Hydrogen bonds and the structure of perchlorates of phosphorylated diazacycloalkanes

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Mono- and diperchlorates of phosphorylated diazacycloalkanes (PDAC), *viz.* 1,5-bis(2-diphenylphosphorylethyl)-1,5-diazacyclooctanes (**1a**, **1b**), 1,4-bis(2-diphenylphosphorylethyl)-1,4-piperazine (**2a**), and 1-methyl-4-(2-diphenylphosphorylethyl)-1,4-piperazines (**3a**, **3b**), were prepared. The formation of inter- and intramolecular hydrogen bonds in PDAC perchlorates and some model compounds in the solid state and in solution was investigated by IR spectroscopy. The dependence between the effect of the hydrogen bond formation and association of the ions in solution was analyzed. Conformational analysis of the cations of PDAC was carried out.

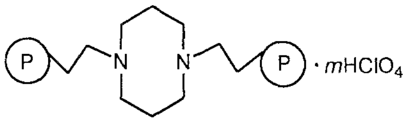
Key words: phosphorylated diazacycloalkanes, perchlorates, structure of protonation products, H-bonds, IR spectroscopy, conformational analysis.

Phosphorylated diazacycloalkanes (PDAC), cyclopendant complexing agents with diphenylphosphoryl groups in the pendants, have several basicity sites (N and P=O), which may be involved in protonation. In the study of the acid-base properties of PDAC (see Ref. 1), assumptions concerning the protonation sites and the order in which they are protonated have been made on the basis of the analysis of the p*K* values. The increase in the basicity of some PDAC in the aprotic solvent compared with their nonphosphorylated analogs was explained by additional stabilization of the corresponding cations owing to intramolecular hydrogen bonds (IMHB).

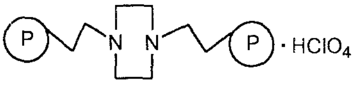
To confirm these assumptions we synthesized in the present work perchlorates of the corresponding PDAC of 1 : 1 and 1 : 2 composition and studied the IR spectra of their crystalline samples (KBr pellets) and solutions in acetonitrile (an aprotic dipolar solvent similar in properties to nitromethane in which the acid-base properties of PDAC (see Ref. 1) have been studied) and also the IR spectra of some model compounds.

In the IR spectra of the starting PDAC (**1—3**), the CH_2 group exhibits two characteristic bands,[2] ν_{as} 2948±18 cm^{-1} and ν_s 2875±10 cm^{-1}, and the N—CH_2 group is responsible for the band at 2810 cm^{-1}, the intensity of which increases when the CH_3 group (compound **3**) is replaced by the $CH_2CH_2P(O)Ph_2$ group (compound **2**), which confirms the assignment made. The $Ph_2P(O)$ group accounts for a number of characteristic bands of the phenyl rings:[3] 1595, 1490, 1440, and 1125 cm^{-1} in the spectrum; the bands corresponding to the P=O stretching vibrations lie in the range of 1180—1185 cm^{-1}.

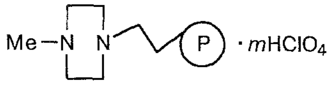
Protonation of PDAC occurs at the nitrogen atom in all cases. This results in the appearance of an intense band at 1100 cm^{-1} associated with the ClO_4^- anion and a broad band between 2600 and 3300 cm^{-1} correspond-



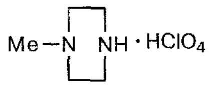
1a (*m* = 1)
1b (*m* = 2)



2a



3a (*m* = 1)
3b (*m* = 2)



4a

5a

= $Ph_2P(O)$

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Table 1. The data of the IR spectra of PDAC perchlorates and some their analogs (ν/ cm^{-1})

Salt	KBr pellets		MeCN solution		Amine	KBr pellets	MeCN solution
	N$^+$—H	P=O	N$^+$—H	P=O		P=O	P=O
1a	2800—2400	1185 1163	2700, 3020, 3035^a	1185, 1163	**1**	1180	1180^a
1b	2900—2400	1165	3015	1165	**1**	1180	1180
2a	2800—2450	1180, 1160	3035^a	1180, 1165^a	**2**	1180	1180^a
3a^b	3100	1185	3015, 3440	1190, 1175	**3**	1185	1195 1180
3b^c	2900—2400	1160sh	3015	1165	**3**	1185	1195, 1180
4^d	2400—3000	—	2400—3000	—	**4**	—	—
5a	2700	1160	2700, 3085	1195, 1180	**5**	1195	1195

[a] A solution in chloroform.

