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C-PHOSPHORYLATED FURAZANO-[3,4-*b*]PIPERAZINES

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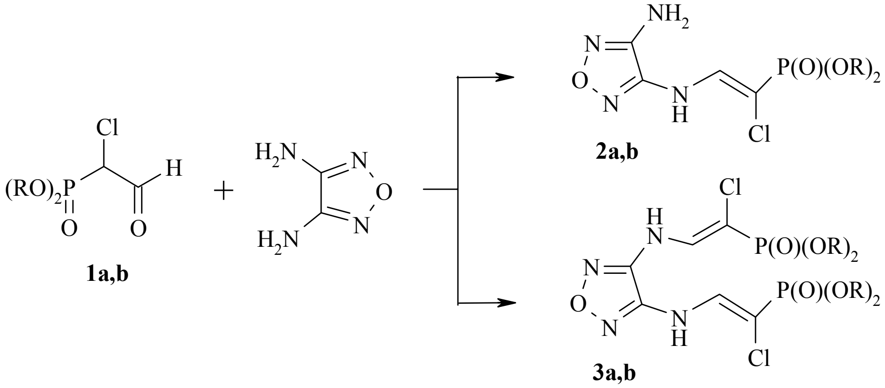
The reaction of phosphorylated α-chloroacetaldehydes with 3,4-diaminofurazane gives enamines, bisenamines, semiaminals, and O,N-acetals, whose cyclization leads to previously unreported phosphorylated furazano[3,4-b]piperazines.

Keywords: O,N-acetal, bisenamines, 3,4-diaminofurazane, enamines, semiaminal, phosphorylated α-chloroacetaldehydes, furazano[3,4-*b*]piperazines.

Derivatives of furazano[3,4-*b*]piperazines are used as energy-rich materials, intermediates in organic synthesis, and biologically active compounds. However, preparative methods for obtaining these compounds and the chemical properties of these derivatives, which may have potential as biologically active compounds, have not been studied adequately [1, 2].

With the aim of synthesizing C-phosphorylated furazanopiperazines, we studied the reactions of α-chloroacetaldehydes **1** with diaminofurazane. The condensation of phosphorylmonochloroacetaldehydes **1a**,**b** with 3,4-diaminofurazane proceeds in ethanol at reflux and leads to the formation of monoenamine **2** and bisenamine **3** depending on the ratio of the starting reagents.



2, 3 a R = Et, **b** R = *i*-Pr

Enamines **2** and **3** are white crystalline compounds. The IR band for their amino group is found at 3350 cm^{-1} and is superimposed on the stretching band of the secondary amino group to give a complex overall shape. The low value for ν_{NH_2} in KBr pellets indicates hydrogen bonding of this group.

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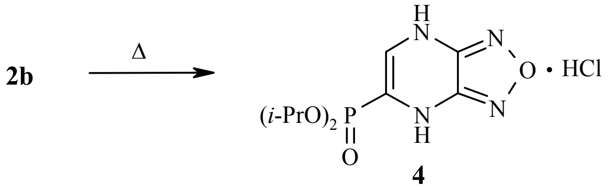
The protons of the NH–CH=CCl fragment in the ^{1}H NMR spectra of **2** and **3** in DMSO-d$_6$ and acetone-d$_6$ are seen as a characteristic group of signals: a doublet at 7.7-7.8 ppm (CH=) with $^3J_{PH} = 12.5$ Hz and downfield doublet at 8.9-9.0 ppm (NH).

The methine group proton in the ^{1}H NMR spectrum of **3** is not shifted downfield and the broad signal corresponding to NH$_2$ group protons is not seen.

As assumed, at higher temperature in xylene at reflux, **2b** undergoes heterocyclization as the result of intramolecular nucleophilic substitution to give hydrochloride **4**.

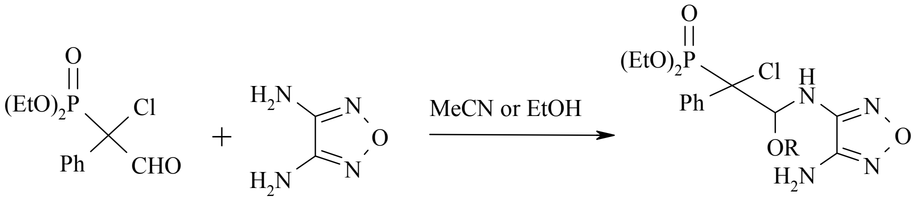


4

The ^{1}H NMR spectrum of **4** in DMSO-d$_6$ shows a doublet of doublets for the =CH group proton at 7.75 ppm as well as two doublets at 8.10 ($^+$NH$_2$) and 9.00 ppm (NH) with 2:1 intensity ratio. The singlet characteristic for NH$_2$ group protons at 6.2 ppm (for **2b**) completely disappears. The signal in the ^{31}P NMR spectrum is shifted from 9.89 to 11.00 ppm.

The IR spectrum of **4** has stretching bands for the phosphoryl group at 1280 cm^{-1}, C=C bond at 1635 cm^{-1}, secondary amino group at 3100 cm^{-1}, and $^+$NH$_2$ group at 3280 cm^{-1}.

