Analysis and exploration of Structural Disorder in a new diazaphospholane compound: $(ClCH_2CH_2)_2NPO[(ClCH_2CH_2)N(CH_2)_2NC(O)C_6H_4(p\text{-}NO_2)]$

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A new diazaphospholane compound, 2-bis(2-chloroethyl)amino-1-(4-Nitrobenzoyl)-1,3,2-diazaphospholane-2-oxide (DIAZ compound), have been synthesized and characterized by IR and NMR spectroscopy and X-ray crystallography. This compound is produced from the reaction of phosphoramidic dichlorides and bis(2-chloroethyl) amine and contains three-terminal CH_2Cl groups. From the thermodynamic point of view, the formation of the DIAZ compound is more probable than phosphoric triamide. The X-ray analysis of this compound represents a structural disorder in only one of these terminal groups. The question is why disorder can be seen for some parts of the molecular structure and do not appear for the other part. In this paper, we have used density functional theory calculations to find the reason for such a phenomenon. Thus, we have shown that this phenomenon is due to the very close space structural isomers of the molecule which, can be appeared in the crystalline form. The harmonic vibrations computed for the DIAZ compound by the DFT method agree with the observed IR spectral data.

Keywords: DFT calculation, structural disorder, rotational barrier, diazaphospholane.

1. Introduction

Diazaphospherinane and diazaphospholane are important groups of heterocyclic phosphorus compounds that are of great importance in chemical and biological sciences. These compounds are effective light stabilizers for organic materials, especially for polymers. In addition, they have antioxidant and/or flame-retardant properties. [1]. They are suitable catalysts for the carbodiimidization reaction [2] and have antitumor pharmaceutical potential [3]. Heterophospholanes and heterophosphorinanes, in which phosphorus is surrounded by two other heteroatoms (oxygen, sulfur, and nitrogen), have been thoroughly studied [4–6]. However, these compounds can also contain NCH_2CH_2Cl as part of their structures, which open a door to possible applications for drugs to cure cancer [7,8]. Unfortunately, the stereochemistry, and crystal structures of these materials are not completely studied [9,10]. The study of the cyclophosphamides structures can help us to understand the pharmacological effects of these compounds. One of the diazaphospholane compounds is 2-bis(2-chloroethyl) amino-1-(4-Nitrobenzoyl)-1,3,2-diazaphospholane-2-oxide which, we call it as DIAZ compound.

In the present research, the DIAZ compound is synthesized and spectroscopically characterized. Additionally, an X-ray analysis on its single-crystal indicated a disorder in the structure. Although, disorder has been reported in many organophosphorus crystalline structures [11-14], the reason for the formation of this phenomenon has not been discussed in the literature. Therefore, the focus of this article is to study and possibly explain the root cause of this anomaly. To confirm the disorder, complete DFT calculations involving structural optimization and vibrational frequencies are performed. From this information, the corresponding Gibbs free energy of DIAZ compound and the barrier energy of rotation around C-N bonds are calculated. The results indicated that the CH_2Cl group in the vicinity of the heterocycle ring possesses less barrier energy. Therefore, the disorder observation may be associated with rotation around the corresponding C-N bond. One may expect that the reaction of 4-nitrobenzoyl phosphoramidic dichloride and bis(2-chloroethyl) amine to initially yield phosphoric triamide. Hence, this compound has not seen in the product, a DFT calculation has been performed to find the reason. This calculation shows that phosphoric triamide has lower stability than the DIAZ compound.