[b] The band of the ClO_4^- anion in the crystalline sample is split into two components: 1100 and 1060 cm^{-1}.

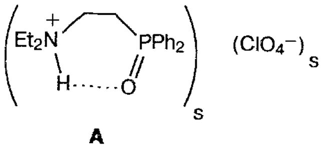
[c] The band of the ClO_4^- anion in an acetonitrile solution is split into two components: 1100 and 1050 cm^{-1}.

[d] The band of the ClO_4^- anion in the crystalline sample is broadened and split into two components: 1100 and 1150 cm^{-1}; in the solution, it is broadened: 1100 cm^{-1}.

ing to the N$^+$—H groups in the spectra of the corresponding salts. The formation of the H-bonds of the N$^+$—H...O=P type is manifested as the displacement of the bands associated with the N$^+$—H and P=O groups, and the presence of type N$^+$—H...$OClO_3^-$ contact ion pairs is exhibited as splitting of the band at 1100 cm^{-1} corresponding to the perchlorate anion.

Diethyl(2-diphenylphosphorylethyl)ammonium perchlorate (5a). The spectrum of salt **5a** contains no band at 2810 cm^{-1} corresponding to N—CH_2, which is recorded in the spectrum of the starting base **5**; it exhibits instead a broad band of N$^+$—H centered at 2700 cm^{-1}, which is typical of ammonium salts.[2] The band corresponding to the P=O groups shifts to lower frequencies by 35 cm^{-1} (Table 1). These data imply that N$^+$—H...O=P intermolecular hydrogen bonds are formed in the crystal.

In the spectrum of a solution of salt **5a** in acetonitrile, the band at 2700 cm^{-1} associated with vibrations of the N$^+$—H groups involved in the intermolecular H-bonds is partly retained, and an additional band at 3085 cm^{-1}, which may be assigned to vibrations of the N$^+$—H groups involved in the intramolecular H-bond (IMHB), appear.



A

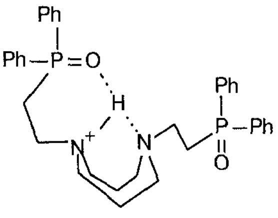
s means solvated by molecules of the solvent

The P=O vibrations in the spectrum of the solution of salt **5a** are exhibited as three bands: 1195, 1180, and 1160 cm^{-1}. The 1195 cm^{-1} band corresponds to free P=O groups (see Table 1), the 1160 cm^{-1} band is recorded as well in the spectrum of a solid sample and relates to the P=O groups involved in the intermolecular H-bond. This is also indicated by the fact that the band at 2700 cm^{-1} is retained in the spectrum of the solution. Hence, the band at 1180 cm^{-1} can be assigned to vibrations of the P=O groups involved in the intramolecular H-bond (structure **A**). When the solution is diluted twofold, all three of the bands corresponding to P=O vibrations remain in the spectrum, but some redistribution of their intensities occurs: the intensity of the 1195 cm^{-1} band increases somewhat and that of the 1160 cm^{-1} band decreases. Thus, an equilibrium between the free cations, the cations containing the IMHB (structure **A**), and ion associates in which the cations are linked by intermolecular H-bonds exists in a solution of the perchlorate **5a**. In the range of concentrations studied, the perchlorate anion is not associated with the cations, as indicated by the fact that its narrow band at 1100 cm^{-1} does not change when the solution is diluted or concentrated.

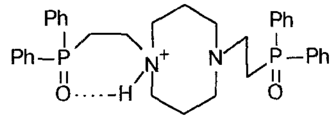
1,5-Bis(2-diphenylphosphorylethyl)-1-azonia-5-azacyclooctane perchlorate (1a). The N$^+$—H vibrations are manifested in the spectrum of solid monoprotonated salt **1a** as a number of broad bands in the 2400—2800 cm^{-1} region, *viz.* 2850, 2700, and 2550 cm^{-1}. The bands at 1185 and 1163 cm^{-1} correspond to vibrations of the free P=O groups and those involved in the intermolecular H-bonds of the N$^+$—H...O=P type, respectively (Table 1).