In previous work [3], we showed that diethoxyphosphorylphenyl-α-chloroacetaldehyde in a polar solvent (acetonitrile) reacts with diaminofurazane to give semiaminal **5a** but this reaction in ethanol gives O,N-acetal **5b**, whose structure was demonstrated by X-ray diffraction structural analysis.



5a,b

a R=H, **b** R=Et

Since the crystal of **5b** is centrosymmetric, this compound exists as a racemate (Fig. 1).

The conformation along the P–C$_{(12)}$ and C$_{(8)}$–C$_{(12)}$ bonds is staggered, perhaps due to steric effects; steric hindrance is minimal in this conformation. The P=O and C–Cl bonds in **5b** are in *gauche* arrangement, while the C$_{(8)}$–C$_{(12)}$ bond is *trans* to the phosphoryl bond. The phenyl substituent at C$_{(12)}$ is in an eclipsed conformation with the C$_{(12)}$–Cl bond, probably due to steric hindrance arising from the bulky substituents at C$_{(12)}$. The aminofurazane substituent has planar conformation. The N$_{(2)}$–C$_{(3)}$–N$_{(7)}$–C$_{(8)}$ torsion angle is 11.5(4)°, resulting from conjugation of the unshared electron pair of N$_{(7)}$ with the π-system of the furazane ring. The C$_{(3)}$–N$_{(7)}$ bond length (1.345(4) Å) corresponds to this conjugation.

The bond lengths and valence angles in the phosphonate fragment, benzene ring, and furazane ring are ordinary.

The crystal of **5b** is stabilized by N–H···O and N–H···N hydrogen bonding (Fig. 2) between the aminofurazane group and phosphoryl group oxygen atom N$_{(7)}$–H···O$_{(21')}$ ($3/2$-x, $1/2$+y, $1/2$-z), N$_{(7)}$–H 0.93, N$_{(7)}$···O$_{(21')}$ 3.042(3); H···O$_{(21')}$ 2.15 Å, angle N$_{(7)}$–H···O$_{(21')}$ 161° and also between the amino NH$_2$ group, phosphoryl group, and one of the nitrogen atoms of the furazane ring: N$_{(6)}$–H$_{(61)}$···O$_{(21')}$, N$_{(6)}$–H$_{(61)}$ 0.75,

$N_{(6)}\cdots O_{(21')}$ 2.903(4), $H_{(61)}\cdots O_{(21')}$ 2.16 Å, angle $N_{(6)}–H_{(61)}\cdots O_{(21')}$ 173°; $N_{(6)}–H_{(62)}\cdots N_{(5'')}$ (2-*x*, 2-*y*, -*z*), $N_{(6)}–H_{(62)}$ 1.12, $N_{(6)}\cdots N_{(5'')}$ 3.019(4), $H_{(62)}\cdots N_{(5'')}$ 1.94 Å, angle $N_{(6)}–H_{(62)}\cdots N_{(5'')}$ 161°.

A two-dimensional molecular layer is formed in the *X0Z* plane (perpendicular to the *0Y* axis) due to these hydrogen bonds.

The parallel packing of these layers in the crystal leads to the formation of molecular stacks.

Fig. 3 shows that the arrangement of the benzene and furazane rings in these stacks suggests a stacking effect. However, the geometrical parameters do not correspond to those formally adopted for π–π interactions.

TABLE 1. Characteristics of the Products Synthesized

Com-pound	Empirical formula	Found, % / Calculated, %			mp, °C	Yield, %
		Cl	N	P		
2a	$C_8H_{14}ClN_4O_4P$	11.88 11.97	18.81 18.89	10.49 10.45	130-132	85
2b	$C_{10}H_{18}ClN_4O_4P$	10.91 10.94	17.22 17.26	9.44 9.55	155-158	87
3a	$C_{14}H_{24}Cl_2N_4O_7P_2$	14.36 14.40	11.28 11.36	12.53 12.58	145-146	78
3b	$C_{18}H_{32}Cl_2N_4O_7P_2$	12.87 12.93	10.17 10.20	11.23 11.29	168-170	81
4	$C_{10}H_{18}ClN_4O_4P$	10.88 10.94	17.16 17.26	9.48 9.55	220-221	83
5a	$C_{14}H_{20}ClN_4O_5P$	9.18 9.09	14.27 14.34	7.98 7.94	152-153	83
5b	$C_{16}H_{24}ClN_4O_5P$	8.57 8.48	13.44 13.38	7.55 7.41	158-159	80
6	$C_{16}H_{23}N_4O_5P$	—	14.34 14.66	8.22 8.12	150-151	76
7	$C_{14}H_{20}ClN_4O_4P$	9.24 9.09	14.42 14.34	8.01 7.94	166-167	69