2. Experimental:

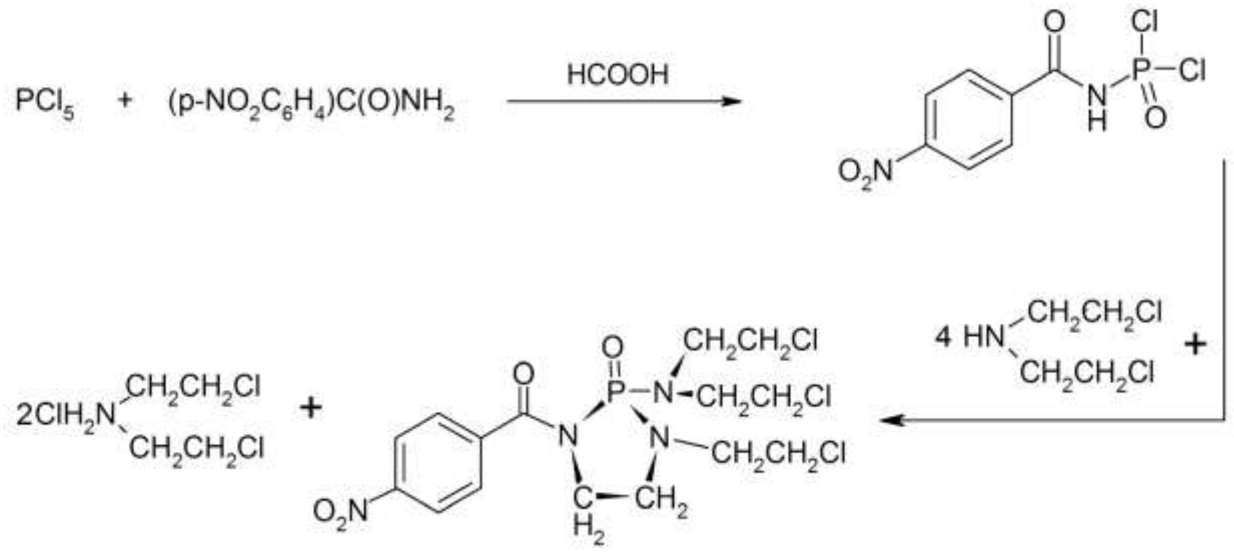
2.1. Materials and Methods

To prepare the single crystal of the DIAZ compound, the chemicals were purchased commercially and used without further purification. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker (Avance DRS) 500 spectrometer. ^{1}H and ^{13}C chemical shifts were determined relative to internal TMS. For ^{31}P NMR, 85% H_3PO_4 is used as external standard An IR spectrum (KBr pellet) is attained using a Shimadzu, IR-60 model spectrometer.

X-ray data of the DIAZ compound is collected on a four-cycle diffractometer Gemini equipped with CCD detector Atlas. In the single-crystal diffractometer a graphite monochromatic Cu Kα radiation (λ = 1.54184Å) was used. The structure is solved by direct methods and refined with the Jana2006 program [15].

2.2. Synthesis of 2-bis(2-chloroethyl)amino-1-(4-Nitrobenzoyl)-1,3,2-diazaphospholane-2-oxide

For the synthesis of the DIAZ compound, we first prepared the intermediate compound (p-NO2-C6H4)C(O)N(H)P(O)Cl2 using the Kirsanov method [16]. This compound is produced from the reaction of phosphorus pentachloride with 4-nitrobenzamide and then treatment with formic acid. Substituted phosphoramidic dichlorides and amines are ideal precursors for preparing carbacylamidophosphate species. Thus, the DIAZ compound was synthesized by reacting 4-nitrobenzoyl phosphoramidic dichloride and bis(2-chloroethyl) amine (nitrogen mustard), as shown in Scheme 1. Synthesis is performed by adding dropwise 4.0 mmol of bis(2-chloroethyl) amine to a stirred solution of 1.0 mmol of 4-nitrobenzoyl phosphoramidic dichloride in dry acetonitrile (20 ml) at 268 K. After 8 hours of stirring, the product was filtered off and then washed with distilled water and recrystallized from a mixture of chloroform/acetonitrile. Yield: 75%. δ_H (500.13 MHz, $CDCl_3$): 2.93 (2H, m, CH_2(ring)), 3.11 (2H, m, CH_2(ring)), 3.36 (2H, m, CH_2), 3.41-3.53 (6H, m, CH_2, CH_2Cl), 3.71 (2H, t, *J* 6.0 Hz, CH_2Cl), 3.84 (1H, m, CH_2Cl), 3.99 (1H, m, CH_2Cl), 7.97 (2H, d, *J* 8.4 Hz, Ar-H), 8.30 ppm (2H, d, *J* 8.6 Hz, Ar-H); δ_C (125.76 MHz, $CDCl_3$): 41.92 (C-12), 42.05 (C-10 and C-8), 43.10 (C-13), 43.58 (C-14), 46.46 (C-15), 49.16 (C-9 and C-11), 123.307 (C-3 and C-5), 129.68 (C-2 and C-6), 140.21 (C-1), 149.40 (C-4), 169.17 ppm (C-7); δ_P (202.46 MHz, $CDCl_3$): 19.06 ppm (br); ν_{max}: 2935 (C-H), 1659 (C=O), 1511 (NO_2), 1345 (C-NO_2), 1225 (P=O), 1137 (C-N_{amide}), 1094 ($(P\text{-}N)_{ring}$), 978 (P-N), 762 cm^{-1} (C-Cl).