When the salt is dissolved in chloroform or acetonitrile, the absorption in the 2400—2800 cm^{-1} region is partially retained (a broad band at ~2700 cm^{-1}), and an additional band at 3020 cm^{-1}, which should be assigned to the N^+—H groups involved in the IMHB, appears. Both P=O bands, 1185 and 1170 cm^{-1}, do not shift following dilution of the solution, which allows the former band to be assigned to vibrations of the free P=O groups, and the latter band can be assigned to vibrations of the P=O groups involved in the IMHB. The intense band at 1100 cm^{-1} associated with the ClO_4^- anion does not change upon dilution as well. Thus, in solutions of the concentrations studied, perchlorate **1a** exists as the nonassociated anion and the cation containing an IMHB.

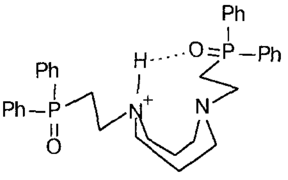
The problem of the structure of the cation of monoprotonated salt **1a** has been discussed in detail in the previous paper.[1] Based on the data of conformational analysis, three possible structures for this cation, **B**, C, and **D**, were considered.



B



C



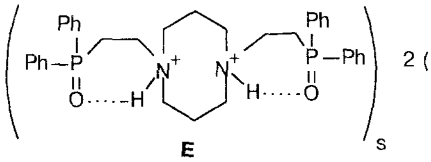
D

The unusually high basicity of compound **1** at the first step of protonation in nitromethane compared with other PDAC, whose cations are stabilized by the N^+—H...O=P IMHB completing a six-membered chelate-type ring (type **A** and **C** structures), was explained by a more efficient stabilization of cation **1a** due to a three-center H-bond (structure **B**). Unfortunately, the data of IR spectra do not allow one to make a justified choice between structures **B**, **C**, and **D**. The ^{31}P NMR spectra of solutions of salts **1a** and **2a** also provide no information due to rapid proton exchange processes. Notice that cations **B**, **C**, and **D** can coexist in solution in a certain equilibrium.

1,5-Bis(2-diphenylphosphorylethyl)-1,5-diazoniacyclooctane diperchlorate (1b). In the spectrum of solid **1b**, the vibrations of the N^+—H groups are manifested by a broad band between 2400 and 2900 cm^{-1}, having maxima at 2720 and 2620 cm^{-1}. Unlike the spectrum of the monoprotonated salt **1a**, this spectrum exhibits one P=O band at 1165 cm^{-1}, while the band corresponding to the free P=O groups is missing, and the band at 1100 cm^{-1} due to the perchlorate anion has an increased intensity. This indicates that intermolecular H-bonds of the N^+—H...O=P type involving both P=O groups are formed in the crystal.

In the spectrum of an acetonitrile solution of salt **1b**, the N^+—H and P=O bands are changed compared with those in the spectrum of the solid salts. This reflects destruction of the intermolecular H-bonds and formation of the intramolecular H-bonds in the cation. The N^+—H band is recorded at 3015 cm^{-1} and the band for P=O vibrations is at 1165 cm^{-1}. Their positions do not change upon dilution, and therefore they can be assigned to vibrations of the groups involved in the intramolecular H-bonds of the N^+—H...O=P type with the closure of the six-membered chelate ring.

These data together with the results of the conformational analysis and the study of basicity[1] allow one to assume that salt **1b** forms solvent-separated ion pairs in solution, the cations of which are stabilized by two IMHB (structure **E**):



E

It should be noted that salt **1b** turned out to be unstable and with time it is converted into salt **1a**. An absorption band at 1185 cm^{-1} associated with the free P=O groups appears in the spectrum of solid **1b** within approximately a month, and then, in the course of time, the spectrum becomes identical to that of the monoprotonated salt **1a**. This conversion is also confirmed by the fact that the IR spectra of solutions of the salts and the data of elemental analysis coincide for both salts.

1,4-Bis(2-diphenylphosphorylethyl)-1-azonia-4-azacyclohexane perchlorate (2a). The spectrum of solid **2a** is similar to that of perchlorate **1a**: it contains two P=O bands at 1180 and 1160 cm^{-1} and a broad N^+—H absorption band in the range of 2450—2800 cm^{-1}, which is typical of the case when N^+—H...O=P intermolecular bonds are formed.