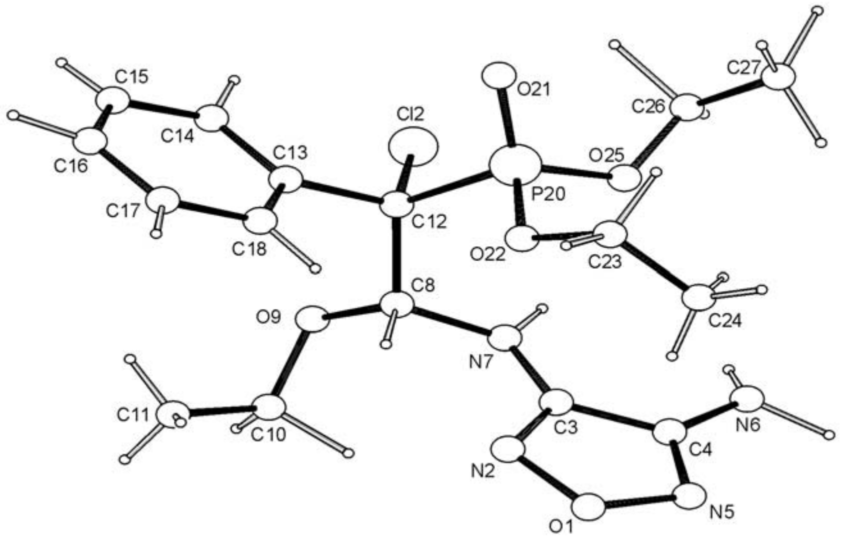


Fig. 1. Geometry of **5b** in the crystal.

TABLE 2. IR, ^{1}H and ^{31}P NMR Spectra of Products Synthesized

Compound	IR spectrum, ν, cm^{-1}	^{1}H NMR spectrum, δ, ppm. (*J*, Hz)*	^{31}P NMR spectrum, δ, ppm
2a	1280 (P=O), 1610 (C=C), 3100 (NH), 3350 (NH$_2$)	1.25 (6H, t, $^{3}J_{HH}$ = 12.5, 2CH$_3$); 4.00 (4H, m, 2OCH$_2$); 6.00 (2H, br. s, NH$_2$); 7.70 (1H, dd, $^{3}J_{HH}$ = 8.75, $^{3}J_{PH}$ = 12.5, =CH); 8.90 (1H, d, $^{3}J_{HH}$ = 12.5, NH)	9.8
2b	—	1.25 (12H, dd, $^{3}J_{HH}$ = 7.5, 4CH$_3$); 4.60 (2H, m, 2OCH); 6.20 (2H, br. s, NH$_2$); 7.75 (1H, dd, $^{3}J_{HH}$ = 7.5, $^{3}J_{PH}$ = 12.5, =CH); 9.00 (1H, d, $^{3}J_{HH}$ = 10.0, NH)	9.89
3a	1280 (P=O), 1605 (C=C), 3140 (NH)	1.20 (12H, dt, $^{3}J_{HH}$ = 12.5, 4CH$_3$); 4.00 (8H, m, 4OCH$_2$); 7.75 (2H, dd, $^{3}J_{PH}$ = $^{3}J_{HH}$ = 12.5, 2CH=); 8.90 (2H, d, $^{3}J_{HH}$ = 12.5, 2NH)	12.3
3b	—	1.25 (24H, dt, , $^{3}J_{HH}$ = 15, 8CH$_3$); 4.70 (4H, m, 4OCH); 7.80 (2H, dd, $^{3}J_{PH}$ = 12.5, $^{3}J_{HH}$ = 17.5, 2CH=); 9.00 (2H, d, $^{3}J_{HH}$ = 10.0, 2NH)	12.5
4	1280 (P=O), 1635 (C=C), 3100 (NH), 3280 (H$_2$N$^+$)	1.20 (12H, dt, $^{3}J_{HH}$ = 17.5, 4CH$_3$); 4.60 (2H, m, 2OCH); 7.75 (2H, dd, $^{3}J_{HH}$ = 7.5, $^{3}J_{PH}$ = 10.0, CH=); 8.10 (2H, d, $^{3}J_{HH}$ = 10.0, $^{+}$NH$_2$); 9.00 (1H, d, NH)	11.0
5a	1280 (P=O), 1650 (CH–O), 3100 (NH), 3250 (NH$_2$), 3340 (OH)	1.10 (6H, dt, $^{3}J_{HH}$ = 22.5, 2CH$_3$); 3.90 (4H, m, 2OCH$_2$); 5.50 (1H, d, $^{3}J_{PH}$ = 5, OCH); 6.00 (2H, br. s, NH$_2$); 7.25 (3H, m, C$_6$H$_5$); 7.60 (2H, m, C$_6$H$_5$); 10.30 (1H, br. s, OH); 11.50 (1H, br. s, NH)	15.0
5b	1280 (P=O), 1640 (CH–O), 3100 (NH), 3250 (NH$_2$)	1.0 (9H, dt, $^{3}J_{HH}$ = 20, 3CH$_3$); 3.75 (4H, m, 2OCH$_2$); 4.00 (2H, q, $^{3}J_{HH}$ = 12.5, OCH$_2$); 5.75 (1H, d, $^{3}J_{PH}$ = 5, OCH); 6.10 (2H, br. s, NH$_2$); 7.30 (3H, m, C$_6$H$_5$); 7.80 (2H, m, C$_6$H$_5$); 11.70 (1H, br. s, NH)	15.15, 15.20
6	1280 (P=O), 1620 (C–O), 3250 (NH)	1.15 (9H, dt, $^{3}J_{HH}$ = 22.5, 3CH$_3$); 3.80 (4H, m, 2OCH$_2$); 4.10 (2H, q, $^{3}J_{HH}$ = 10.0, OCH$_2$); 5.00 (1H, dt, $^{3}J_{HH}$ = 7.5, $^{3}J_{PH}$ = 10.0, OCH); 5.50 (2H, s, NH$_2$); 7.35 (3H, m, C$_6$H$_5$); 7.50 (2H, m, C$_6$H$_5$)	20.83, 20.91
7	1287 (P=O), 1570 (C–O), 3200 (NH)	1.15 (6H, dt, $^{3}J_{HH}$ = 20, 2CH$_3$); 4.00 (4H, m, 2OCH$_2$); 5.30 (1H, dd, $^{3}J_{HH}$ = 7.5, $^{3}J_{PH}$ = 12.5, OCH); 7.25 (3H, m, C$_6$H$_5$); 7.50 (2H, m, C$_6$H$_5$); 8.20 (2H, d, $^{3}J_{PH}$ = 7.5, $^{+}$NH$_2$); 9.00 (1H, d, $^{3}J_{HH}$ = 12.5, NH); 10.50 (1H, d, $^{3}J_{HH}$ = 10.0, OH)	19.8