Scheme 1. The preparation route of the DIAZ compound involves the formation of the (p-NO2-C6H4)C(O)N(H)P(O)Cl2 intermediate and then the formation of the final product by adding bis(2-chloroethyl) amine.

2.3. Crystal structure determination

Single crystal of DIAZ compound is obtained from a solution of chloroform and acetonitrile after slow evaporation at room temperature. The volume ratio of solvents is 2 to 1, respectively. The molecular structure of the compound is presented in Fig. 1, and the experimental details are given in table 1.

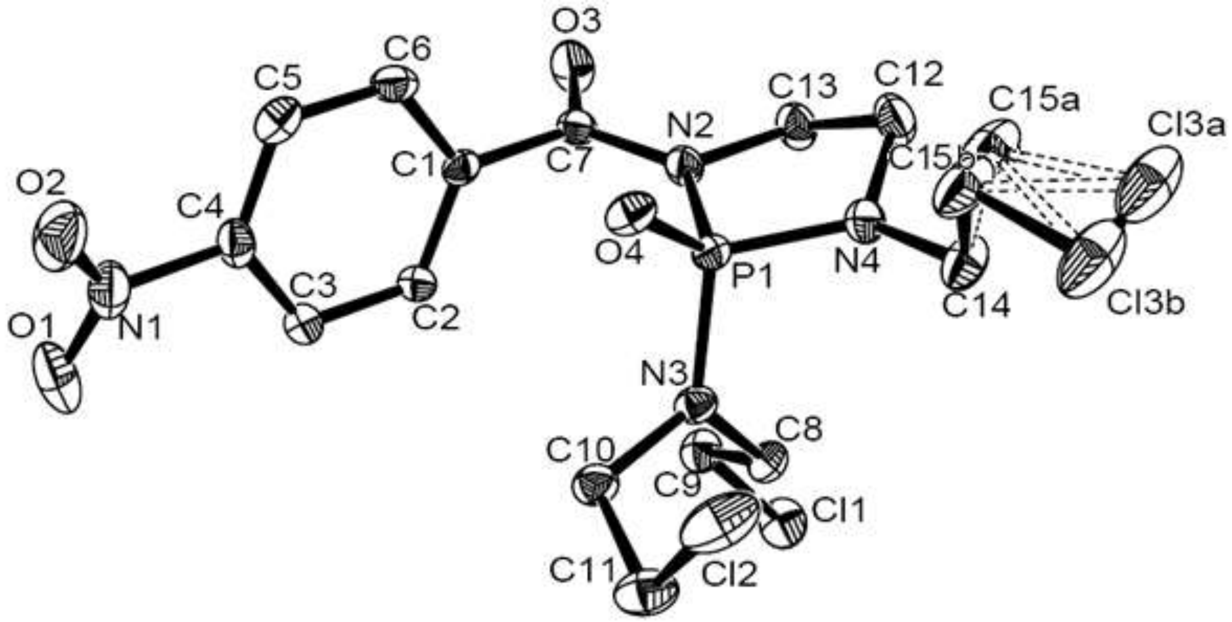


Fig. 1 Molecular structure of DIAZ compound, showing 50% probability displacement ellipsoids.

2.4. Computational methods

Quantum chemical calculations were performed with the Gaussian 03 program package [17]. The molecular geometry, vibrational frequencies, ^{1}H- and ^{13}C-NMR spectra of the compound in the ground state have been calculated using the density functional theory method (B3LYP) [18] with 6-311++G (d,p) basis set. The design of the structure and the vibrational modes of molecules are obtained using GaussView03 software [19].

