

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy



journal homepage: www.elsevier.com/locate/saa

Infrared, ¹H and ¹³C NMR spectra, structural charcterization and DFT calculations of novel adenine-cyclodiphosp(V)azane derivatives

Tarek A. Mohamed^{a,*}, Wajdi M. Zoghaib^b, Ibrahim A. Shaaban^{a,1}, Rabei S. Farag^a, Abd Elnasser M.A. Alajhaz^a

^a Department of Chemistry, Faculty of Science (Boys), Al-Azhar University, Nasr City 11884, Cairo, Egypt ^b Department of Chemistry, Sultan Qaboos University, P.O. Box 36, Al Khod, Muscat, Oman

ARTICLE INFO

Article history: Received 29 July 2011 Received in revised form 21 August 2011 Accepted 22 August 2011

Keywords: Adenine-cyclodiphospha(V)zanes Vibrational assignments ¹H NMR ¹³C NMR and theoretical calculations

ABSTRACT

Adenine tetrachlorocyclodiphospha(V)zane derivatives (III_{a-c}) were prepared by the reaction of hexachlorocyclodiphospha(V)zane derivatives (II_{a-c}) and adenine (II) as precursors. The synthesized compound's and their structures (III_{a-c}) were firmly characterized (based on the presence of an inversion center) using FT-IR (4000–200 cm⁻¹), UV–vis. (190–800 nm), ¹H, ¹³C NMR and Mass spectral measurements in addition to C, H, N, P elemental analysis. The compounds (III_{a-c}) were found to be a 1:2 molar ratio of (I_{a-c}) and adenine (II) adducts, respectively. Confident and complete vibrational assignments are proposed for nearly all fundamental vibrations, along with detailed interpretation for all observed signals in both ¹H and ¹³C NMR spectra of the investigated phospha(V)zanes (III_{a-c}). In addition, unconstrained geometry optimization of III_{a-c} were carried out by means of DFT-B3LYP/3-21G(d) calculations to provide new insight into the structural parameters and molecular geometries of compounds III_{a-c} . The results are reported herein and compared with similar molecules whenever appropriate.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Cyclodiphosphazane derivatives are an important family of inorganic heterocyclic compounds containing a saturated fourmembered P_2N_2 ring which gained considerable interest in synthesis and structural investigations [1–3]. This is due to the organic and inorganic properties of theses compounds particularly the ability of the inorganic rigid P–N framework to combine with organic substituents. Moreover, the ability of these compounds to form transition metal complexes with remarkable chemical and biological properties is also of great interest [4–7]. The high reactivity of hexachlorocyclodiphospha(V)zane toward nucle-ophilic substitution provides for chlorine atom(s) substitution by nucleophiles. Therefore, several cyclodiphospha(V)zanes containing active methylene, alcohols, thiols [3,8], aromatic and aliphatic amines [9–11] have already been synthesized and characterized. However, no one article provides a comprehensive interpretation and vibrational assignment for all observed frequencies. Moreover, little computational studies have been extended to cyclodiphosp-hazanes [12].

We aimed at synthesizing novel adenine-cyclodiphospha-(V)zane derivatives via amination of hexachlorocyclodiphospha(V)zane derivatives with adenine hoping the derivatives possess some important biological features. Furthermore, the synthesized compound's structures were characterized using elemental analysis and spectroscopic measurement including IR, UV, Mass Spec, ¹H and ¹³C NMR. In the context of our most recent work on P₃N₃Cl₆ [13] and adenine [14] we carried out computational calculations for **III**_{a-c} using Density Functional Theory (DFT) [15] in order to provide an efficient approach to their structures configurationally and structural parameters as well.

2. Experimental

2.1. Materials

Adenine, actonitrile, dimethylformamide (DMF), and dimethylsulfoxide (DMSO) were purchased from Aldrich Chemical Company. All reagents with 99% purity grade were used without further purification.

^{*} Corresponding author at: University of Nizwa, College of Arts and Sciences, Post Code 616, P.O. Box 33, Nizwa, Oman. Tel.: +202 38503918; fax: +202 22629356. *E-mail address:* tarek_ama@hotmail.com (T.A. Mohamed).

¹ Taken in part from the Master Thesis of Ibrahim A. Shaaban which was submitted to Chemistry Department, Faculty of Science, Al Azhar University, Nasr City, Cairo 11884, Egypt.

^{1386-1425/\$ -} see front matter © 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.saa.2011.08.035



Fig. 1. Synthesis of adenine-cyclodiphosph(V)azane derivatives (III_{a-c}).

2.2. Synthesis of adenine-tetrachlorocyclodiphospha(V)zanes (III_{a-c})

The hexachlorocyclodiphosphazane compounds (I_{a-c}) were prepared using the provided scheme (Fig. 1) and purified using known procedures [16]. Solid adenine (1.35 g, 0.01 mol) was added in small portions to a well stirred solution of 0.005 mol hexachlorocyclodiphosphazane derivatives (I_{a-c}) in 100 mL acetonitrile for 0.5 h. The hot reaction mixture was refluxed for 2 h in a fume hood with continuous stirring while evolving HCl gas. The reaction mixture was filtered and the resulting solid was washed several times with acetonitrile and diethyl ether before drying under vacuum.

2.3. Instrumentation

2.3.1. Elemental analysis

Carbon, hydrogen and nitrogen elemental analyses were carried out at the Micro Analytical Center, Cairo University, Giza, Egypt. While, the phosphorus percent was determined gravimetrically as phosphorous ammonium molybdate using Voy's method [17]. Analytical data for the adenine-tetrachlorocyclodiphosphazane derivatives (\mathbf{III}_{a-c}) are listed in Table 1.

2.3.2. IR and UV-vis spectra

The mid-infrared spectra (4000–200 cm⁻¹) of solid adenine and the synthesized compounds (III_{a-c}) were recorded on a Perkin Elmer Spectrum 100 FT-IR Spectrometer using CsI disk technique (Fig. 2). To improve the S/N ratio, forty scans were collected utilizing 0.5 cm⁻¹ resolution. The observed IR bands of adenine and the compounds (III_{a-c}) are listed in Table 2. The ultraviolet–visible spectra (190–800 nm) were measured using a Perkin Elmer Lambda 35 spectrophotometer with the samples dissolved in DMF (Fig. 3).

2.3.3. Mass spectra

Mass spectra (Supplement Fig. S-1) for compounds (III_{a-c}) were acquired on a Quattro Ultima Pt (Waters Corp., Milford, MA, USA), Tandem Quadrupole mass spectrometer using chemical ionization technique. Samples were initially dissolved in DMSO and serial dilutions were carried out in 50/50 (v/v) acetonitrile/water. The samples were infused using a Harvard syringe pump (Harvard, CA, USA) at a flow rate of 10 μ L per minute into the mass spectrometer.

2.3.4. NMR spectra

¹H (Fig. 4) and ¹³C (Fig. 5) NMR spectral measurements were performed with the samples (III_{a-c}) dissolved in DMSO- d_6 at 25 °C using a Bruker Avance 400 MHz NMR spectrometer equipped with

a Magnex Scientific superconducting magnet, and Top Spin 1.3 software. Tetramethylsilane (TMS) was used as an internal reference. To identify and ascertain the NH peaks in ¹H NMR spectra of the compounds under investigation, D_2O was added to the NMR sample with vigorous shaking to either reduce or eliminate the NH signal (proton deuterium exchange). To reduce the signal to noise ratio, 10,000 scans were acquired for ¹³C NMR measurements and 16 scans for ¹H NMR analysis with a 5 s relaxation delay time using a 10 k data point file. The ¹H and ¹³C chemical shifts of compounds (III_{a-c}) are listed in Tables 3 and 4, respectively.



Fig. 2. FT-IR solid spectrum of adenine and adenine-cyclodiphosph(V)azane derivatives in CsI; (A) adenine; (B) III_a ; (C) III_b ; (D) III_c .

Analytical and	nhysical dat	of adapting	cyclodiphosph	(V)	derivatives ()	
Analytical and	physical uata	a of adefinite-	cyclouipilospi	I(V)dZdIIC	uerivatives (I	a_{a-c}

Comp. No.	Reactants (mol, g)	Molecular m.p.		Color	Elemental anal	lysis; found/calculated		
	Hexachlorocyclodiphosph(V)azane derivatives and adenine	formula	(°C)	(%Yield)	%С	%Н	%N	%P
III _a	[(C ₆ H ₆)NPC1 ₃] ₂ (I _a): adenine (II) (0.01, 4.57): (0.02, 2.70)	C ₂₂ H ₁₈ Cl ₄ N ₁₂ P ₂ (654 g/mol)	283-285	White 80.20%	39.74/40.39	3.01/2.77	26.00/25.69	9.22/9.47
III _b	[(<i>p</i> -CH ₃ C ₆ H ₅)NPC1 ₃] ₂ (I _b): adenine (II) (0.01, 4.85): (0.02, 2.70)	C ₂₄ H ₂₂ Cl ₄ N ₁₂ P ₂ (682 g/mol)	260-263	Greenish 81.80%	41.81/42.25	3.12/3.25	25.00/24.64	8.84/9.08
III _c	[(<i>p</i> -ClC ₆ H ₅)NPC1 ₃] ₂ (I _c): adenine (II) (0.01, 5.26): (0.02, 2.70)	C ₂₂ H ₁₆ Cl ₆ N ₁₂ P ₂ (723 g/mol)	272–275	White 76.90%	36.50/36.54	2.50/2.23	24.01/23.24	8.34/8.57

3. Computational procedure

In order to obtain structural details about the prepared adenine-tetrachlorocyclodiphospha(V)zane derivatives (III_{a-c}), unconstrained geometry optimizations were performed while excluding the inversion center for compounds III_{a-c} using DFT [15] calculations. The calculations were carried out with B3LYP method in which Becke's non-local exchange [18] and the Lee–Yang–Parr correlation functiona [19] were applied with a 3-21G(d) basis set [20]. We could not implement larger basis sets owing to the lack of advanced computational facilities and the presence of eighteen

heavy atoms other than carbon and hydrogen which require Unix systems or work stations. Energy minima with respect to the nuclear coordinates were obtained by the simultaneous relaxation of all geometrical parameters for molecules (III_{a-c}) using Pulay's gradient method [21] with Gaussian-98 computational package [22] running on a PC, 2.0 GHz Pentium processor, 2 MB Ram. The bond lengths, bond angles, dihedral angles and selected structural parameters (SPs) are presented in Table 5. ¹H (Table 3) and ¹³C (Table 4) chemical shifts for adenine-cyclodiphospha(V)zanes (III_{a-c}) were also predicted using Chem Draw Ultra v8 [23].