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* Solvents: (CD$_3$)$_2$SO for **2a, 4, 5a,b, 7** and (CD$_3$)$_2$CO for **2b, 3a,b,** and **6**.

In previous work [3], we reported that the reaction of ester **5b** with sodium ethylate in ethanol gives a high yield of a condensed heterocyclic compound, namely, 4-diethoxyphosphoryl-5-ethoxy-4-phenyl-3,4,5,6-tetrahydrofurazano[3,4-*b*]piperazine (**6**), which is the first reported phosphorylated furazano[3,4-*b*]piperazine.

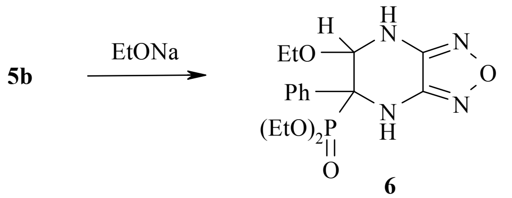

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TABLE 3. Lengths of Major Bonds (*d*) in **5b**

Bond	*d*, Å	Bond	*d*, Å
$Cl_{(2)}–C_{(12)}$	1.801(3)	$N_{(7)}–C_{(3)}$	1.345(4)
$P_{(20)}–O_{(21)}$	1.464(2)	$N_{(7)}–C_{(8)}$	1.452(4)
$P_{(20)}–O_{(22)}$	1.561(2)	$C_{(3)}–C_{(4)}$	1.435(4)
$P_{(20)}–O_{(25)}$	1.553(2)	$C_{(8)}–C_{(12)}$	1.542(4)
$P_{(20)}–C_{(12)}$	1.842(3)	$C_{(10)}–C_{(11)}$	1.409(9)
$O_{(1)}–N_{(2)}$	1.382(4)	$C_{(12)}–C_{(13)}$	1.541(4)
$O_{(1)}–N_{(5)}$	1.399(4)	$C_{(13)}–C_{(14)}$	1.386(5)
$O_{(9)}–C_{(8)}$	1.406(4)	$C_{(13)}–C_{(18)}$	1.399(5)
$O_{(9)}–C_{(10)}$	1.437(5)	$C_{(14)}–C_{(15)}$	1.420(5)
$O_{(22)}–C_{(23)}$	1.458(5)	$C_{(14)}–H_{(14)}$	1.06(3)
$O_{(25)}–C_{(26)}$	1.458(5)	$C_{(15)}–C_{(16)}$	1.346(6)
$N_{(2)}–C_{(3)}$	1.305(4)	$C_{(16)}–C_{(17)}$	1.338(6)
$N_{(5)}–C_{(4)}$	1.299(4)	$C_{(17)}–C_{(18)}$	1.375(5)
$N_{(6)}–C_{(4)}$	1.345(4)	$C_{(23)}–C_{(24)}$	1.463(8)

In a continuation of a study of the reactivity of semiaminals **5** and in an attempt to obtain new condensed C-phosphorylated heterocyclic furazane derivatives, we investigated the intramolecular heterocyclization of O,N-acetal **5a** under vigorous conditions. Heating **5a** in toluene at reflux leads to an intramolecular nucleophilic reaction and formation of furazano[3,4-*b*]piperazine hydrochloride **7**.