Table 1. Crystal data and structure refinement for DIAZ compound.

Crystal data	
chemical formula	C15 H20 Cl3 N4 O4 P1
M_r	457.7
Crystal system, Space group	monoclinic, C1c1
Temperature (K)	120
a, b, c (Å)	18.9703(4), 11.5159(2), 10.7380(3)
α, β, γ (°).	90, 121.5425(30), 90
V (Å^3)	1999.234(101)
Z	4
Radiation type	Cu Kα
μ (mm^{-1})	5.176
Crystal form, size (mm)	Irregular shape, 0.3521 × 0.2390 × 0.2253
Data collection	
Diffractometer	Oxford Diffraction CCD
Data collection method	'Rotation method data acquisition using ω scans'
Absorption correction	multi-scan
T_{min}	0.325
T_{max}	1.000
No. of measured, independent and observed reflections	17757, 3429, 3402
Criterion for observed reflections	$I > 3\sigma(I)$
R_{int}	0.032
θ_{max}(°)	66.93
Refinement	
Refinement on	F
$R[F^2 › 2\sigma(F^2)]$, $wR(F^2)$, S	0.023, 0.036, 1.70
No. of reflections	3429
No. of parameters	250
H-atom treatment	Constrained to parent site
$(\Delta/\sigma)_{max}$	0.043
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.34, -0.2

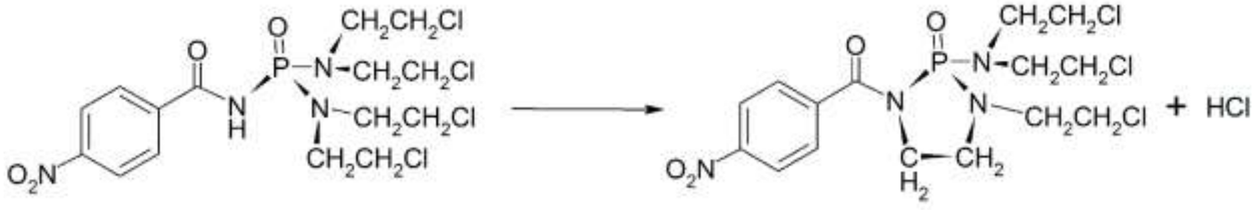
3. Results and discussion

3-1. X-ray Crystallography

The crystal structure of the DIAZ compound contains a five-membered ring made of one phosphorus, two nitrogen and two carbon atoms. The tetrahedral configuration around phosphorus atom was distorted (the angles in the range of 106.65-121.12˚). The short P-N bond lengths, of 1.640-1.717 Å, are of interest compared with the typical P-N bond distances, whose value is 1.77 Å [20]. In contrast with the previously reported similar compounds, the endocyclic nitrogen atoms surprisingly have a planar environment with the sum of the angles near 360˚. As indicated in figure 2, there seems to be a disorder in Cl(3)-C(15) and their carbon associated protons.

3-2. Structural analysis using DFT calculations

In the present study, nitrogen mustard is reacted with 4-nitrobenzoyl phosphoramidic dichloride. Normally, one expects a phosphoric triamide to be produced (Scheme 2). However, the amid-nitrogen atom will nucleophilic attack one of the carbon atoms connected to the chlorine atom. As a result, HCl gas is released and a hetero-cycle in the molecule's structure is generated to prepare a new type of cyclophosphamide compound (DIAZ). Careful observation of Fig. 1 reveals that the Cl(3)-C(15) in the molecule shows a disordered phenomenon.



Scheme 2. The evolution of HCl gas and the formation of cyclophosphamide compound (DIAZ) from phosphoric triamide.

To clarify the reason for forming cyclophosphamide compound and the disordered product, two different types of DFT calculations are performed on the molecules;

- Thermodynamic stability of the DIAZ compound is compared with phosphoric triamide compound.
- Rotational energy of Cl(3)-C(15) group around C-N bond is compared with one of the other equivalent Cl-C groups.

The above computations are described below in details.