Table 2

Vibrational assignments of adenine-cyclodiphosph(V)azane derivatives (III_{a-c}) compared with adenine.^a

Vibrational assignment	Adenine [14]	$III_a(Y=H)$	$III_b(Y=p-CH_3)$	III _c (Y=p-Cl)
PCl ₂ wag PCl ₂ Scissor N-H wag	250 w	209 vs 217 s 254 m	209 vs 228 s 251 sh	225 vs 254 w
N-H wag	230 W	265 sh	$\begin{cases} 271 \text{ vw} \\ 284 \text{ sh} \end{cases}$	267 vw
Pyrimidine ring puckering	337 s	{ 325 sh 335 m,s	{326 sh 335 s	{ 321 sh 335 s
Benzene ring puckering		387 w	371 w	$\int 382 \text{ w}$
P-Cl stretch		425 w, br	{ 410 w 420 sh	425 br, sh
PNP in plane deformation Imidazole NH wagging	513 sh	473 m, s { 497 m 522 sh	$\begin{cases} 465 \text{ w} \\ 486 \text{ sh} \\ 492 \text{ s} \\ 502 \text{ sh} \\ 513 \text{ sh} \end{cases}$	450 br, sh 496 m, br
Pyrimidine ring puckering	543 s	535 vs	{ 535 vs 539 sh	{ 535 s { 541 sh
NPN in plane deformation		563 w	{563 w 570 sh	563 w
Imidazole ring puckering	621 s, sh	{ 609 sh 620 s	{610 s 619 m	619 m
Imidazole ring in plane deformation	667 s, br	{637 s 655 sh	∫ 637 s ∫ 543 sh	$\begin{cases} 637 \text{ m} \\ 650 \text{ sh} \end{cases}$
C–N wagging	683 m	683 s	680 m 700 sh	681 m
Pyrimidine ring breath	723 vs	{ 711 s 719 sh	{ 711 s 720 sh	{ 711 m 720 sh
C-Cl inplane deformation				744 m, br
Benzene C-H wagging		{ 742 s 755 sh 774 m, sh	{753 m, br 776 m	{ 754 m, br 783 vw, sh
Pyrimidine ring in plane bending	797 m	∫ 789 m,sh,spl. 800 sh	789 w, sh	791 vw, sh

Table 2 (Continued)				
Vibrational assignment	Adenine [14]	III _a (Y=H)	$III_b(Y=p-CH_3)$	$III_{c}(Y=p-Cl)$
Methyl rocking Imidazole C–H wagging Pyrimidine ring bending Imidazole ring bending Pyrimidine C–H wagging	846 m, s 872 s 913 vs 939 vs	(860 br, sh) ^b (860 br,sh) 898 m 946 s	811 s (858 m, br) (858 m, br) 893 s {946 s 965 sh	(870 sh, br) (870 sh, br) 898 m 946 s
Benzene C=C-C stretches		982 m, br 1015 sh, br 1029 sh	$\begin{cases} 999 \text{ br} \\ 1017 \text{ w, sh} \\ 1021 \text{ w, sh} \end{cases}$	{984 w, sh 1016 m
C-Cl stretch				{1067 sh, w 1096 m
NH ₂ rocking	1025 s			
Methyl rock Imidazole CN ring stretch	1126 s	$\begin{cases} 1112 \text{ max, br} \\ 1123 \text{ max, br} \end{cases}$	1075 m { 1112 w 1121 sh	{1113 max, sh 1119 max, sh
P-N stretch		{ 1140 sh 1170 sh	{ 1137 m { 1173 m	{ 1138 sh 1156 sh
P–N stretch		{ 1185 m 1193 sh	{1186 m {1202 sh	{ 1185 s 1200 sh
Imidazole C–H in plane bending Methyl in plane deformation	1253 vs	1242 s	1242 s 1259 s	1242 s, br
Benzene C–H in plane bending Pyrimidine C–N stretch	1309 vs	1288 sh 1306 w	1285 vw, sh {1306 w 1319 w	1281 sh 1305 m
Imidazole ring stretch (v CN) C–N stretch	1335 vs 1368 s	1331 m	1331 m	1331 m
Benzene C=C-C stretches		{ 1382 sh 1399 w, sh	{ 1384 m 1398 m	1398 m, sh
Pyrimidine C–H in plane bending	1420 vs	{ 1413 m 1421 sh	{ 1413 s { 1419 sh	{1413 vs 1418 sh
Methyl in plane deformation			1441 m	
Pyrimidine CC ring stretch Imidazole CN ring stretch	1451 s 1506 w	1465 w, br 1493 m	1466 w, br ∫1496 s ∫1508 sh	1467 w, br 1493 vs
Benzene C=C-C stretches		{ 1520 vw, sh 1550 vw, sh 1574 m	{ 1531 vw 1556 w, sh 1576 s	{1539 sh, br 1576 s
Pyrimidine CN and CC ring stretch	1603 vs	{ 1602 sh 1611 m 1651 w, sh	{ 1592 w 1611 vs 1654 vw, sh	1611 vs, br
NH ₂ Scissor	1675 vs	C . =	6	C
N-H in plane bending		1701 vs, br 1789 vw	1702 vs, br 1790 w] 1698 v.br] 1789 w
Benzene C–H stretch	2000 -	(2955 s, br)	(2954 s, br)	(2953 s, br)
Pyrimidine C–H stretch	2980 s	(2955 S, br) 3033 s, br	(2954 s, br) 3033 s, br	(2953 s, br) 3033 s br
Imidazole C–H stretch	3119 vs	3085 sh	3138 sh	(3102 vbr)
NH ₂ symmetric stretch	3296 vs			
N-H stretch		(3253 s, sh)	(3255 s)	3315 sh, br
Imidazole N–H stretch NH ₂ antisymmetric stretch	3347 sh 3426 vw	(3253 s, sh)	(3255 s)	3375 sh

^a Vibrational assignment of adenine taken from Ref. [14].

^b Bands between brackets are used for two fundamentals modes.

4. Result and discussion

4.1. Electronic absorption spectral analysis

Analytical data and selected physical properties of the prepared adenine-cyclodiphospha(V)zane derivatives (III_{a-c}) are presented in Table 1. Comparison of calculated and experimental elemental analysis percentages indicates that the composition of compounds (III_{a-c}) coincides well with the structures proposed.

Electronic absorption bands (Fig. 3) observed in the 193–262 nm range were assigned to $\pi \rightarrow \pi^*$ transitions within the benzene and purine rings [24]. However, the recorded absorption bands at 268, 268 and 268 nm were attributed to the $n \rightarrow \pi^*$ (adenine moiety) transition of III_a, III_b and III_c, respectively, in agreement

Table 3

Characteristic ¹H NMR chemical shift (δ , ppm) of adenine-cyclodiphosph(V)azane compounds (III_{a-c}).

T (1 1 4 ^a	III _a (Y	(= H)	III _b (Y	′= p-CH ₃)	III _c (Y	= p-Cl)
Types of hydrogen atoms	Calc. ^b	Obs.	Calc. ^b	Obs.	Calc. ^b	Obs.
H _(a) (exocyclic N–H)	4.0	(9.01 br) ^c	4.0	8.92 br ^c	4.0	(8.87 br) ^c
H _(b) (N–H imidazole)	13.65	$(9.01 \text{ br})^{c}$	13.65	9.19 br ^c	13.65	(8.87 br) ^c
H _(c) (C–H pyrimidine)	8.16	8.42 (s)	8.16	8.42 (s)	8.16	8.37 (s)
H _(d) (C–H imidazole)	7.86	8.41 (s)	7.86	8.41 (s)	7.86	8.36 (s)
H _(e) (C–H <i>o</i> -benzene)	6.63	7.27 ^d	6.51	7.158 ^d	6.57	6.72 (doublet) 6.74
H _(f) (C–H <i>m</i> -benzene)	7.20	7.38 ^e	6.98	7.19 ^d	7.24	7.06 (doublet) 7.09
$H_{(g)}$ (C–H <i>p</i> -benzene)	6.81	7.30 ^e				
H _(g) (C–H Methyl)			2.34	2.22 (s)		
Correlation Coeff. (R ²)	0.	56		0.59	0.	58

^a For hydrogen atoms numbering, see Fig. 1.

^b ¹H NMR were calculated by Chem. Office [23].

^c These signals were disappeared after adding D₂O.

^d These signals are well resolved to doublet upon the addition of D_2O , see Fig. 4.

 $^{\rm e}$ These signals are well resolved to triplet upon the addition of D_2O , see Fig. 4.

Table 4

Characteristic ¹³C NMR chemical shift (δ , ppm) of adenine-cyclodiphosph(V)azane derivatives (III_{a-c}).

Types of carbon atoms ^a	III _a (Y=H)		III_b (Y=p-CH ₃)		III _c (Y=p-Cl)	
	Calc. ^b	Obs.	Calc. ^b	Obs.	Calc. ^b	Obs.
C ₁₀ (Methyl group)			21.3	21.35		
C ₇ (o-benzene)	116.3	115.17	116.2	115.31	117.7	115.49
C ₄ (purine)	119.4	123.63	119.4	123.88	119.5	118.99
C ₉ (<i>p</i> -benzene)	122.4	128.49	131.2	131.01	124.3	123.8
C ₈ (<i>m</i> -benzene)	129.5	130.59	129.8	129.69	129.7	129.68
C ₅ (imidazole)	138.7	133.27	138.7	138.67	144.7	143.90
C ₁ (purine)	144.8	144.27	144.8	146.08	144.8	(146.82) ^c
C ₆ (benzene)	146.7	146.21	143.7	144.32	144.8	(146.82)
C ₃ (purine)	151.2	149.98	151.2	149.96	153.9	152.46
C ₂ (pyrimidine)	152.4	152.18	152.4	152.10	152.4	150.22
Correlation Coeff. (<i>R</i> ²)	0.9488		0.9983		0.9916	

^a For carbon atoms numbering, see Fig. 1.

^b ¹³C NMR were calculated by Chem Draw Ultra [23].

^c Signal between brackets was assigned to two different carbons.



Fig. 3. Ultraviolet spectrum of a denine-cyclodiphosph(V)azane derivatives; (A) III_a; (B) III_b; (C) III_c.

with those reported for adenine [25]. The reported bands between 270 and 290 nm [3,26,27] are characteristic of delocalized electrons within the phospha(V)azo four-membered ring (dimeric structure). Therefore the observed bands at 275, 273 and 273 nm were for compounds III_a , III_b and III_c , respectively.

4.2. Mass spectral analysis

The recorded mass spectrum of adenine-cyclodiphospha-(V)zane (III_a ; calculated formula weight is 654 amu) is provided in Supplement Fig. S-1A. Fragment ion peaks of 2–100% abundances are attributed to the corresponding fragmentation patterns resulting from bond cleavage at different positions in adeninecyclodiphospha(V)zane derivatives (III_{a-c}). Supplement Figs. S-2, S-3 and S-4 summarize the calculated/found molecular weight of compounds III_{a-c} and the proposed fragmentation pathways corresponding to their masses and relative intensities. As can be deduced from Supplement Figs. S-2, S-3 and S-4, the recorded peak intensities are directly proportional to fragment stability.

The decomposition and the common fragmentation features of III_a are presented in Supplement Fig. S-2. The parent peak appeared at m/z = 656 (3%) is attributed to ³⁷Cl isotope (M+2). The most intense ion (base peak) at m/z = 460 (100%) is attributed to fragment [C₂₀H₁₈N₁₀P₂]⁺. In addition, the observed peaks at m/z = 460.8 (27%), 442 (55.1%), 399.5 (14%) and 376.5 (44.2%) best describe [C₁₆H₁₇ClN₁₁P₂]⁺, [C₁₄H₁₅Cl₂N₉P₂]⁺, [C₈H₉Cl₃N₉P₂]⁺ and

Table 5

B3LYP structural parameters for adenine-cyclodiphosph(V)azane derivatives (III_{a-c}) utilizing 3-21G(d) basis set.