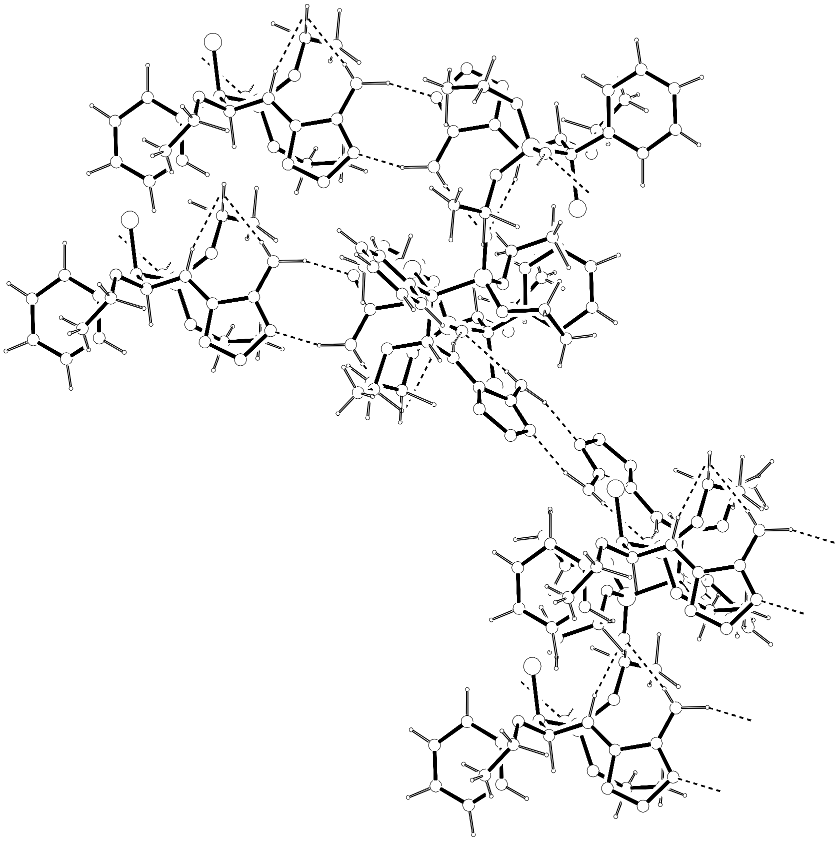


Fig. 2. Hydrogen bonding system in the crystal of **5b**.

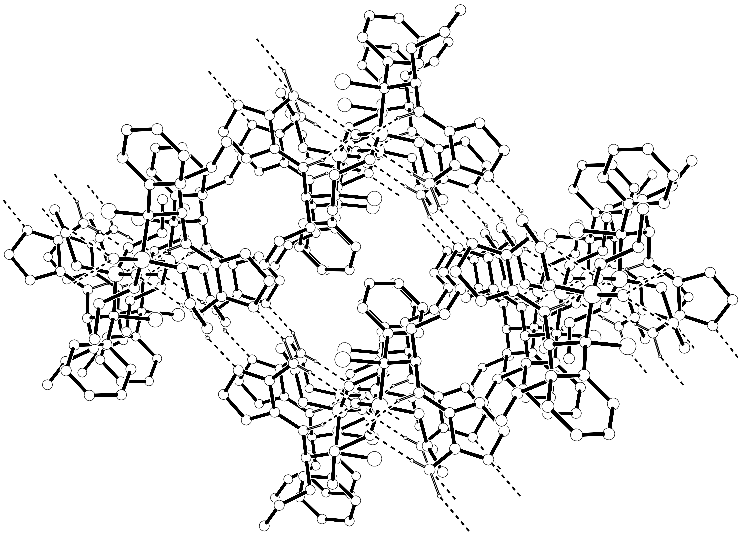
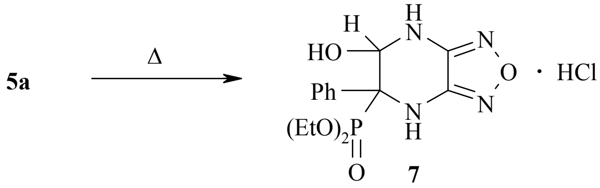


Fig. 3. Stacking of molecules in the crystal of **5b**.



Heterocycle **7** is a white crystalline compound with good solubility in ethanol, DMSO, and acetonitrile. The reaction proceeds with involvement of the furazane NH_2 group and α-halogen atom and is complete after 8 h at 105-110°C.

The IR spectrum of **7** shows a band at 1570 cm^{-1} due to stretching vibrations of the CH–O group as well as bands at 1287 (P=O), 3200 (NH), 3250 ($^+NH_2$), and 3340 cm^{-1} (OH).

The phosphorus signal in the ^{31}P NMR spectrum of this compound is shifted from 15.0 to 19.8 ppm, indicating a heterocyclization reaction. The finding of two signals in the ^{31}P NMR spectrum shows formation of a mixture of diastereomers.

The signal for the semiaminal proton in the ^1H NMR spectrum of **7** is shifted upfield from 5.50 to 5.30 ppm. The broad singlet for the NH_2 group protons in the vicinity of 6.00 ppm in **5a** disappears and a doublet appears at 8.20 ppm, probably indicative of protons of the $^+NH_2$ group. While the OH and NH group proton signals in the starting semiaminal are seen as broad singlets at 10.30 and 11.50 ppm, respectively, these signals for heterocycle **7** appear as a doublet at 10.50 and 9.00 ppm, respectively.