3-2-1. Thermodynamic stability calculation

Ab initio calculations are performed to understand better the reason for getting the DIAZ compound. The molecular geometry and vibrational frequencies of compounds in the ground state are calculated using the density functional theory method (B3LYP) with 6-311++G(d,p) basis set, which is implemented in

Gaussian 03 package. The molecular geometry (The optimized bond lengths and bond angles) of the DIAZ compound in the ground state is similar to the data obtained from X-ray crystallography (Table 2). The harmonic vibrations computed for the DIAZ compound by the DFT method agree with the observed IR spectral data (Table 3). The experimental infrared spectrum of the DIAZ compound is compared with that of the theoretical spectrum calculated at the 6-311G++(d,p) level of theory (Fig 2). It is noted that the experimental results are obtained at the solid phase and the theoretical calculations at the gaseous phase. The computed vibrational frequencies were scaled with 0.967 for high and 1.0100 for low-frequency vibrations [21].

The Gibbs free energies of molecules in the displayed reaction (Scheme 2) are illustrated in Table 4. To compare the thermodynamic stability of the DIAZ compound with that of phosphoric triamide, the Gibbs free energy of each compound in the reaction must be calculated in kJ/mol (-8628468.1 for phosphoric triamide, -7418566.5 for DIAZ compound and -1209949.3 for HCl). From these values, the ΔG of the reaction is calculated (-47.70793 kJ/mol), which is a negative number.

In other words, from the thermodynamic point of view, the formation of the DIAZ compound is more probable than phosphoric triamide. Therefore, after the reaction of 4-nitrobenzoyl phosphoramidic dichloride with bis(2-chloroethyl) amine and formation of phosphoric triamide, nitrogen of the amide through an intra-molecular nucleophilic attack the carbon atom, C(15), associated with one of the terminal CH_2Cl. This gives rise to the release of HCl which forms a five-membered ring in the structure. This product is the DIAZ compound having more stability than phosphoric triamide.

Table 2. Selected bond distances (A˚) and angles (°) for the DIAZ compound.

Bonds or angles	B3LYP/6-311++G**	X-ray
P=O	1.487	1.469
P-N$_{amide}$	1.742	1.717
P-N$_{amine}$	1.6767	1.640
P-N$_{amine}$(ring)	1.6771	1.641
C=O	1.221	1.220
C-N$_{amide}$	1.389	1.364
C-N$_{amide}$(ring)	1.480	1.480
C-N$_{amine}$(ring)	1.466	1.468
RMSD	0.023	
O=P-N$_{amide}$	115.75	113.88
O=P-N$_{amine}$	110.62	110.19
O=P-N$_{amine}$(ring)	119.54	121.12
P-N$_{amide}$-C	129.61	127.85
P-N$_{amide}$-C(ring)	112.15	112.73
P-N$_{amine}$-C(ring)	112.99	114.70
RMSD	1.4	

Table 3. Selected experimental and calculated vibrational data (cm^{-1}) for DIAZ compound.

Tentative assignment	Experimental	B3LYP/6-311++G**
ν(C=O)	1659 vs	1646
$\nu_a(NO_2)$	1511 w	1528
$\nu(C\text{-}NO_2)$	1345 vs	1327
ν(OC-N)	1329 vs	1327
ν(P=O)	1225 s	1198
$\nu(C\text{-}N_{ring})$	1137 s	1148
$\nu_s(C\text{-}CO\text{-}N_{ring})$	1094	1114
$\nu_a(PN_3)$	978 m	980