head sequenceisindisindisindP-Netterin-Pro137115701570P-Netterin-Pro127115701570P-Consell-Cons205620562056P-Consell-Cons1331-13811382-14031331-1381C-H benzene ring)1331-13821382-14031331-1381C-H benzene ring)1331-13821341-13651301C-H persene ring)128612851286C-H persene ring)128613881351Ny-field-Prof138313881361Ny-field-Prof138313881381Ny-field-Prof138313821382Ny-field-Prof138413841382Ny-field-Prof134213421342Ny-field-Prof134213421342Ny-field-Prof140714071407Ny-field-Prof138213821382Ny-field-Prof138213821382Ny-field-Prof138213821382Ny-field-Prof138213821382Ny-field-Prof138213821382Ny-field-Prof138213821382Ny-field-Prof138213821382Ny-field-Prof138213821382Ny-field-Prof138213821382Ny-field-Prof138213821382Ny-field-Prof138213821382Ny-field-Prof138213821382Ny-fie	Structural parameter ^a	III _a (Y=H)	III _b (Y=p-CH ₃)	III _c (Y=p-Cl)
μ-N-min-1- μ-N-min-2- μ-N-	Bond lengths in Å			
P ₁ -N ₀ =P ₁ -C ₀ 1.6701.6701.670P ₁ -C ₀ =P ₁ -C ₁ 2.6562.6562.656P ₁ -C ₀ =P ₁ -C ₁ 1.3421.4401.341C=C1.3471.3411.3411.341C=C1.3411.3411.3411.341C=C0.561.3511.3411.341C=C0.571.3411.3411.341C=C0.571.3601.3611.361P ₁ -N ₂ -C ₁ +N ₂ -C ₁ 1.3611.3621.361N ₁ -C ₁ =N ₂ -C ₂ -C ₁ 1.3321.3321.331N ₁ -C ₁ =N ₂ -C ₂ -C ₂ 1.3381.3361.334N ₁ -C ₁ =N ₂ -C ₂ -C ₂ 1.3321.3321.332N ₁ -C ₁ =N ₂ -C ₂ -C ₂ 1.4071.4071.407C ₁ -C ₁ =C ₂ -C ₁ -C ₂ 1.4021.4011.401C ₁ -C ₁ =C ₂ -C ₁ -C ₂ 1.4021.4021.401C ₁ -C ₁ =C ₂ -C ₁ -C ₂ 1.4021.4021.401C ₁ -C ₂ =C ₂ -C ₂ -C ₃₄ 1.4021.3321.337N ₂ -C ₂ =N ₂ -C ₃₄ 1.4021.4021.401C ₁ -C ₂ =C ₂ -C ₁ -C ₁ 1.4021.4021.401C ₁ -C ₂ =C ₂ -C ₁ -C ₁ 1.4021.4021.401C ₂ -N ₂ =C ₂ -C ₃₄ 1.4021.4021.402C ₁ -C ₂ =C ₂ -C ₁ -C ₁ 1.4021.4021.401C ₂ -N ₂ =C ₂ -C ₁ -H ₁ 1.4021.4021.401C ₂ -N ₂ =C ₂ -C ₁ -H ₁ 1.4021.4021.401C ₂ -N ₂ =C ₂ -C ₁ -H ₁ 1.4021.4021.402 <td>$P_1 - N_2 \equiv N_3 - P_4$</td> <td>1.811</td> <td>1.810</td> <td>1.813</td>	$P_1 - N_2 \equiv N_3 - P_4$	1.811	1.810	1.813
PC.G.B.PC.G.P. C.C.G.PC.G.PC.G.PC.G.P.2.0562.0562.056NC.S.PC.G.PC.G.1.2392.2402.236NC.S.PC.G.PC.G.1.2391.3291.329C.C.G.P.C.G.PC.G.1.3291.3291.329C.C.S.P.C.G.P.C.G.1.3291.3291.320NC.S.P.N.C.G.1.3201.3281.321NC.S.P.N.C.G.1.3361.3381.337NC.S.P.N.C.G.1.3561.3381.337NC.S.P.N.C.G.1.3421.3421.342NC.S.P.N.C.G.1.3421.3421.342NC.S.P.N.C.G.1.3421.3421.342NC.S.P.N.C.G.1.3421.3421.342C.S.C.S.P.S.C.G.C.1.3421.3421.342C.S.C.S.C.S.C.S.C.S.C.S.C.S.C.S.C.S.C.S	$P_1 - N_3 \equiv N_2 - P_4$	1.671	1.670	1.670
P ₁ -C ₀ =P ₁ -C ₀ 2.2392.2402.286P ₁ -C ₀ =P ₁ -C ₀ 1.4421.4401.439C=C (baracer ring)1.081-1.0821.081-1.0831.082C=C (-C_1)1.081-1.0821.081-1.0821.081N=C (-P_1)1.7051.7061.700N=C (-P_1)1.7051.7051.706N=C (-P_1)1.7051.7051.706N=C (-P_1)1.7051.7051.706N=C (-P_1)1.7051.7051.706N=C (-P_1)1.7051.7061.707N=C (-P_1)1.7561.7561.756N=C (-P_1)1.7561.7561.756N=C (-P_1)1.7561.7561.756N=C (-P_1)1.7561.7561.756N=C (-P_1)1.7561.7561.756N=C (-P_1)1.7561.7421.756N=C (-P_1)1.7561.7621.767N=C (-P_1)1.8001.8001.800C=C (-P_1)1.8001.8001.800C=C (-P_1)1.8001.8001.800N=C (-P_1)1.8001.8001.800N=C (-P_1)1.8001.8001.800N=C (-P_1)1.8001.8001.800N=C (-P_1)1.8001.8001.800N=C (-P_1)1.8001.8001.800N=C (-P_1)1.8001.8001.800N=C (-P_1)1.8001.8001.800N=C (-P_1)1.8001.8001.800N=C (-P_1)1	$P_1 - Cl_{40} \equiv P_4 - Cl_{38}$	2.056	2.056	2.056
N ₁ -C ₂ m ² , C ₁ 144214401439C-C (benzer ring)1.391-1.3931.391-1.4031.391-1.368C-R (benzer ring)1.391-1.3981.3911.391C-C ₁ m ² C ₁ -C ₁ 1.7051.7061.700N ₁ -C ₁ m ² M ₂ -C ₂ 1.3891.3081.301N ₁ -C ₁ m ² M ₂ -C ₂ 1.3801.3581.331N ₁ -C ₁ m ² M ₂ -C ₂ 1.3581.3581.351N ₁ -C ₁ m ² M ₂ -C ₂ 1.3581.3531.351N ₁ -C ₂ m ² M ₂ -C ₂ 1.3421.4491.342N ₁ -C ₂ m ² M ₂ -C ₂ 1.3421.4491.342Q ₁ -C ₂ m ² M ₂ -C ₂ 1.3421.4491.342Q ₁ -C ₂ m ² M ₂ -C ₂ 1.4401.4401.440Q ₁ -C ₂ m ² M ₂ -C ₂ 1.4401.4401.440Q ₁ -C ₂ m ² M ₂ -C ₂ 1.4401.4401.440Q ₁ -C ₂ m ² M ₂ -C ₂ 1.4401.4401.440Q ₁ -C ₂ m ² M ₂ -C ₂ 1.4401.4401.440Q ₁ -C ₂ m ² M ₂ -C ₂ 1.3471.3971.397Q ₂ -M ₂ -C ₂ m ² M ₂ 1.3471.3971.396N ₁ -C ₂ m ² M ₁ -C ₂ -M ₁ 1.2561.2561.256Q ₁ -M ₂ -M ₁ -M ₁ (midzoid eff)1.0151.0131.013Q ₁ -M ₂ -M ₂ -M ₁ -M ₁ 1.0561.0051.008N ₁ -M ₂ -M ₂ -M ₂ -M ₁ 1.0251.2561.256Q ₁ -M ₂ -M ₁ -M ₁ -M ₁ 1.1351.1351.135Q ₁ -M ₁ -M ₁ -M ₁ 1.1551.1571.256Q ₁ -M ₂ -M ₁ -M ₁ -M ₁ 1.152	$P_1 - Cl_{20} \equiv P_4 - Cl_{27}$	2.239	2.240	2.236
Call Distance imag) 1333-1388 1332-1403 1331-1388 Call Distance imag) 1081-1082 1081-1085 1082 Call Distance imag) 1205 1205 1205 Nar, GamMSy, Ga 1389 1388 1391 Nar, GamMSy, Ga 1388 1381 1391 Nar, GamMSy, Ga 1388 1381 1381 Nar, GamMSy, Ga 1342 1342 1342 Nar, GamMSy, Ga 1402 1402 1402 Nar, GamMy, Ga 1342 1342 1342 Nar, GamMy, Ga 1342 1342 1345	$N_2 - C_5 \equiv N_2 - C_{11}$	1 442	1 440	1 439
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	C = C (benzene ring)	1 393_1 398	1 392_1 403	1 391_1 368
C - μ C - μ	C H (bonzono ring)	1.091 1.092	1.091 1.095	1.092
λip - 1.706 1.706 1.706 λip - 1.808, - 1.1026 1.206 1.206 λip - 1.808, - C4 1.206 1.206 λip - 1.808, - C4 1.358 1.338 1.337 Nip - C1, - Nip - C4, - Nip 1.356 1.366 1.368 Nip - C1, - Nip - C2, - Nip 1.342 1.342 1.342 C1, - Nip - C2, - C2, - C2, - C2, - C4, - 1.402 1.407 1.407 C1, - C1, - C2, - C2, - C2, - 1.407 1.407 1.407 C1, - C1, - C2, - C2, - C2, - 1.407 1.402 1.208 C1, - Mis - C2, - Nip 1.337 1.397 1.397 C1, - Mis - C2, - Nip 1.326 1.226 1.226 C1, - Mis - C2, - Nip 1.337 1.397 1.396 C1, - Mis - C2, - Nip 1.337 1.397 1.396 C1, - Mis - C2, - Nip 1.337 1.397 1.396 Nip - Hill, -	C = C = C	1.081-1.082	1.001-1.005	1.082
r r r degram 1.489 1.088 1.088 r r r degram 1.899 1.689 1.688 N r - Hwy - Hexopetit NH) 1.389 1.338 1.337 N r - Hwy - Hexopetit NH) 1.388 1.338 1.338 See	$C_{10} - C_{57} = C_{16} - C_{61}$	1 705	1,440	1 700
Ny-1-angle - Ny-1-angle - Angle - Angl	$P_1 - N_{23} = P_4 - N_{17}$	1.705	1.700	1.201
N ₁ -HPN ₂ -H1(EXOC)CIU NI) 1.025 1.025 1.025 N ₁ -C ₂ -HV ₂ -HN ₂ 1.336 1.338 1.337 N ₁ -C ₂ -HV ₂ -HN ₂ 1.336 1.338 1.337 N ₁ -C ₂ -HV ₂ -HN ₂ 1.336 1.336 1.337 N ₁ -C ₂ -HV ₂ -C ₂ 1.407 1.407 1.407 C ₂ -C ₂ -C ₂ -C ₂ 1.407 1.407 1.407 C ₂ -C ₂ -HV ₂ -C ₂ 1.407 1.407 1.407 C ₂ -TV ₂ -C ₂ -C ₂ 1.407 1.402 1.401 C ₂ -HV ₂ -C ₂ -C ₄ 1.402 1.401 1.402 1.401 C ₂ -HV ₂ -C ₂ -H(I) 1.336 1.335 1.380 1.380 N ₂ -C ₂ -HV ₂ -C ₃ 1.336 1.336 1.326 1.336 1.326 N ₂ -H=N ₂ -H(I) 1.013 1.013 1.013 1.013 1.013 C ₂ -H=C ₂ -H(I) IIIII 1.037 1.037 1.037 1.037 C ₂ -H=C ₂ -H(I) IIIIIIII 1.013 1.013 1.013 1.013 C ₂ -H=C ₂ -H(I)	$N_{17} - C_{18} \equiv N_{23} - C_{24}$	1.389	1.388	1.391