Thus, the products of the reaction of phosphorylated chloro aldehydes with diaminofurazane, namely, enamines **2** and **3**, semiacetal **5a**, and O,N-acetal **5b** are convenient starting compounds for the synthesis of phosphorylated furazano[3,4-*b*]piperazines.

TABLE 4. Bond Angles (ω) in **5b**

Bond angle	ω, deg.	Bond angle	ω, deg.
$O_{(21)}-P_{(20)}-O_{(22)}$	116.2(1)	$C_{(8)}-C_{(12)}-C_{(13)}$	109.2(2)
$O_{(21)}-P_{(20)}-O_{(25)}$	114.2(1)	$C_{(12)}-C_{(13)}-C_{(14)}$	123.3(3)
$O_{(21)}-P_{(20)}-C_{(12)}$	112.2(1)	$C_{(12)}-C_{(13)}-C_{(18)}$	117.8(3)
$O_{(22)}-P_{(20)}-O_{(25)}$	104.2(1)	$C_{(14)}-C_{(13)}-C_{(18)}$	118.9(3)
$O_{(22)}-P_{(20)}-C_{(12)}$	100.8(1)	$C_{(13)}-C_{(14)}-C_{(15)}$	117.5(3)
$O_{(25)}-P_{(20)}-C_{(12)}$	108.0(1)	$C_{(14)}-C_{(15)}-C_{(16)}$	122.3(4)
$N_{(2)}-O_{(1)}-N_{(5)}$	110.5(2)	$C_{(15)}-C_{(16)}-C_{(17)}$	119.3(4)
$C_{(8)}-O_{(9)}-C_{(10)}$	114.6(3)	$C_{(16)}-C_{(17)}-C_{(18)}$	121.7(4)
$P_{(20)}-O_{(22)}-C_{(23)}$	119.1(2)	$C_{(13)}-C_{(18)}-C_{(17)}$	120.2(3)
$P_{(20)}-O_{(25)}-C_{(26)}$	124.6(2)	$N_{(5)}-C_{(4)}-C_{(3)}$	109.5(3)
$O_{(1)}-N_{(2)}-C_{(3)}$	106.1(3)	$N_{(6)}-C_{(4)}-C_{(3)}$	126.5(3)
$O_{(1)}-N_{(5)}-C_{(4)}$	105.3(3)	$O_{(9)}-C_{(8)}-N_{(7)}$	112.4(2)
$C_{(3)}-N_{(7)}-C_{(8)}$	120.8(2)	$O_{(9)}-C_{(8)}-C_{(12)}$	106.3(2)
$N_{(2)}-C_{(3)}-N_{(7)}$	124.1(3)	$N_{(7)}-C_{(8)}-C_{(12)}$	113.7(2)
$N_{(2)}-C_{(3)}-C_{(4)}$	108.6(3)	$O_{(9)}-C_{(10)}-C_{(11)}$	111.0(5)
$N_{(7)}-C_{(3)}-C_{(4)}$	127.3(3)	$Cl_{(2)}-C_{(12)}-P_{(20)}$	103.1(1)
$N_{(5)}-C_{(4)}-N_{(6)}$	123.9(3)	$Cl_{(2)}-C_{(12)}-C_{(8)}$	108.8(2)
$Cl_{(2)}-C_{(12)}-C_{(13)}$	111.4(2)	$O_{(22)}-C_{(23)}-C_{(24)}$	110.0(4)
$P_{(20)}-C_{(12)}-C_{(8)}$	114.7(2)	$O_{(25)}-C_{(26)}-C_{(27)}$	110.7(4)
$P_{(20)}-C_{(12)}-C_{(13)}$	109.5(2)		