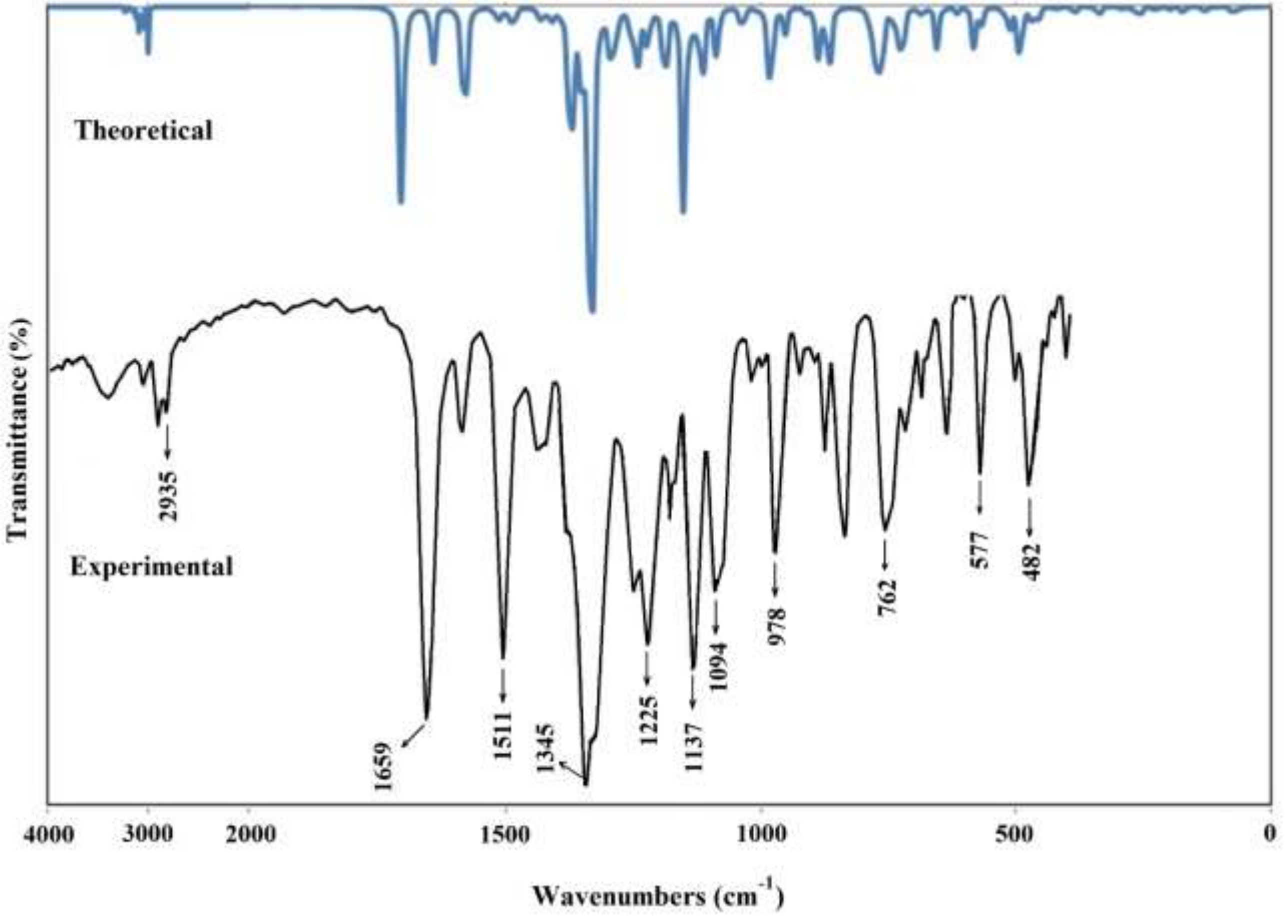


Fig. 2 Comparison between the experimental infrared spectrum of the DIAZ compound in the solid phase with that of the theoretical spectrum in the gas phase calculated at B3LYP/6-311++G(d,p) level of theory.

Table 4. The Gibbs free energy of all compounds and reaction illustrated in the Scheme 2.

Compound	Phosphoric triamide	DIAZ	HCl	$\Delta G_{reaction}$
Energy (kJ/mol)	-8628468.08277	-7418566.5262	-1209949.2645	-47.70793

3-2-2 Energy barrier calculation

As it can be seen, in Fig. 1 there exist three chloroethyl groups in the structure of the molecule. However, the disordered phenomenon is observed for only one of the chloroethyl groups that are adjacent to the heterocycle ring. The reason for observing the disorder for a group in the network may be related to its uncertain spatial position. Therefore, during the crystallization, it is assumed that due to easier rotation around one of the C-N bonds on one side of the molecule which makes two structural isomers with very close energies and existing of these isomers makes the disorder phenomena in the X-ray data. In other words, during the ordering of the crystal, the molecules have been able to take different angles which in the course of crystallography caused a disturbance in the X-ray dispersion, and hence disorder effect has occurred. Molecular energy values for dihedral angles due to rotation around two of the three C-N bonds are calculated. The rotational energy of the Cl(3)-C(15) group around the C-N bond is compared with one of the other equivalent Cl-C groups. That is, the C-N bound adjacent to the heterocycle ring and one of the other two equivalent bonds (C(11)-Cl(12) or C(9)-Cl(10)). The scanning step is chosen to be 10° between the -180° to +180° range for ∠PNCC or ∠CNCC dihedral angles. Table 5 and Fig. 3 illustrate these molecular energy values in relation to the different dihedral angles. The values are all normalized to the most stable molecule which is considered the ground state.