Cash 3g = Cash 3g = Cash 3g 1.338 1.338 1.338 Cash 3g = Cash 3g 1.349 1.349 1.349 Car 0ha Cash Cash 3g 1.342 1.342 1.342 Cash Cash Cash 3g 1.407 1.407 1.407 Cash Cash Cash 3g 1.402 1.402 1.401 Cash Cash Cash 3g 1.338 1.336 1.330 Cash Cash 2g = Cash 3g 1.342 1.342 1.342 Cash 1g = Cash 3g 1.336 1.330 1.330 Cash 1g = Cash 3g 1.337 1.336 1.330 Na - Cash 3g 1.337 1.337 1.336 Na - Cash 3g 1.337 1.337 1.336 Na - Cash 3g 1.013 1.013 1.013 Na - Hang Ag 1.0066 1.006 1.008 Na - Hang Ag 1.0013 1.013 1.013 Cash 1g = Cash 1g = Cash 1g 1.006 1.00.8 1.008 Na - Hang Ag Ag 1.026 1.026 1.026 1.026 Na - Cash 1g = Na - Na	$N_{17}-H \equiv N_{23}-H$ (exocyclic NH)	1.026	1.025	1.026
Na ₁ -C ₁ mba ₂ -C ₇ 1.356 1.356 1.358 Na ₁ -C ₁ mba ₂ -C ₇ 1.349 1.349 1.349 1.344 Na ₁ -C ₂ mba ₁ -C ₂ 1.342 1.342 1.342 C ₁ -C ₁ mb ₂ -C ₂ -C ₁ 1.407 1.407 1.407 C ₁ -C ₁ mb ₂ -C ₂ -(type) 1.342 1.342 1.342 C ₁ -C ₁ mb ₂ -C ₂ -(type) 1.307 1.337 1.380 C ₂ -M ₂ -C ₂ -(S ₂ -C ₂) 1.337 1.337 1.336 C ₂ -M ₂ -C ₂ -M ₁ 1.326 1.337 1.356 N ₂ -C ₂ -M ₂ -C ₂ -M ₁ 1.013 1.013 1.013 N ₂ -C ₂ -M ₂ -C ₂ -M ₁ 1.076 1.076 1.076 C ₂ -M=C ₂ -M (Inicity)CH) 1.076 1.087 1.076 C ₂ -M=C ₂ -M ₁ 1.013 1.013 1.013 1.013 M ₂ -M=M ₂ -M ₂ -M ₁ -M ₁ 1.013 1.013 1.013 1.013 C ₂ -M=C ₂ -M ₁ 1.013 1.013 1.013 1.013 1.013 M ₁ -M ₁ -M ₁ -M ₁ 1.013 1.013 1.013 1.	$C_{18} - N_{33} \equiv C_{24} - N_{29}$	1.338	1.338	1.337
C ₁ -M ₂ -C ₂ ^{-M₀ 1.349 1.342 1.342 1.342 C₀-C₀-C₂-C₀ 1.407 1.407 1.407 1.407 C₀-C₀-C₂-C₀-C₀ 1.402 1.402 1.402 1.401 C₀-H₀-C₀-C₀-C₀ 1.384 1.385 1.380 1.380 C₀-M₀-C₀-M₀-C₀-M₀ 1.397 1.397 1.397 1.397 C₀-M₀-C₀-M₀-C₀-M₀ 1.397 1.386 1.386 1.386 N₀-C₀-M₀-C₀-M₀-C₀ 1.397 1.396 1.397 1.396 N₀-C₀-M₀-C₀-M₀-C₀ 1.397 1.396 1.396 1.396 N₀-C₀-M₀-M₀-C₀ 1.397 1.396 1.396 1.396 N₀-M₀-M₀-M₀-M₀-M₁ 1.013 1.016 1.016 1.016 C₀-M₀-M₀-M₀-M₀-M₁ 1.006 1.006 1.008 1.008 M₀-M₀-M₀-M₀-M₁ 1.026 1.020 1.020 1.020 M₀-M₀-M₀-M₀-M₁-M₁ 1.026 1.020 1.020 1.020 N₁-M}	$N_{33}-C_{21}\equiv N_{29}-C_{27}$	1.356	1.356	1.358
N ₃ -C ₃ =N ₃ -C ₃ 1.342 1.342 1.342 N ₃ -C ₃ =N ₂ -C ₃ 1.407 1.407 1.407 C ₁ -H ⁻ C ₂ -H(D ₁)(V ₁ midlac CH) 1.00 1.000 1.000 C ₀ -T ₁ -H ⁻ C ₂ -H(D ₁)(V ₁ midlac CH) 1.384 1.387 1.380 C ₂ -N ₂ -C ₃ -N ₂ -C ₃ 1.397 1.397 1.397 1.396 C ₂ -N ₂ -C ₃ -C ₃ 1.397 1.397 1.396 1.336 N ₂ -G ₂ -H ₂ -C ₃ -H(Imdizote NH) 1.013 1.013 1.013 1.013 N ₂ -H ₂ -H ₂ -H(Imdizote NH) 1.013 1.016 1.076 1.076 C ₂ -H ₂ -H ₂ -H(Imdizote NH) 1.013 1.013 1.013 1.013 M ₂ -H ₂ -H ₂ -H ₂ -H ₃ -H ₃ 1.006 1.006 1.008 1.008 N ₂ -H ₁ -H ₂ -H ₂ -H ₃ -H ₃ 1.013 1.013 1.013 1.013 1.013 M ₂ -H ₂ -H ₂ -H ₃ -H ₃ -H ₃ 1.006 1.006 1.008 1.008 1.008 1.008 1.008 1.008 1.008 1.008 1.008 1.008 1.008 1.008 <	$C_{21}-N_{34}\equiv C_{27}-N_{30}$	1.349	1.349	1.348
Cac Cag Cag Cag Cag1407140714071407Ca Cag Cag Cag Cag140214011401Ca Cag Cag Cag Cag1380138013801380Nas Cag Nag Cag Nag Cag1397139713971397Cag Nag Cag Nag Cag Nag Cag1397139713961397Nag Cag Nag Cag Nag Cag Nag Cag1397139713961397Nag Cag Nag Cag Nag Cag13971397139610131013Cag Cag Nag Cag Nag Cag1076107610761076Cag Cag Cag Cag1076107610761076Cag Cag Cag Cag1076107610761076Nag Cag Cag Cag Cag2640°2639°2639°2639°Bond angles in100.6100.8100.8100.8Nag Pa, Nag Pa,	$N_{34}-C_{20}\equiv N_{30}-C_{26}$	1.342	1.342	1.342
C.gC.gG.gC.g.1.4021.4021.4021.4021.402C.gLH.C.gH.V.g./H.V.J.1.3841.3851.380C.gN.gC.gNS.1.3371.3971.397C.gN.gC.g.NC.g.1.3371.3971.366S.gC.gN.JC.g.1.3971.3971.366N.gC.gN.JC.g.1.3971.3971.366N.gC.gN.JC.g.1.0131.0131.013C.gH.C.gH.(midzole NH)1.0131.0131.013C.gH.C.gH.(midzole NH)1.0161.0761.076C.GC.GC.G.1.0971.0761.008Mard angle n'1.0971.0131.013N.gH.N.J.P.N.G.2.640*2.639*2.630*Sand angle n'1.096100.61.008N.gH.N.J.P.N.G.1.0241.0351.035Mard angle n'1.0241.0351.035N.gL.N.J.P.N.S.P.N.1.0251.0301.035N.gL.N.J.P.N.S.P.N.1.0241.0351.036N.gL.N.J.P.N.S.N.S.C.T.N.S.1.0251.0251.025N.gL.N.J.P.N.S.N.S.C.T.N.S.1.0251.0251.025N.gC.J.S.S.C.T.N.S.C.T.N.S.1.0251.0251.025N.gC.J.S.S.C.T.N.S.C.T.N.S.C.T.N.S.1.0251.0251.025N.gC.J.N.S.C.T.N.S.C.T.N.S.C.T.N.S.1.0251.0251.025N.gC.J.N.S.C.T.N.S.C.T.N.S.C.T.N.S.C.T.N.S.1.0251.0251.025N.gC.G.T.N.S.C.G.N.S.C.T.N.S.C.T.N.S.C.T.N.S.C.T.N.S.1.0251.025 <td>$C_{20}-C_{19}\equiv C_{25}-C_{26}$</td> <td>1.407</td> <td>1.407</td> <td>1.407</td>	$C_{20}-C_{19}\equiv C_{25}-C_{26}$	1.407	1.407	1.407
$C_n - Hercy - H(pyrimidine CH)1.0801.0801.080C_n - N_{narcy - Ry0}1.3971.3851.380N_3 - C_2 - N_{3} - C_3 - N_31.3971.3971.397N_3 - C_2 - N_{3} - C_3 - N_31.3971.3961.326N_{32} - C_{30} - N_{31} - C_31.0131.0131.013C_2 - H=C_3 - H(midazle CH)1.0761.0761.076C_2 - H=C_3 - H(midyl CH)1.0761.0761.076C_2 - H=C_3 - H(midyl CH)1.0761.0361.00.8N_3 - N_1 - N_2 - N_2 - N_21.00.61.00.61.00.8N_1 - H_N_2 = N_1 - N_1 - H_N_2 = N_1 - M_1 - M_2 - M_11.01.61.00.8N_1 - H_N_2 = N_2 - C_3 - H_11.00.61.00.81.00.8N_1 - N_1 - N_2 - N_2 - P_1 - N_2 - R_31.02.81.00.8N_1 - N_1 - N_2 - N_2 - P_1 - N_2 - R_31.02.81.00.8N_2 - C_3 - H_2 - R_1 - N_2 - R_31.02.81.00.8N_2 - C_3 - N_2 - R_3 - R_1 - N_2 - R_31.02.81.00.8N_2 - C_3 - N_3 - R_3 - R_1 - N_2 - R_31.02.11.02.8N_1 - N_2 - N_2 - R_3 - R_1 - N_2 - R_31.02.11.02.1N_2 - C_3 - N_3 - C_3 - N_31.13.51.03.6N_2 - C_3 - N_3 - C_3 - N_31.13.51.03.6N_2 - C_3 - N_3 - C_3 - N_31.13.51.04.1N_2 - C_3 - N_3 - C_3 - N_31.02.71.02.8N_3 - C_3 - N_3 - C_3 - N_31.03.11.03.1N_3 - C_3 - N_3 - C_3 - N_31.03.11.04.1N_3 - C_3 - N_3 - C_3 - N_3$	$C_{19} - C_{18} \equiv C_{25} - C_{24}$	1.402	1.402	1.401
$ \begin{array}{c} \zeta_{g} n_{g} = \zeta_{g} = \zeta_{g} - \zeta_{g} = $	C_{21} -H= C_{27} -H (pyrimidine CH)	1.080	1.080	1.080
Ng-C_2 C_2-Ng=C_2-Ng-C_2 C_2-Ng=C_2-Ng-C_21.3971.3971.397Ng-C_2-Ng=C_2-Ng-C_2 C_2-Ng=C_2-Ph(midazole CH)1.3971.3261.326Ng-C_2-H=C_2-H(midazole CH)1.0761.0761.076C_2-H=C_2-H(midazole CH)1.0761.0761.076C_2-H=C_2-H(midazole CH)1.0761.0761.076C_2-G_2=C_2-C_31.0971.0761.076Ng-T_2-P_2-P_1(meth)CH)1.0761.0761.076Dead angles in1.0971.0761.008Ng-T_2-P_2-P_2-P_31.006100.6100.8Ng-T_2-P_2-P_2-P_31.021.0301.028Ng-T_2-P_2-P_2-P_31.021.0301.028Ng-T_3-C_3-P_2-P_3-P_31.021.0301.028Ng-T_3-C_3-P_2-P_31.021.0301.028Ng-T_3-C_3-P_3-P_3-P_31.021.0301.028Ng-C_3-P_3-P_3-P_3-P_31.031.0301.04Ng-C_3-P_3-P_3-P_3-P_31.031.0301.04Ng-C_3-P_3-P_3-P_3-P_31.031.031.04Ng-C_3-P_3-P_3-P_3-P_31.031.031.04Ng-C_3-P_3-P_3-P_3-P_31.031.041.06Ng-C_3-P_3-P_3-P_3-P_3-P_31.031.041.06Ng-C_3-P_3-P_3-P_3-P_3-P_31.041.021.06Ng-C_3-P_3-P_3-P_3-P_31.041.041.06Ng-C_3-P_3-P_3-P_3-P_31.041.021.02Ng-C_3-P_3-P_3-P_3-P_31.041.021.02Ng-C_3-P_3-P_3-P_3-P_31.041.02 <td>$C_{20} - N_{35} \equiv C_{26} - N_{32}$</td> <td>1.384</td> <td>1.385</td> <td>1.380</td>	$C_{20} - N_{35} \equiv C_{26} - N_{32}$	1.384	1.385	1.380
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$N_{25} - C_{22} \equiv N_{22} - C_{28}$	1 397	1 397	1 397
$\begin{array}{ccccccc} \mbox{C} 1 = 1 & 1 = 0 & 1 & 1 = 0 & 1 & 1 = 0 & 1 & 1 = 0 & 1 & 1 = 0 & 1 & 1 = 0 & 1 & 1 = 0 & 1 & 1 = 0 & 1 & 1 & 1 = 0 & 1 & 1 & 1 = 0 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 &$	$C_{22} = N_{22} = C_{20} = N_{21}$	1 326	1 326	1 326