TABLE 5. Torsion Angles (τ) in **5b**

Torsion angle	τ, deg.	Torsion Angle	τ, deg.
$O_{(21)}-P_{(20)}-O_{(22)}-C_{(23)}$	-60.5(3)	$N_{(7)}-C_{(8)}-C_{(12)}-Cl_{(2)}$	68.9(3)
$O_{(25)}-P_{(20)}-O_{(22)}-C_{(23)}$	66.1(3)	$N_{(7)}-C_{(8)}-C_{(12)}-P_{(20)}$	-46.0(3)
$C_{(12)}-P_{(20)}-O_{(22)}-C_{(23)}$	177.9(3)	$N_{(7)}-C_{(8)}-C_{(12)}-C_{(13)}$	-169.3(2)
$O_{(21)}-P_{(20)}-O_{(25)}-C_{(26)}$	-19.57(3)	$O_{(1)}-N_{(2)}-C_{(3)}-N_{(7)}$	-179.0(3)
$O_{(22)}-P_{(20)}-O_{(25)}-C_{(26)}$	-147.3(3)	$O_{(1)}-N_{(2)}-C_{(3)}-C_{(4)}$	0.4(3)
$C_{(12)}-P_{(20)}-O_{(25)}-C_{(26)}$	106.1(3)	$O_{(1)}-N_{(5)}-C_{(4)}-N_{(6)}$	177.9(3)
$O_{(21)}-P_{(20)}-C_{(12)}-Cl_{(2)}$	74.5(2)	$O_{(1)}-N_{(5)}-C_{(4)}-C_{(3)}$	-1.5(4)
$O_{(21)}-P_{(20)}-C_{(12)}-C_{(8)}$	-167.3(2)	$C_{(8)}-N_{(7)}-C_{(3)}-N_{(2)}$	11.5(4)
$O_{(21)}-P_{(20)}-C_{(12)}-C_{(13)}$	-44.2(2)	$C_{(8)}-N_{(7)}-C_{(3)}-C_{(4)}$	-167.8(3)
$O_{(22)}-P_{(20)}-C_{(12)}-Cl_{(2)}$	-161.2(1)	$C_{(3)}-N_{(7)}-C_{(8)}-O_{(9)}$	-116.6(3)
$O_{(22)}-P_{(20)}-C_{(12)}-C_{(8)}$	-43.1(2)	$C_{(3)}-N_{(7)}-C_{(8)}-C_{(12)}$	122.5(3)
$O_{(22)}-P_{(20)}-C_{(12)}-C_{(13)}$	80.1(2)	$N_{(2)}-C_{(3)}-C_{(4)}-N_{(5)}$	0.7(4)
$O_{(25)}-P_{(20)}-C_{(12)}-Cl_{(2)}$	-52.3(2)	$N_{(2)}-C_{(3)}-C_{(4)}-N_{(6)}$	-178.7(3)
$O_{(25)}-P_{(20)}-C_{(12)}-C_{(8)}$	65.9(2)	$Cl_{(2)}-C_{(12)}-C_{(13)}-C_{(14)}$	-1.6(4)
$O_{(25)}-P_{(20)}-C_{(12)}-C_{(13)}$	-171.0(2)	$Cl_{(2)}-C_{(12)}-C_{(13)}-C_{(18)}$	178.7(2)
$N_{(5)}-O_{(1)}-N_{(2)}-C_{(3)}$	-1.4(3)	$P_{(20)}-C_{(12)}-C_{(13)}-C_{(14)}$	111.9(3)
$N_{(2)}-O_{(1)}-N_{(5)}-C_{(4)}$	1.8(3)	$P_{(20)}-C_{(12)}-C_{(13)}-C_{(18)}$	-67.9(3)
$C_{(10)}-O_{(9)}-C_{(8)}-N_{(7)}$	78.6(3)	$C_{(8)}-C_{(12)}-C_{(13)}-C_{(14)}$	-121.8(3)
$C_{(10)}-O_{(9)}-C_{(8)}-C_{(12)}$	-156.4(3)	$C_{(8)}-C_{(12)}-C_{(13)}-C_{(18)}$	58.5(3)
$C_{(8)}-O_{(9)}-C_{(10)}-C_{(11)}$	93.4(5)	$C_{(12)}-C_{(13)}-C_{(14)}-C_{(15)}$	-179.2(3)
$P_{(20)}-O_{(22)}-C_{(23)}-C_{(24)}$	-103.0(4)	$C_{(18)}-C_{(13)}-C_{(14)}-C_{(15)}$	0.5(5)
$P_{(20)}-O_{(25)}-C_{(26)}-C_{(27)}$	94.7(4)	$C_{(12)}-C_{(13)}-C_{(18)}-C_{(17)}$	179.8(3)
$N_{(7)}-C_{(3)}-C_{(4)}-N_{(5)}$	-179.9(3)	$C_{(14)}-C_{(13)}-C_{(18)}-C_{(17)}$	0.03(6)
$N_{(7)}-C_{(3)}-C_{(4)}-N_{(6)}$	0.7(5)	$C_{(13)}-C_{(14)}-C_{(15)}-C_{(16)}$	-0.8(6)
$O_{(29)}-C_{(8)}-C_{(12)}-Cl_{(2)}$	-55.3(3)	$C_{(14)}-C_{(15)}-C_{(16)}-C_{(17)}$	0.5(6)
$O_{(9)}-C_{(8)}-C_{(12)}-P_{(20)}$	-170.2(2)	$C_{(15)}-C_{(16)}-C_{(17)}-C_{(18)}$	0.2(6)
$O_{(9)}-C_{(8)}-C_{(12)}-C_{(13)}$	66.5(3)	$C_{(16)}-C_{(17)}-C_{(18)}-C_{(13)}$	-0.4(6)

EXPERIMENTAL

The IR spectra were taken in vaseline mull or KBr pellets on a UR-20 spectrometer. The X-ray diffraction structural analysis was carried out on an Enraf-Nonius CAD-4 automatic four-circle diffractometer at 20°C. The ^{1}H NMR spectra for solutions in acetone-d_6 and DMSO-d_6 were taken on a Tesla BW-567 (100 MHz, HMDS), and ^{31}P NMR spectra on a Bruker WR-80 spectrometer at 32 MHz with 85% H_3PO_4 as the reference.