Table 5. The different dihedral angles rotation around the C-N bonds (º) and the corresponding molecular energy values (KJ/mol).

Dihedral angle	Molecular energy^a	Molecular energy^b	Dihedral angle	Molecular energy^a	Molecular energy^b	Dihedral angle	Molecular energy^a	Molecular energy^b
-180	116.006	49.040	-50	11.591	602.526	80	0.786	124.219
-170	119.369	28.741	-40	15.155	802.966	90	3.856	203.680
-160	118.008	14.219	-30	19.059	785.1576	100	8.163	341.315
-150	94.333	6.178	-20	22.876	628.020	110	13.216	396.480
-140	57.491	1.918	-10	26.094	578.171	120	19.985	299.340
-130	29.033	0	0	26.833	771.421	130	32.524	173.066
-120	14.838	0.123	10	24.533	1052.506	140	56.792	100.595
-110	9.0466	2.738	20	20.172	1210.474	150	90.254	79.015
-100	6.830	8.953	30	14.661	1234.934	160	114.982	76.381
-90	5.699	23.332	40	9.342	874.702	170	118.997	67.841
-80	5.535	58.462	50	4.850	526.156	180	116.006	49.040
-70	6.528	144.380	60	1.552	302.268			
-60	8.639	327.715	70	0	155.280			

a. the rotational N-Chloroethyl is adjacent to the heterocycle ring, b. the rotational N-Chloroethyl is far from the heterocycle ring.

As the data in table 5 and figure 3 represent, there seems to be symmetry in the shape of the rotational energy of the N-Chloroethyl, which is adjacent to the heterocycle ring. Its barriers are located at -170°, 0°, and 170°. The three barriers of the N-Chloroethyl that are farther from the heterocycle ring are at -40, 30, and 110 degrees. Here we found the relative energy barriers around C(14)N(4) bond concerning the C(8)N(3) is about 10. Doing a scan optimization rotational energy barrier calculation would reproduce lower energies. And, this would happen for both the energy barrier and the relative energy do not change a lot. Therefore the disorder is due to the smaller energy barrier around C(14)N(4) bond.