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$V_{22} = V_{36} = V_{28} = V_{31}$	1 307	1 307	1 306
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\frac{1}{36} - \frac{1}{619} - \frac{1}{1031} - \frac{1}{625}$	1.012	1.012	1.012
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$N_{32} - \Pi = N_{35} - \Pi (\Pi \Pi \Pi \Pi Z O I e I N \Pi)$	1.015	1.015	1.015
$C_27 \rightarrow H_{23} = H_{1} + (Hettry)(H)$ 1097 $C_3 - C_1 = C_1 = C_1 + (Hettry)(H)$ 1.761 $N_1 \dots H_{23} = N_3 - C_1 + N_3 + N_1 + N_2$ 2.640°2.639° $D nd angles in'1.00.61.00.8N_2 - P_1 - N_3 = N_2 - P_4 - N_390.290.390.3P_1 - N_3 = N_2 - P_4 - N_1 - H1.351.35.01.35.1N_2 - P_1 - N_3 = N_2 - C_{13} + N_1 - H_11.35.11.35.11.35.1N_2 - C_2 = N_2 - S_{12} - N_1 - H_11.93.11.93.11.93.1N_2 - C_2 - N_2 = N_1 - N_1 - H_11.91.11.90.11.90.1N_2 - C_2 - N_2 = N_1 - N_1 - H_11.91.11.90.11.90.1N_2 - C_2 - N_2 = N_2 - C_2 - N_2 -$	C_{22} -H= C_{28} -H (Imidazole CH)	1.076	1.076	1.076
$C_0 - Ck_0 = (C_1 - C_1)$ 1.64 1.630° $Bord angles in'V2.630^{\circ}2.630^{\circ}Bord angles in'VVVVP_1 - N_2 = P_1 - N_2 - P_4100.6100.6100.8N_2 - P_1 - N_3 = P_4 - N_3 - P_4100.6100.6100.8N_2 - P_1 - N_3 = P_4 - N_1 - C_{10} = C_{12} - P_4 - C_{13}90.290.390.3P_1 - N_2 - C_4 = P_4 - N_1 - C_{16}129.8130.0129.8P_1 - N_2 - C_4 = P_4 - N_1 - C_{16}129.8130.0129.8P_1 - N_2 - C_4 = P_4 - N_1 - C_{16}121.2121.3121.3C_2 - C_4 - N_2 = C_1 - N_3119.3119.3119.4N_2 - C_4 - N_2 = C_1 - N_3 - C_{11}119.1119.1119.1N_3 - C_5 - N_3 - C_{11} - N_4126.8126.8126.7N_2 - C_2 - N_2 = C_1 - N_3 - C_{11}125.6125.6125.6C_5 - C_1 - N_3 - C_{21}116.4116.4116.4N_3 - C_{21} - N_3 - C_{22}110.4116.4116.4N_3 - C_{21} - N_3 - C_{22}110.7107.0107.0N_3 - C_{22} - N_2 - N_2 - N_2 - N_2 - N_2110.7112.5125.6N_3 - C_{22} - N_2 - N_2 - N_2110.7110.7110.7N_3 - C_{22} - N_2 - N_2 - N_2110.7107.0107.0N_3 - C_{22} - N_2 - N_2 - N_2110.7112.5125.5C_3 - N_2 - N_2 - N_2 - N_2119.1 - 120.7$	C_{57} -H \equiv C ₆₁ -H (methyl CH)		1.097	
Na1HN23=HS36HN17 2.640° 2.639° 2.630° Bond angles in* HN27 2.630° 2.630° P_1-N_2-P_4=P_1-N_2-P_4 100.6 100.6 100.8 D_2-P_1-N_3=P_1-N_2-P_4 79.4 79.4 79.2 Cl ₃₀ -P_1-CL ₆₀ =Cl ₃₇ -P_4-Cl ₃₈ 90.2 90.3 90.3 P_1-N2_2-C_4=P_4-N17-Cl ₄₈ 129.8 130.0 129.8 N_31-C-41,Pa=N17-Cl ₁₈ -N33 113.5 113.5 113.5 N_32-C-42,Pa_9=N17-Cl ₁₈ -N33 121.2 121.3 119.4 C ₃₂ -C ₄₂ -N ₂₉ =N17-Cl ₃₁ -N33 119.3 119.4 126.6 C ₃₂ -C ₄₂ -N ₂₉ =N3x-C ₂₁ -N34 126.8 126.6 126.6 C ₃₂ -C ₄₂ -C ₄₉ =N3x-C ₂₁ -N34 126.6 126.6 126.6 C ₃₂ -C ₄₂ -C ₄₉ =N3x-C ₂₁ -N44 126.6 126.6 126.6 C ₃₂ -C ₄₂ -C ₄₉ =N3x-C ₂₁ -N44 126.6 126.6 126.6 C ₃₂ -C ₄₂ -C ₄₉ =N3x-C ₂₁ -N4 126.6 126.6 126.6 C ₃₂ -C ₄₂ -C ₄₉ =N3x-C ₂₁ -N4 126.6 126.6 126.6 126.6	$C_{10} - Cl_{58} \equiv C_6 - Cl_{57}$	h	h	1.761
Bond angles in" p-Np-Rp-Rp-Np-Np-Np-Np-Np-Np-Np 100.6 100.8 Np-Pp-Rp-PNp-Pp-Np-Np-Np-Np 79.4 79.4 79.2 Clyo-Pr-CLag=Clyr-P4-Cl3s 90.2 90.3 90.3 P-Nb2-Cg2=P4-N17-Cls 129.8 130.0 129.8 P-Nb2-Cg2=P4-N17-Cls 121.3 121.3 121.3 Cg2-Cg4-Np=Mp-Tr-H 113.5 113.5 121.3 Cg2-Cg4-Np=Mp-Tr-Gls-Ng3 121.2 121.3 121.3 Cg2-Cg4-Np=Mp-Tr-Gls-Ng3 122.6 126.8 126.7 Cg2-Cg4-Np=Mp-Cg-Cg-Ng=Ng3-Cg1-Ng4 126.8 126.7 122.6 Cg2-Cg2-Cg2=Cg1-Ng4-Cg0 12.7 12.8 10.4 Sg4-Cg2-Cg3=Cg1-Ng4-Cg0 12.6 125.6 125.6 Cg2-Ng1-Cg2=Mg4-Cg0-Cg3 12.5 125.6 125.6 Cg2-Ng1-Cg3=Mg4-Cg0-Cg3 10.4 10.4 16.4 Cg3-Ng1-Cg3=Mg4-Cg0-Cg3 10.7 10.7 10.4 Cg3-Ng1-Cg3=Mg4-Cg0-Cg3 10.7 10.7 10.7 Sg4-Cg2-TB-Mg3-Cg2 104.5 10.6 1	$N_{31}\cdots HN_{23} \equiv N_{36}\cdots HN_{17}$	2.640 ^b	2.639 ^b	2.630 ^b
$\begin{split} P_1 - P_2 - P_4 = P_1 - P_3 - P_4 & 100.6 & 100.6 & 100.6 \\ IO.6 & 100.8 & 100.8 & 100.8 & 100.8 & 100.8 \\ IO.6 & 100.8 & 100.8 & 100.8 & 100.8 \\ IO.6 & 100.8 & 100.8 & 100.8 & 100.8 & 100.8 \\ IO.6 & 100.8 & 100.8 & 100.8 & 100.8 & 100.8 & 100.8 \\ IO.6 & 100.8 & 100.8 & 100.8 & 100.8 & 100.8 & 100.8 & 100.8 \\ IO.6 & 100.8 & 10$	Bond angles in°			
$N_2-P_1, N_3 = M_2 - P_4, N_3$ 79.479.479.479.2 $N_3-P_1 - C_1_0 = C_1_3 - N_3$ 90.290.390.3 $P_1 - N_{22} - C_{24} = P_4 - N_{17} - C_{18}$ 129.8130.0129.8 $N_3 - C_4 - N_2 = M_1 - C_{18} - N_3$ 121.2121.3121.3 $C_3 - C_4 - N_2 = C_{18} - N_3$ 119.3119.3119.4 $C_3 - C_4 - N_2 = C_{18} - N_3$ 119.3119.1119.0 $N_2 - C_4 - N_2 = C_{18} - N_3 - C_2$ 119.1119.1119.0 $N_2 - C_2 - N_3 = C_{18} - N_3 - C_2$ 126.8126.8126.7 $C_2 - N_3 - C_2 - C_{18} - N_3 - C_2$ 125.6125.6125.6 $N_3 - C_2 - C_2 - N_3 - C_{20}$ 104.5104.5104.9 $N_3 - C_2 - C_3 - N_3 - C_{20}$ 107.0107.0107.0 $N_3 - C_2 - N_3 - C_{20}$ 107.0107.0107.0 $N_3 - C_2 - N_3 - C_{20}$ 107.0107.0107.0 $N_3 - C_2 - N_3 - C_2 - N_3 - C_2116.2116.5116.2N_3 - C_2 - N_3 - C_2 - N_3 - C_2119.9 - 120.2118.5 - 120.8119.1 - 121.0C_3 - N_3 - C_3 - N_3 - C_3 - M_3 - C_2 - M_3 - 119.5125.5125.5125.5C_2 - C_4 - H_3 - C_4 - H_3 - C_5 - 129.3119.4 - 120.1119.3 - 120.7119.5 - 120.8N_1 - C_2 - M_3 - C_4 - M_3 - C_5 - 129.3129.1129.1129.1129.1C_2 - C_4 - H_4 $	$P_1 - N_2 - P_4 \equiv P_1 - N_3 - P_4$	100.6	100.6	100.8
Cl3p=P,-Cl_0=Clp-P_4-Cl3p 902 90.3 90.3 P_1-N23-H=Q_4-N17-Cl3P 129.8 130.0 129.8 N37-C24=P20-N17-Cl3P 113.5 113.5 113.5 N37-C24+P30=N17-Cl3P-N33 121.2 121.3 121.3 C32-C34-N30=N17-Cl3P-N33 19.3 119.3 119.4 C32-C34-N30=Cl3P-Cl3P-N33-C21 110.1 119.1 119.0 N30-C32-N30=R33-C21-N34 126.8 126.8 126.7 N30-C32-C35=N34-C30-C30 112.7 112.7 112.8 N30-C32-C32=N34-C30-C9-C19 125.6 125.6 125.6 S26-C32-C32=C30-C9-C19-C19 125.6 125.6 125.6 S26-C32-C32=N34-C30-C19-C19 104.5 104.9 104.9 N31-C32=N32=N36-C22-N35 112.5 125.5 125.6 S26-S3-C3-Q3-C3-C3 107.0 107.0 107.0 N31-C32=N32=N36-C22-N35 116.2 125.5 116.2 S26-S2-C3-Q3-C3-LH 125.5 125.5 125.5 S25-C32-C3-HS-C42-H 125.5 125.5 125.	$N_2 - P_1 - N_3 \equiv N_2 - P_4 - N_3$	79.4	79.4	79.2
P ₁ -N ₂₃ -C ₄ =P ₄ -N ₁₇ -C ₁₈ 128.8 130.0 128.8 P ₁ -N ₂₃ -H=P ₄ -N ₁₇ -H 113.5 113.5 113.5 N ₂₃ -C ₄ -N ₂₉ =N ₁₇ -C ₁₈ -N ₃₃ 121.2 121.3 121.3 C ₂₄ -N ₂₉ =C ₁₉ -C ₁₈ -N ₃₁ -C ₂₁ 119.3 119.4 126.8 C ₂₄ -N ₂₉ -C ₂₇ =C ₁₈ -N ₃₃ -C ₂₁ 119.1 119.0 119.0 C ₂₄ -N ₂₉ -C ₂₇ =C ₁₈ -N ₃₃ -C ₂₁ 126.8 126.7 128.7 C ₂₇ -N ₃₉ -C ₅₂ =C ₁₉ -N ₃₄ -C ₂₀ 125.6 125.6 125.6 C ₂₆ -C ₂₅ -C ₂₄ =C ₂₀ -C ₁₉ -C ₁₈ 116.4 116.4 164.7 C ₃₇ -N ₃₉ -C ₅₂ =C ₂₉ -N ₃₅ -C ₂₀ 107.0 107.0 107.0 S ₂₉ -C ₂₇ -C ₂₉ =N ₃₅ -C ₂₀ -N ₂₅ 12.5 12.5 12.5 C ₃₈ -N ₃₂ -C ₂₆ =C ₂₂ -N ₃₅ -C ₂₀ 107.0 107.0 107.0 N ₂₉ -C ₂₇ -H=N ₃₅ -C ₂₁ -H 125.4 125.4 125.3 C ₂₆ -N ₂₉ -P ₁₉ -N ₃₉ -C ₂₂ -H 125.5 125.5 125.5 C ₂₇ -C ₁₉ -C ₁₉ -H 125.1 118.5 120.1 19.1 C ₂₆ -C ₁₀ -C ₁₀ -C ₁₁ -H 125.3 125.3<	$Cl_{39}-P_1-Cl_{40}\equiv Cl_{37}-P_4-Cl_{38}$	90.2	90.3	90.3