The unit cell parameters of colorless monoclinic prisms of $C_{16}H_{24}ClN_4O_5P$ were: $a = 10.312(6)$, $b = 11.529(5)$, $c = 17.51(1)$ Å; $\beta = 92.33(6)°$; $V = 2080(2)$ Å^3; $d_{calc} = 1.25$ g/cm^3; $Z = 4$; space group $P2_1/n$.

The unit cell parameters and intensities of 4612 reflections were measured, of which 3155 reflections with $I \geq 3\sigma$ were used, employing CuKα radiation ($\lambda = 1.54184$ Å), a graphite monochromator, and $\omega/2\theta$-scanning, $\theta \leq 74°$. No drop in intensity of control reflections was observed during the exposure. An empirical absorption correction was used μCu = 2.639 mm^{-1}. The structure was solved by the direct method using the SIR program [4] and refined initially isotropically and then anisotropically. The hydrogen atoms were found from the electron density difference maps. Their contribution to the structural amplitudes were considered with fixed positional and isotropic temperature parameters. The final $R = 0.052$ and $R_w = 0.066$ were found using 2899 independent reflections. All the calculations were carried out using the MOLEN program package [5] on an AlphaStation 200 computer. Analysis of the intermolecular interactions and figures of the structures were obtained using the PLATON program [6]. The atomic coordinates and geometrical parameters are given in Tables 3-5.

Synthesis of Enamines and Bisenamines 2, 3 (General Procedure). A mixture of aldehyde **1a**,**b** (0.02 mol) and 3,4-diaminofurazane (0.02 mol) was heated at reflux for 16 h in the corresponding alcohol. The solvent was removed in vacuum and the crystalline precipitate of 3-amino-4-[(2-dialkoxyphosphoryl)-2-chloroethenyl-amino)]furazanes **2a**,**b** were filtered off, washed with ethanol, and dried. The yield of **2a** was 85% and the yield of **2b** was 87%.

3,4-Bis[(2-dialkoxyphosphoryl)-2-chloroethenylamino]furazanes 3a,b were obtained analogously from aldehyde **1a**,**b** (0.04 mol) and 3,4-diaminofurazane (0.02 mol) in 78 and 81% yield, respectively.

3H,6H-4-(diisopropoxyphosphoryl)furazano[3,4-*b*]piperazine Hydrochloride (4). A solution of **2b** (3.25 g, 0.01 mol) in xylene (20 ml) was heated at reflux for 12 h. The solvent was distilled off in vacuum. The crystalline precipitate of **4** was filtered off, washed with ether, and dried to give 2.7 g (83%).

Diethyl Ester of 2-[(4-Amino-3-furazanyl)amino]-1-chloroethyl-2-hydroxy-1-phenylphosphoric Acid (5a). A mixture of diethoxyphosphorylphenyl derivative of α-chloroacetaldehyde (5.81 g, 20 mmol) and 3,4-diaminofurazane (2 g, 20 mmol) in acetonitrile (30 ml) was heated at reflux for 12 h. The solvent was evaporated off and 10 ml 1:1 ether–ethanol was added. The crystalline precipitate was filtered off, dried, and recrystallized from ethanol to give 6.48 g (83%) of compound **5a**.

Diethyl Ester of 2-[(4-Amino-3-furazanyl)amino]-1-chloro-2-ethoxyethyl-1-phenylphosphonic Acid (5b). A mixture of diethoxyphosphorylphenyl derivative of α-chloroacetaldehyde (5.81 g, 20 mmol) and 3,4-diaminofurazane (2 g, 20 mmol) in ethanol (30 ml) was heated at reflux for 10 h. The solvent was removed and 10 ml 1:1 ether–acetonitrile was added to the residue. The crystalline precipitate of **5b** was filtered off, washed with ether, and recrystallized from acetonitrile to give 6.7 g (80%).

4-(Diethoxyphosphoryl)-5-ethoxy-4-phenyl-3,4,5,6-tetrahydrofurazano[3,4-*b*]piperazine (6). A solution of **5b** in ethanol (10 ml) was added dropwise to a stirred solution obtained from metallic sodium (0.23 g, 10 mmol) in ethanol (20 ml) at 50°C. The reaction mixture was heated at reflux for 8 h. The solvent was evaporated off and ether (15 ml) was added to the residue. The precipitate of NaCl was filtered off. The filtrate was evaporated in vacuum. The crystalline precipitate of **6** was filtered off and recrystallized from acetone to give 2.9 g (76%).

4-Diethoxyphosphoryl-5-hydroxy-4-phenyl-3,4,5,6-tetrahydrofurazano[3,4-*b*]piperazine Hydrochloride (7). A solution of **5a** (3.9 g, 0.01 mol) in toluene (20 ml) was heated at reflux for 8 h. The solvent was distilled off and 6 ml 1:1 ether–hexane was added to the residue. The crystalline precipitate of **7** was filtered off, washed with ether, and dried to give 2.7 g (69%).

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