4	82.6	81.9	80.6	82.7	81.7	83.3	82.0	82.8
$P^1C^1P^2$	94.4	94.5	96.7	97.6	93.3	93.4	97.5	98.6	90.3	89.9	93.0	97.3	89.9
$X^1P^1P^2$	86.8	84.8	91.2	89.9	92.1	89.5	101.2	99.4	131.9	132.5	91.1	101.0	132.8
$X^2P^2P^1$	120.9	122.6	91.2	89.9	128.1	128.9	101.2	99.4	131.9	132.5	128.9	101.0	132.8
$X^1P^1C^1$	97.4	97.1	97.8	97.5	102.2	101.3	102.7	101.9	106.9	106.2	101.8	102.8	107.2
$X^2P^2C^1$	103.2	103.5	97.8	97.5	107.4	107.0	102.7	101.9	106.9	106.2	107.6	102.8	107.2
$P^1C^1Cl^1$	114.5	113.9	115.2	114.5	117.2	116.5	117.8	117.0	111.1	111.1	117.5	118.0	111.0
$P^2C^1Cl^1$	112.8	112.6	115.2	114.5	112.1	111.8	117.8	117.0	111.1	111.1	112.1	118.0	111.0
$P^1C^1Cl^2$	109.1	108.7	109.2	108.8	107.0	106.8	106.7	106.3	116.9	116.5	107.1	106.7	117.3
$P^2C^1Cl^2$	114.9	114.9	109.2	108.8	117.5	117.4	106.7	106.3	116.9	116.5	117.7	106.7	117.3
$Cl^1C^1Cl^2$	110.4	111.3	110.6	111.7	109.2	110.2	109.2	110.4	109.4	110.3	108.9	109.0	109.2
$P^1C^2P^2C^1$	19.6	21.8	13.9	15.2	21.2	23.5	8.6	9.7	27.8	30.3	21.9	9.1	28.3

180° in **I** and 0° in **II** and **III**. The $P^1C^2P^2C^1$ angles in isomers **II** are considerably smaller than in isomers **I** and **III**.

A specific feature of *trans* isomers as compared to the *cis* isomers is that in the *trans* form the related structural elements of two "halves" of diphosphetidine molecules $(XP–CCl_2)_2$ with P^1 and P^2 phosphorus atoms differ in geometric characteristics (e.g., $P^1–X^1$ and $P^2–X^2$ bonds, $C^1P^1C^2$ and $C^1P^2C^2$ angles) owing to the different directions of the P–X bonds. Molecules **I** have the C_s symmetry, with the symmetry plane passing through X^1, P^1, P^2, and X^2 atoms. The *cis* isomers (**II**, **III**) have no such structural differences, both "halves" are equivalent (Table 1). Correspondingly, molecules **II** and **III** have the C_{2v} symmetry, with one of two symmetry planes being the same as in the *trans* isomer and the other plane passing through the carbon atoms and chlorine atoms bound to them. As in all the three isomers there is a symmetry plane passing through X^1, P^1, P^2, and X^2 atoms, only the parameters related to one half of the molecule are listed in Table 1.

The bond lengths and angles calculated by the RHF and MP2 methods differ insignificantly (Table 1). Only the larger P–F bond lengths (by 0.035 Å) obtained by the MP2 method can be noted. The geometric parametrs of molecules **I**–**III** with X = F in some cases considerably differ from the respective parameters of the molecules with X = Cl and Br, whereas in isomers with X = Cl and Br all the parameters are very close, with the natural exception of P–X bonds which, as expected, regularly increase in the order F–Cl–Br.

One of the specific manifestations of nonplanarity of the P_2C_2 ring in *trans* and *cis* isomers is the elongation of the exocyclic P–X bonds located from the "concave" side of the ring as compared to the related bonds on the opposite side. The exocyclic C–Cl bonds are also different. In the *trans* isomers, the bonds located on the "concave" side of the ring are shorter, and in the *cis* isomers the shortest C–Cl and P–X bonds are located on the same side of the ring. The endocyclic $P^1–C$ and $P^2–C$ bonds in the molecules with the given X are equal in the *cis* isomers and differ in the *trans* isomer (Table 1).