$P_1-N_2-H=P_2-N_1-H$ 113.5113.5113.5 $N_{22}-C_4-N_{22}=N_1-C_{18}-N_{33}$ 121.2121.3121.3 $C_{24}-N_{22}=C_{19}-C_{18}-N_{33}-C_{21}$ 119.3119.4 $C_{24}-N_{22}-C_{27}-N_{30}-C_{21}-N_{34}-C_{20}$ 119.1119.1 $C_{27}-N_{30}-C_{26}=C_{21}-N_{34}-C_{20}$ 122.6125.6 $C_{27}-N_{30}-C_{26}=C_{22}-N_{24}-C_{20}-C_{19}$ 125.6125.6 $C_{27}-N_{30}-C_{26}=C_{22}-N_{24}-C_{20}-C_{19}$ 125.6125.6 $C_{27}-C_{26}=C_{22}-N_{25}-C_{22}-N_{25}$ 104.5104.5 $N_{31}-C_{28}=C_{20}-N_{50}-C_{22}$ 104.5104.5 $N_{31}-C_{28}=C_{20}-N_{50}-C_{22}-N_{35}$ 125.6125.6 $C_{27}-N_{30}-C_{26}=C_{21}-N_{34}-C_{20}$ 107.0107.0 $N_{31}-C_{28}=N_{32}-C_{22}-N_{35}-C_{30}$ 107.0107.0 $N_{31}-C_{28}=N_{32}-C_{31}-H$ 116.2116.5116.2 $C_{27}-N_{20}-N_{25}-C_{21}-H$ 125.4125.3125.5 $C_{27}-N_{20}-N_{27}-H$ 125.5125.5125.5 $C_{27}-C_{10}-H_{20}-N_{27}-H$ 119.9-120.2118.5-120.8119.1-121.0 $N_{11}-C_{20}-H=N_{20}-C_{5}-H$ 129.1129.1129.1 $V_{27}-H=N_{27}-H_{2}-H_{2}-C_{5}129.3129.1129.1V_{27}-H=N_{27}-H_{2}-H_{$	$P_1 - N_{23} - C_{24} = P_4 - N_{17} - C_{18}$	129.8	130.0	129.8
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$P_1 - N_{23} - H = P_4 - N_{17} - H$	113.5	113.5	113.5
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$N_{23}-C_{24}-N_{29} \equiv N_{17}-C_{18}-N_{33}$	121.2	121.3	121.3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$C_{25} - C_{24} - N_{29} \equiv C_{19} - C_{18} - N_{33}$	119.3	119.3	119.4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$C_{24} - N_{20} - C_{27} = C_{19} - N_{22} - C_{21}$	1191	1191	119.0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$N_{24} = N_{22} = N_{22} = N_{23} = N_{24} = N_{24}$	126.8	126.8	126.7
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\Gamma_{29} = \Gamma_{30} = \Gamma_{33} = \Gamma_{33} = \Gamma_{34}$	112 7	110.0	112.0.7
$\begin{split} & 130 - 226^{-}C_25 - 374^{-}C_20 - C_{19} & 12.50 & 10.50$	$C_{2}/N_{30} C_{26} = C_{21}/N_{34} C_{20}$	125.6	125.6	125.6
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$N_{30} - C_{26} - C_{25} = N_{34} - C_{20} - C_{19}$	116 4	116 4	125.0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$L_{26} - L_{25} - L_{24} = L_{20} - L_{19} - L_{18}$	1045	1045	1040
$\begin{array}{cccc} & 112.5 & 112.5 & 112.5 & 112.5 & 112.5 & 112.5 & \\ & & & & & & & & & & & & & & & & & $	$C_{25} - N_{31} - C_{28} = C_{19} - N_{36} - C_{22}$	104.5	104.5	104.9
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$N_{31} - C_{28} - N_{32} \equiv N_{36} - C_{22} - N_{35}$	112.5	112.5	112.5
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$C_{28} - N_{32} - C_{26} \equiv C_{22} - N_{35} - C_{20}$	107.0	107.0	107.0
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$N_{29}-C_{27}-H \equiv N_{33}-C_{21}-H$	116.2	116.5	116.2
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$C_{26}-N_{32}-H \equiv C_{20}-N_{35}-H$	125.4	125.4	125.3
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$N_{31}-C_{28}-H = N_{36}-C_{22}-H$	125.5	125.5	125.5
$\begin{array}{llllllllllllllllllllllllllllllllllll$	C=C-C (benzene ring)	119.9–120.2	118.5–120.8	119.1-121.0
$\begin{array}{cccc} C_{10}-C_{57}-H = C_{16}-C_{61}-H & 111.0 & \\ H-C_{27}-H = H-C_{61}-H & 108.4 & \\ P_1-N_3-C_{11} = P_4-N_2-C_5 & 129.3 & 129.3 & 129.1 & \\ P_4-N_3-C_{11} = P_1-N_2-C_5 & 129.1 & 129.1 & \\ Dihedral angles in^{\circ} & & & \\ N_2-P_1-N_3-P_4 & 0.00 & 0.00 & 0.00 & 0.0 & \\ N_{17}-P_4-N_2-P_1 = N_{23}-P_1-N_2-P_4 & 92.1 & 91.9 & 92.2 & \\ P_1-N_{23}-C_24-N_{29} = P_4-N_{17}-C_{18}-N_{33} & 4.5 & 3.5 & 5.6 & \\ C_7-C_5-N_2-P_1 & 91.2 & 90.7 & 91.7 & \\ C_{12}-C_{11}-N_3-P_4 & 88.4 & 88.5 & 88.3 & \\ P_1-N_{23}-H-C_{24} = P_4-N_{17}-H-C_{18} & 159.9 & 160.5 & 159.2 & \\ Benzene ring & 0.13-1.29 & 0.1-1.2 & 0.23-1.04 & \\ \end{array}$	C=C-H (benzene ring)	119.4–120.1	119.3–120.7	119.5-120.8
$\begin{array}{cccc} H - C_{27} - H = H - C_{61} - H & 108.4 & 129.3 & 129.1 & 12$	$C_{10} - C_{57} - H \equiv C_{16} - C_{61} - H$		111.0	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$H-C_{27}-H=H-C_{61}-H$		108.4	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$P_1 - N_3 - C_{11} \equiv P_4 - N_2 - C_5$	129.3	129.3	129.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$P_4 - N_2 - C_{11} \equiv P_1 - N_2 - C_5$	129.1	129.1	129.2
Distribution00.000.000.0 $N_2-P_1 \to N_2 - P_1 = N_{22} - P_1 - N_2 - P_4$ 92.191.992.2 $P_1 - N_{23} - C_{24} - N_{29} = P_4 - N_{17} - C_{18} - N_{33}$ 4.53.55.6 $C_7 - C_5 - N_2 - P_1$ 91.290.791.7 $C_{12} - C_{11} - N_3 - P_4$ 88.488.588.3 $P_1 - N_{23} - H - C_{24} = P_4 - N_{17} - H - C_{18}$ 159.9160.5159.2Benzene ring0.15 - 0.40.17 - 0.520.07 - 0.68Purine ring0.13 - 1.290.1 - 1.20.23 - 1.04	Dihedral angles in ^o			
$N_{17}-P_4-N_2-P_1=N_{23}-P_1-N_2-P_4$ 90.000.0 $N_{17}-P_4-N_2-P_1=N_{23}-P_1-N_2-P_4$ 92.191.992.2 $P_1-N_{23}-C_{24}-N_{29}=P_4-N_{17}-C_{18}-N_{33}$ 4.53.55.6 $C_7-C_5-N_2-P_1$ 91.290.791.7 $C_12-C_{11}-N_3-P_4$ 88.488.588.3 $P_1-N_{23}-H-C_{24}=P_4-N_{17}-H-C_{18}$ 159.9160.5159.2Benzene ring0.15-0.40.17-0.520.07-0.68Purine ring0.13-1.290.1-1.20.23-1.04	$N_{0} = P_{1} = N_{0} = P_{1}$	00.0	00.0	00.0
$n_{17}-r_4-n_{22}-r_1-n_{22}-r_1-n_{22}-r_4}$ 52.191.592.2 $P_1-N_{23}-C_{24}-N_{29}\equiv P_4-N_{17}-C_{18}-N_{33}$ 4.53.55.6 $C_7-C_5-N_2-P_1$ 91.290.791.7 $C_{12}-C_{11}-N_3-P_4$ 88.488.588.3 $P_1-N_{23}-H-C_{24}\equiv P_4-N_{17}-H-C_{18}$ 159.9160.5159.2Benzene ring0.15-0.40.17-0.520.07-0.68Purine ring0.13-1.290.1-1.20.23-1.04	$N_{-} D$, $N_{-} D$, $M_{-} D$, $M_{-} D$, $N_{-} D$	00.0	01.0	02.0
$r_1 - r_{123} - c_{24} - r_{129} = r_4 - r_{17} - c_{18} - r_{133}$ 4.55.5 $C_7 - C_5 - N_2 - P_1$ 91.290.791.7 $C_{12} - C_{11} - N_3 - P_4$ 88.488.588.3 $P_1 - N_{23} - H - C_{24} = P_4 - N_{17} - H - C_{18}$ 159.9160.5159.2Benzene ring0.15 - 0.40.17 - 0.520.07 - 0.68Purine ring0.13 - 1.290.1 - 1.20.23 - 1.04	$1 v_1 / -1 4 - 1 v_2 - r_1 - 1 v_2 - r_1 - 1 v_2 - r_4$ D N C N - D N C N	J2.1 4 5	91,9 25	56
$C_7-E_5-iN_2-P_1$ 91.2 90.7 91.7 $C_{12}-C_{11}-N_3-P_4$ 88.4 88.5 88.3 $P_1-N_{23}-H-C_{24}=P_4-N_{17}-H-C_{18}$ 159.9 160.5 159.2 Benzene ring $0.15-0.4$ $0.17-0.52$ $0.07-0.68$ Purine ring $0.13-1.29$ $0.1-1.2$ $0.23-1.04$	$r_1 - i v_{23} - c_{24} - i v_{29} = r_4 - i v_{17} - c_{18} - i v_{33}$	4.J 01.2	5.5 00 7	J.U 01.7
$C_{12}-C_{11}-N_3-P_4$ 88.488.588.3 $P_1-N_{23}-H-C_{24}\equiv P_4-N_{17}-H-C_{18}$ 159.9160.5159.2Benzene ring0.15-0.40.17-0.520.07-0.68Purine ring0.13-1.290.1-1.20.23-1.04	$C_7 - C_5 - N_2 - P_1$	91.2	90.7	91./
$P_1 - N_{23} - H - C_{24} \equiv P_4 - N_{17} - H - C_{18}$ 159.9160.5159.2Benzene ring0.15 - 0.40.17 - 0.520.07 - 0.68Purine ring0.13 - 1.290.1 - 1.20.23 - 1.04	$C_{12} - C_{11} - N_3 - P_4$	88.4	88.5	88.3
Benzene ring 0.15-0.4 0.17-0.52 0.07-0.68 Purine ring 0.13-1.29 0.1-1.2 0.23-1.04	$P_1 - N_{23} - H - C_{24} \equiv P_4 - N_{17} - H - C_{18}$	159.9	160.5	159.2
Purine ring 0.13-1.29 0.1-1.2 0.23-1.04	Benzene ring	0.15-0.4	0.17-0.52	0.07-0.68
	Purine ring	0.13-1.29	0.1–1.2	0.23-1.04