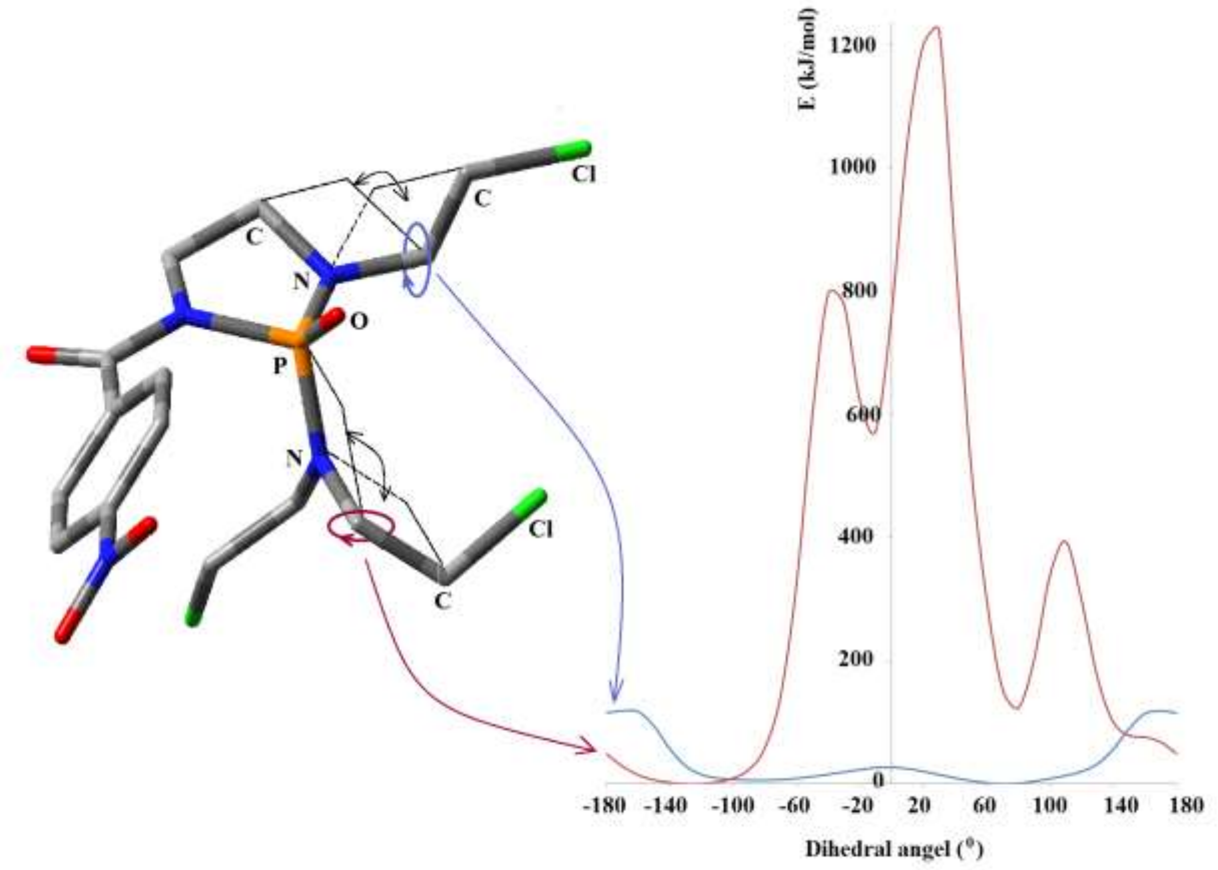


Fig. 3 molecular energy values with respect to the different dihedral angles rotation around the C-N bonds.

Careful consideration of the above study shows that the energy barrier of the rotation around the C-N bond in N-Chloroethyl, which is adjacent to heterocycle, is the lowest one. This means that the rotation around this C-N bond is easier. Therefore, the initial assumption that during crystallization, part of the molecule was able to present a different spatial position is correct. Since, the length and the order of the C-N bond in the two discussed groups are not that different, the main reason for the difference in their energy barriers is caused by the steric hindrance of the surrounding groups. In other words, the two chloroethyl groups, which are far from the heterocycle ring inhibit rotation around the C-N bond. However, the chloroethyl next to the heterocycle ring presents less hindrance and the associated rotation is easier and has a much lower energy barrier.

4. Conclusions

In reaction of 4-nitrobenzoyl phosphoramidic dichloride with bis(2-chloroethyl) amine, 2-bis(2-chloroethyl)amino-1-(4-Nitrobenzoyl)-1,3,2-diazaphospholane-2-oxide (DIAZ compound) was produced although one expects to obtain a phosphoric triamide. Due to the intramolecular nucleophilic attack of the amidic nitrogen group (-CONH-) to one of the terminal carbons of the chloroethyl substituted ($-CH_2CH_2Cl$) DIAZ compound has resulted. The Gibbs free energy calculations of the DIAZ compound and phosphoric triamide verify DIAZ is more stable. The optimized geometry and calculated vibrational frequencies of the DIAZ compound reveals a good agreement with the experimental values.

The main finding of this research is the proposal that the observed disorder in one of the substituted C-Cl groups of the DIAZ compound can be due to the rotation around the C-N bond. Therefore, we were able to propose a new method to explain the disorder phenomenon in the crystal structure using DFT calculations.

5. Supplementary Material

Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication CCDC876950 for $C_{15}H_{20}Cl_3N_4O_4P$. Copies of the data can be obtained from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033, e-mail: de posit@ ccdc.cam.ac.uk).

Conflict of Interests

The authores declare no conflicts of interests.

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