Table 2. Energies of molecules of *trans* (**I**) and *cis* (**II, III**) isomers of diphosphetidines $(XP–CCl_2)_2$ with X = F, Cl, Br, calculated by RHF/6-31G(d) and MP2/6-31G(d) methods

X	Total energy of molecule, au	*E* (RHF)			*E* (MP2)		
		trans-**I**	*cis*-**II**	*cis*-**III**	*trans*-**I**	*cis*-**II**	*cis*-**III**
F	–(*E*+2790)	3.961928	3.962490	3.962490	5.309698	5.309430	5.309430
Cl	–(*E*+3510)	4.032628	4.029672	4.027235	5.301351	5.296967	5.296312
Br	–(*E*+7730)	4.865814	4.862976	4.860458	–	–	–

Note that, in *trans*-diphosphetidine **Ib**, the calculated structural parameters of the isolated molecule (Table 1) reasonably agree with the experimental X-ray diffraction data [2], taking into account that the diffraction data were obtained for a crystal, which, as a rule, somewhat distorts the molecular geometry.

It is interesting to consider the angles formed by the P–X bonds with the line connecting the phosphorus atoms of the ring. Table 1 shows that the XPP angle largely depends on the ring side on which the P–X bond is located. In both *trans* and *cis* isomers, this angle is significantly larger when the P–X bond is located from the "convex" side of the P_2C_2 ring. For example, in isomers **I**, the $X^2P^2P^1$ angle is considerably larger than the $X^1P^1P^2$ angle, and XPP angles in isomers **III** are appreciably larger than those in isomers **II**. Apparently, the dependence of the XPP and XPC angles and of the P–X and C–Cl bond lengths (Table 1) on the relative orientation of molecular fragments in isomers **I**–**III** is primarily due to steric interactions.

Based on the results of quantum-chemical calculations, we evaluated the conformational stability of the diphosphetidines as the difference in the total energies of isomeric molecules (Table 2). Consideration of the zero-point vibration energy does not appreciably alter these values. Interestingly, in optimization of the geometry of $(FP–CCl_2)_2$ molecule by either RHF or MP2 method, *cis* isomer **IIIa** is not fixed at all. At location of the P–F bonds from the "convex" side of the P_2C_2 ring, its inversion takes place, and P–F bonds become located on the same side of the nonplanar ring as in *cis* isomer **IIa**.

The calculations performed revealed the stable conformers of diphosphetidines with X = Cl and Br. According to the calculations, *trans* isomers **Ib** and **Ic** are energetically more favorable. For the molecule with X = Cl, this is confirmed by both calculation methods. The energy difference between *trans* isomer **Ib** and *cis* isomers **IIb** and **IIIb** is 7.8 and 14.2 kJ mol^{-1}, respectively [with the zero-point vibration energy taken into account, the difference is 7.7 and 14.1 kJ mol^{-1} (RHF), or 11.5 and 13.2 kJ mol^{-1} (MP2), respectively]. X-ray diffraction data show [2] that the crystalline diphosphetidine exists as *trans* isomer **Ib**. With X = Br, RHF calculations show that *trans* isomer **Ic** is more stable than isomers **IIc** and **IIIc** by 7.5 and 14.1 kJ mol^{-1}, respectively. The above differences in the conformer energies adequately reflect their relative stability, as confirmed by published papers in which the results of quantum-chemical calculations of molecular conformations were compared with the experiment (see, e.g., [4]).

At the same time, in the case of diphosphetidine with X = F, no conclusion about the relative stability of the conformers can be made, because the energies of the *trans* and *cis* isomers (Table 2) are very close. The difference is as small as 1.5 (RHF) or 0.7 kJ mol^{-1} (MP2). Similarly to the case of X = Cl, consideration of the zero-point vibration energy does not significantly affect this difference (in RHF calculations, it is 1.4 kJ mol^{-1}).

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