^a For atom numbering, see Fig. 6.

^b Represent intramolecular hydrogen bonding, see Fig. 6.

 $[C_{14}H_{13}ClN_7P_2]^+$ fragment ions, respectively, beside lesser intense fragment peaks with intensities ranging from 3 to 10%.

The calculated formula mass of compound III_b is 682 amu a peak appearing at m/z = 684 (9.1%) is due to the ³⁷Cl isotope (M+2) whereas the observed peak at m/z = 376.6 (100%) is attributed to fragment ion [C₁₄H₁₃ClN₇P₂]⁺ (Supplement Fig. S-3). The fragment at m/z = 609.9 (22.4%) is due to ion [C₂₄H₂₁Cl₂N₁₂P₂]⁺ resulting from

Cl₂ and H loss from the parent molecule. The ion peak recorded at m/z = 527 (22.4%) belongs to fragment $[C_{19}H_{18}Cl_3N_8P_2]^+$ owing to bond cleavage between the purine moiety and the exocyclic N–H in addition to loss of HCl. On the other hand, the moderately intense ion peaks observed at m/z = 502 (50.3%), and 366.8 (33.9%) are safely assigned to $[C_{18}H_{19}Cl_3N_7P_2]^+$, and $[C_{11}H_{10}Cl_3N_4P_2]^+$ fragments, respectively.



Fig. 4. ¹H NMR spectra (δ , ppm) in DMSO- d_6 solvent; (A) III_a; (B) III_b; (C) III_c.



Fig. 5. ¹³C NMR spectra (δ , ppm) in DMSO- d_6 solvent; (A) III_a; (B) III_b; (C) III_c.

The mass spectrum of adenine-cyclodiphospha(V)zane (III_c; 723 amu) validates the proposed structural formula, Supplement Fig. S-1C. A molecular ion peak at m/z=722 (8%) corresponds to the molecular ion (M–1). The observed fragment at m/z=353 (100%, base peak) fits $[C_{16}H_{15}N_6P_2]^+$ ion fragment, whereas the moderately intense peak (73%) at m/z=446.7 is assigned to $[C_{11}H_{13}Cl_4N_7P_2]^+$ ion fragment. The mass spectrum of III_c reveals a series of peaks at m/z=670, 622, 564.8, 541, etc. corresponding to various fragment ions as explained in Supplement Fig. S-4.

4.3. ¹H and ¹³C NMR spectral interpretations

The characteristic ¹H and ¹³C NMR spectral data for compounds III_{a-c} and their assignments are listed in Tables 3 and 4, respectively. Linear correlations between theoretical and experimental ¹³C chemical shift results for compounds III_{a-c} are reported with a correlation coefficient R^2 equal to 0.9488, 0.9983 and 0.9916, respectively. However, unsatisfactory correlation coefficients were found between observed/calculated ¹H chemical shifts.

4.3.1. ¹H NMR

The ¹H NMR spectra of adenine-cyclodiphospha(V)zane derivatives; III_{a-c} (Fig. 4) were recorded in DMSO- d_6 with tetramethylsilane (TMS) as an internal standard. The intense singlet at 4.0 ppm is attributed inherent water to (D-O-H) in DMSO- d_6 . The observed chemical shifts of the three investigated compounds (III_{a-c}) were found to be somewhat similar owing to the high symmetry of compounds III_{a-c} . In the ¹H NMR spectra of III_a and III_c , the two different N-H singlets (exocyclic N-H and imidazole N-H) were nearly overlapped and therefore assigned to the observed broad signals at 9.01 and 8.87 ppm, respectively (Fig. 4). For III_b, the two distinct peaks at 8.92 and 9.19 ppm are assigned to exocyclic N-H and imidazole N-H, respectively. Addition of D₂O to the previous 3 NMR solutions with vigorous shaking results in diminishing the above mentioned signals due to hydrogen deuterium magnetic exchange. On the other hand, the observed broadness may be attributed to the nuclear quadruple broadening of nitrogen [28]. The singlets at 8.42, 8.42 and 8.37 ppm are assigned to the pyrimidine ring C–H, for III_a, III_b and III_c, respectively. The imidazole ring C–H was assigned to the observed singlets at 8.41, 8.41 and 8.36 ppm in the ¹H NMR spectra of III_a , III_b and III_c , respectively. The ¹H NMR spectrum of III_a exhibits a doublet and two triplets in the spectral range 7.25–7.40 ppm which correspond to o-, m- and p-benzene(C-H e, f and g, respectively). But in case of III_b and III_c, only two doublets were observed in the 6.72-7.20 ppm range which is attributed to o- and *m*-benzene C–H protons. On the other hand, the observed singlet at 2.22 ppm in the III_b spectrum is characteristic of methyl group protons [28].

4.3.2. ¹³C NMR

The ¹³C NMR spectra of adenine-cyclodiphospha(V)zane derivatives (III_{a-c}) dissolved in DMSO- d_6 are provided in Fig. 5. The observed ¹³C peak at 40 ppm is due DMSO- d_6 [28]. The ¹³C peak of tetramethylsilane (TMS) was used as the internal standard. In view of the fact that adenine-cyclodiphospha(V)zanes (III_{a-c}) have an inversion center, the number of observed ¹³C peaks is supposed to be less than the number of carbon atoms present in the molecule.

The ¹³C NMR spectrum of **III**_a (Fig. 5A) displays nine signals. The signals observed at 115.17, 128.49, 130.59 ppm are characteristic of benzene *ortho*-(C_7), *para*-(C_9) and *meta*-(C_8) positions, respectively [28]. The benzene carbon atoms attached to the nitrogen atoms of phospha(V)azo ring (C_6) were assigned to the recorded signal at 146.21 ppm. On the other hand, the remaining five ¹³C signals were due to ten carbon atoms of the two purine rings as seen in Table 4. Ten signals at different chemical shifts appeared



Fig. 6. B3LYP/3-21G(d) optimized structure of adenine-cyclodiphosph(V)azane derivatives; (A) Y=H for III_a; (B) Y=p-CH₃ for III_b; (C) Y=p-Cl for III_c.

in the ¹³C NMR spectrum of **III**_b as seen in Fig. 5B. The intense peak observed at 21.35 ppm corresponds to the methyl group (C_{10}) carbon atom [28]. The peaks observed at 123.88 and 149.96 ppm are attributed to C_4 and C_3 purine ring atoms, respectively. The imidazole carbon atom (C_5) is assigned to the recorded signal at 138.67 ppm [14]. On the other hand, ¹³C NMR spectrum of **III**_c exhibits eight peaks only rather than nine which may be due to the fact that two carbons are predicted at the same chemical shift (Table 4 and Fig. 5C). Therefore, the observed peak at 146.82 ppm is attributed to C_1 (purine ring) and also to C_6 (benzene ring) supported by the calculated ¹³C chemical shifts as seen later.

4.4. Structural parameters

B3LYP/3-21g(d) structural parameters for compounds III_{a-c} are listed in Table 5, whereas atom numbering is given in Fig. 6. All compounds (III_{a-c}) retain inversion center (C_i symmetry) in agreement with earlier crystallographic studies where most *trans*-cyclodiphosphazane molecules were found constrained to C_i symmetry in the solid phase [29–31]. In addition, the sum of calculated internal angles in (P–N)₂ four memberd ring is 360° which agree precisely with the observed X-ray data for *trans*-[ClP(O)NBu^t]₂ [31]. Therefore, the phospha(V)azo four-membered ring is planar. In addition the calculated P–N bond lengths of (P–N)₂ were in agreement within ±0.06–0.01 Å to X-ray values of *trans*-[Cl₅H₁₄N₂PS]₂ [32].

The benzene ring makes a 91.16 and 88.45° dihedral angle with the phospha(V)azo ring which indicates that the benzene ring is perpendicular to the phospha(V)azo ring. On the other hand, the phosphorus atom displays distorted trigonal bipyrimidal geometry owing to the four-membered ring strain. While the nitrogen atoms $(N_{17} \text{ and } N_{23})$ of exocyclic N–H are slightly triagonal pyramidal with a dihedral angle of $(P_1-N_{23}-H-C_{24}\equiv P_4-N_{17}-H-C_{18}) \sim 160^\circ$.

On the other hand, the equilibrium intramolecular distances r (N₃₁···HN₂₃ \equiv N₃₅···HN₁₇) in the optimized structures of III_{a-c} are 0.11 Å shorter than the sum of Van der Waal contact radii for nitrogen and hydrogen atoms (2.75 Å) [33]. This indicates the formation of intramolecular hydrogen bonding between N₃₁ and HN₂₃ also between N₃₅ and HN₁₇ in all three molecules III_{a-c}.

4.5. Vibrational assignment

The mid-FT-IR (4000–200 cm⁻¹) for solid samples of adeninecyclodiphospha(V)zane derivatives (III_{a-c}) are shown in Fig. 2. The recorded wavenumbers and their assignment are collected in Table 2. The assignment of adenine-cyclodiphospha(V)zanes (III_{a-c}) fundamentals are mainly dependant on our recent vibrational interpretation of adenine [14]. Moreover, our focus is on the ν C=C (benzene ring), ν P–N, ν P–Cl, δ PNP, δ NPN and δ PCl₂ vibrational motion. The symmetry coordinates describing the vibration modes are also given in Ref. [14]. A large number of fundamentals were expected in the investigated adenine-cyclodiphospha(V)zane derivatives owing to 3N-6. On the other hand owing to the symmetry of the synthesized compounds (III_{a-c}), these fundamentals are lesser than expected.

In the IR spectrum of the adenine-cyclodiphospha(V)zane derivatives(III_{a-c}) as seen in Fig. 2, the splitting of the observed bands of imidazole, pyrimidine and benzene rings are due to the existence of two molecules of adenine and benzene in the prepared compounds. In addition, the observed bands in the 2980–1795 cm⁻¹ range were attributed to either combination bands or overtones.

4.5.1. NH Fundamentals

Around 3000 cm⁻¹ the observed IR bands in adeninecyclodiphospha(V)zane derivatives; III_{a-c} (Fig. 2) show extensive broadness compared to those observed in adenine (Fig. 2A) which reflects larger hydrogen bonding interaction in cyclophospha(V)zanes (III_{a-c}). Their NH stretches undergo shift to lower frequency ~3253 cm⁻¹. Unfortunately this region is off scale for III_c, thus a maximum center around 3102 cm⁻¹ was chosen. These bands represent all NH stretches as seen in Fig. 2.

The adenine NH₂ wag was assigned earlier [14] to the recorded weak IR band at 250 cm⁻¹, therefore the corresponding NH wag of the adenine-cyclodiphospha(V)zane derivatives (\mathbf{III}_{a-c}) better match the observed IR bands in the 271–251 cm⁻¹ range as seen in Table 2. In addition, the imidazole ring NH wag was assigned to the observed shoulders at 522 and 486 cm⁻¹ for \mathbf{III}_a and \mathbf{III}_b , respectively. Adenine NH₂ scissor mode was assigned to the

band at $1675 \text{ cm}^{-1}(\text{vs})$ [14]. However four N–H in plane bending fundamentals were expected in the prepared compounds III_{a-c} at the observed bands in $1698-1789 \text{ cm}^{-1}$ range. The broadness of these bands may represent more hydrogen bonding interaction in cyclophospha(V)zanes (III_{a-c}) compared to adenine.

4.5.2. CH₃ fundamentals

For each methyl group (C_{3v} local symmetry) there are v_{as} (stretch), v_s , δ_{as} (bending), δ_s , ρ (rock) and τ fundamentals [34]. The methyl stretches (v_{C-H}) in compound III_b are hidden under a very broad band observed around 3000 cm⁻¹. In addition, the observed IR bands in spectrum of III_b (Fig. 2C) at 1441(m) and 1259(s) cm⁻¹ were assigned to the methyl groups bending modes in consistency with Ref. [34]. Similar spectral features are also observed the IR spectrum of adenine as well as compounds III_a and III_c. However, the two methyl rocking modes of III_b are expected in the region of 1000–1100 and 850–800 cm⁻¹[34], thus we concluded that the two methyl rocks (ρ CH₃) for compound III_b are attributed to the observed IR bands at 1075(m) and 811(s) cm⁻¹ (Fig. 2C), see Table 2.

4.5.3. P–Cl, P–N and C–Cl fundamentals

Comparing the infrared spectra of adenine and adeninecyclodiphospha(V)zane derivatives ($III_{a,b}$), the observed band in the range of 217–225 cm⁻¹ is definitely belongs to the PCl₂ scissoring mode, whereas a very strong bands observed at 209 cm⁻¹ are assigned to the PCl₂ wagging modes. However the PCl₂ wagging of III_c seems to be shifted below 200 cm⁻¹, therefore not observed herein. On the other hand, the predicted PCl₂ twisting and rocking modes match those reported earlier at 100 and 50 cm⁻¹, respectively [35], these bands are beyond our experimental capability to detect.

The P–Cl stretching mode is observed in the $410-425 \text{ cm}^{-1}$ range in agreement with Ref. [35]. The P–N stretching modes were assigned to the observed bands in the $1137-1202 \text{ cm}^{-1}$ range, an assignment supported by the absence of these bands in the adenine IR spectrum (Fig. 2A) and compared to the 900–1200 cm⁻¹ for P–O stretch [35]. On the other hand, the observed IR bands in the ranges were assigned to the P–N–P and N–P–N bending modes, in agreement with assignments given for phosphorus compounds [35].

The vibrations belonging to the benzene–halogen bond (C–Cl) are worth discussing here. The mixing of vibrations is possible due to the presence of heavy atoms on the molecule periphery. For carbon halogen vibrations, two sensitive vibrations were found in the 1129–480 cm⁻¹ region, the higher frequency band is assigned for stretching and the lower frequency band for the in plane deformation [36]. Therefore, the C–Cl stretching vibration was assigned to the observed IR medium band at 1096 cm⁻¹ (Fig. 2D; III_c), whereas the recorded band at 744 cm⁻¹ is assigned to the C–Cl in-plane bending mode.

4.5.4. Adenine and purine rings fundamentals

Heteroaromatic and aromatic structures show C–H stretching frequencies in the 3000–3100 cm⁻¹ region [28]. Therefore the IR bands observed in the 2953–3138 cm⁻¹ range were assigned to the C–H stretching fundamentals of benzene, pyrimidine and imidazole rings in adenine-cyclodiphospha(V)zane derivatives (\mathbf{III}_{a-c}) as seen in Table 2. Moreover, the C–H in-plane deformation of pyrimidine rings in \mathbf{III}_{a-c} better fit the recorded IR band in the 1413–1421 cm⁻¹ range which is consistent to that of adenine recorded at 1420 (vs) cm⁻¹. Similarly, δ_{ip} C–H of imidazole rings were assigned to the observed strong band at 1242 cm⁻¹ for \mathbf{III}_{a-c} in analogy to the very strong band at 1253 cm⁻¹ for adenine [14]. However, the observed IR bands in the 1281–1288 cm⁻¹ range were assigned to the ben-

zene rings δ_{ip} C–H of III_{a-c} in contrast to the absence of bands in that region for adenine IR spectra as seen in Fig. 2A.

The observed very strong IR band at 939 cm^{-1} for adenine has been assigned to the pyrimidine ring C–H wagging [14]. Consequently, the observed strong bands at 946 cm⁻¹ for III_{a-c} correlated to pyrimidine ring C–H wagging. However, the imidazole ring C–H wag in the 846–870 cm⁻¹ range overlapped with pyrimidine ring bending modes. The benzene ring C–H wagging modes in III_{a-c} were assigned to the observed bands in the 742–783 cm⁻¹ range of 450-500 cm⁻¹ in agreement with earlier literature [14,37].

The C–N stretching modes for imidazole and pyrimidine rings in adenine were observed at 1126(s) and 1309(vs) cm⁻¹, respectively. Therefore the recorded bands in the 1112–1123 cm⁻¹ and 1305–1306 cm⁻¹ ranges were assigned to v_{C-N} of imidazole and pyrimidine in III_{a-c}, respectively. In addition, benzene ring conjugated C=C-C stretches were observed in the 982-1100 cm⁻¹ spectral range for the phospha(V)zanes (III_{a-c}) along with the recorded bands in the 1382–1399 cm⁻¹ range which is supported by the absence of these bands in the adenine IR spectrum as seen in Fig. 2A. The pyrimidine ring puckering mode of adenine was recorded at 337 cm⁻¹ compared to medium to strong band at 335 cm^{-1} for adenine-cyclodiphospha(V)zane derivatives (III_{a-c}). In addition, the imidazole ring puckering is observed at 621 cm⁻¹ in adenine. Therefore, the recorded bands in the 609–620 cm⁻¹ range would fit the imidazole ring puckering modes in III_{a-c}. However, the observed bands in the $371-392 \text{ cm}^{-1}$ range were consistent with the benzene ring puckering modes.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2011.08.035.

References

- [1] G.G. Briand, T. Chivers, M. Krahn, Coord. Chem. Rev. 233-234 (2002) 237-254.
- [2] P. Chandrasekaran, J.T. Mague, M.S. Balakrishna, Inorg. Chem. 44 (2005) 7925-7932.
- [3] C.M. Sharaby, Spectrochem. Acta 62A (2005) 326–334.
- [4] P. Chandrasekaran, J.T. Mague, R. Venkateswaran, M.S. Balakrishna, Eur. J. Inorg. Chem. 2007 (2007) 4988–4997.
- [5] N. Wheatley, P. Kalck, Chem. Rev. 99 (1999) 3379-3420.
- [6] M. Sakamoto, K. Manseki, H. Okawa, Coord. Chem. Rev. 219–221 (2001) 379–414.
- [7] H.B. Gray, B.G. Malmstroem, Biochemistry 28 (1989) 7499-7505.
- [8] T.H. Afifp, M.A. El Nawawy, Z.H. El Wahab, H.A. Mahdy, Phosphorus, Sulfur, Silicon, Relat. Elem. 132 (1998) 101–108.
- [9] E.H.M. Ibrahim, N.E. Amine, Egypt J. Chem. 22 (1979) 357.
- [10] R.A. Shaw, Pure Appl. Chem. 52 (1980) 1063-1097.
- [11] V. Chandrasekhar, S.S. Krishnamurthy, H. Manohar, A.R.V. Murthy, R.A. Shaw, M. Woods, J. Chem. Soc.: Dalton Trans. (1984) 621–625.
- [12] P. Chandrasekaran, J.T. Mague, M.S. Balakrishna, Tetrahedron Lett. 48 (2007) 5227–5229.
- [13] I.A. Shaaban, W.M. Zoghaib, J. Husband, T.A. Mohamed, Comp. Theor. Chem., submitted for publication.
- [14] T.A. Mohamed, I.A. Shabaan, W.M. Zoghaib, J. Husband, R.S. Farag, A.M.A. Alajhaz, J. Mol. Struct. 938 (2009) 263–276.
- [15] J.K. Labanowski, J.W. Andzelm, Density Functional Methods in Chemistry, Springer Verlag, New York, 1991.
- [16] I.M. Abd-Ellah, A.N. El-Khazandar, Pak. J. Sci. Ind. Res. 31 (1988) 395-397.
- [17] R. Voy, Chem. Ztg. Chem. Apparatus 21 (1897) 441.
- [18] A.D. Becke, Phys. Rev. 38A (1988) 3098-3100.
- [19] C. Lee, W. Yang, R.G. Parr, Phys. Rev. 37B (1988) 785–789.
- [20] W.J. Hehre, L. Radom, P.V.R. Schleyer, J.A. Pople, Ab initio Molecular Orbital Theory, Wiley, New York, 1986.
- [21] P. Pulay, Mol. Phys. 17 (1969) 197-204.
- [22] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon,

E.S. Replogle, J.A. Pople, Gaussian 98 (Revision A.7), Gaussian, Inc., Pittsburgh PA, 1998.

- [23] Chem. Office Ultra, v10, Molecular Modeling and Analysis, Cambridge (2006).
- [24] C.N.R. Rao, Ultra-violet and Visible Spectroscopy Chemical Application, Butterworths, London, 1961.
- [25] S.F. Mason, J. Chem. Soc. (1954) 2071-2081.
- [26] I.M. Abd-Ellah, A.N. El-Khazandar, J. Phosphorous Sulfur 292 (1987) 239.
- [27] C.M. Sharaby, Synth. React. Inorg. Met. -Org. Chem. 35 (2005) 133-142.
- [28] R.M. Silverstein, F.X. Webster, D. Kiemle, Spectrometric Identification of Organic Compounds, John Wiley & Sons, 2004.
- [29] G.J. Bullen, J.S. Rutherford, P.A. Tucker, Acta Cryst. 29B (1973) 1439–1445.
- [30] M.B. Peterson, A.J. Wagner, J. Chem. Soc.: Dalton Trans. (1973) 106–111.
- [31] L. Manojlović-Muir, K.W. Muir, J. Chem. Soc.: Dalton Trans. (1974) 2395–2398.
- [32] T.S. Cameron, C.K. Prout, K.D. Howlett, Acta Cryst. 31B (1975) 2333-2335.
- [33] A. Bondi, J. Phys. Chem. 68 (1964) 441–451.
- [34] T.A. Mohamed, R.S. Farag, Spectrochim. Acta 62A (2005) 800-807.
- [35] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part A, 6th ed., John Wiley & Sons, New York, 2009.
- [36] E.F. Mooney, Spectrochim. Acta 20 (1964) 1021–1032.
- [37] M. Karabacak, D. Karagöza, M. Kurt, Spectrochim. Acta 72A (2009) 1076-1083.