When salt **2a** is dissolved in chloroform, the intermolecular H-bonds are destroyed following dilution, and the corresponding IMHB are formed instead. These are manifested as an N^+—H band at 3035 cm^{-1} and a P=O band at 1165 cm^{-1}; the band corresponding to the free P=O groups (1180 cm^{-1}) also remains in the spectrum. It is likely that in dilute solutions, salt **2a** exists as solvent-separated ion pairs (or solvated ions) in which the cations are stabilized by the IMHB. The probable structures for the cation were analyzed in terms of conformational analysis, in a way similar to what had been done previously for the cations of other PDAC.[1]

Calculations by the method of molecular mechanics (PC Model, Serena Software, Bloomington, IN) showed that a stable conformation in which the piperazine ring exists in a chair form and the N^+...O distance is 3.27 Å is possible for cation **2a** (Fig. 1, *a*). The structure of the

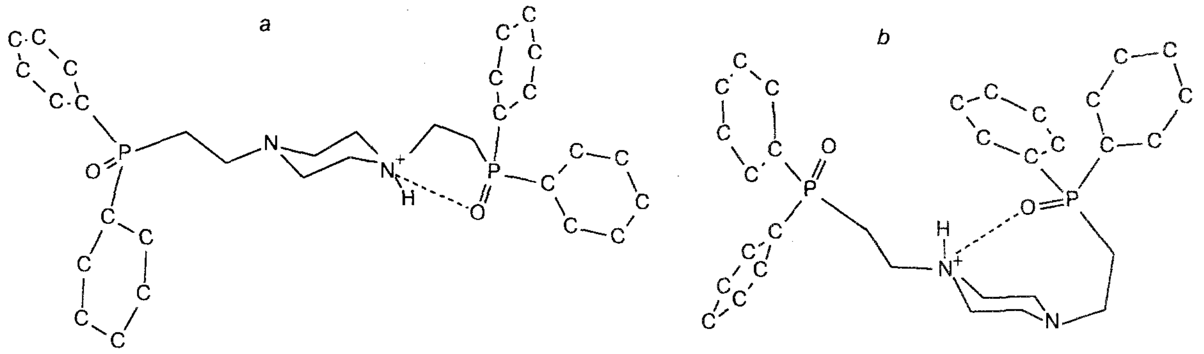
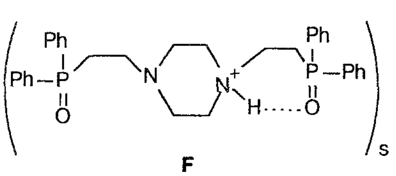


Fig. 1. The conformation of the cation of salt **2** in the region of the global (*a*) or local (*b*) minimum (the distances between the N^+ and O atoms marked with dashed lines are 3.27 Å).

cation was optimized at a specified N^+...O distance of 2.98 Å (which is the typical length of this type of H-bonds[4]) assuming that the IMHB links the proton of the N^+—H group with the oxygen atom of its "own" phosphoryl group. The strain energy for this conformation is as low as 0.1 kcal mol^{-1}. The conformer in which the IMHB involves the O atom of the other phosphoryl group (Fig. 1, *b*) is less stable (ΔE = 12.2 kcal mol^{-1}), and its strain energy calculated under similar conditions is also much greater, *viz*. 6.2 kcal mol^{-1}.

Conformations of cation **2a**, in which the piperazine ring exists in a twist-boat or twist-chair form are less stable than the previously considered conformation where the ring has a chair form (by 6.4 and 7.3 kcal mol^{-1}, respectively) similarly to the reported data on the conformations of the molecule of piperazine.[5] However, in these conformations of cation **2a**, the same relationship between the possibilities of the formation of IMHC holds.

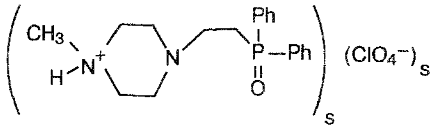
Thus, we believe that salt **2a** exists in solutions as solvent-separated ion pairs, the cations of which are stabilized by two IMHB (structure **F**):



F

1-Methyl-4-(2-diphenylphosphorylethyl)-1-azonia-4-azacyclohexane perchlorate (3a). In the spectrum of a solid sample of salt **3a**, compared with the spectrum of the starting base **3**, the band at 2790 cm^{-1} corresponding to $N—CH_3$ groups[6] disappears, while the $N—CH_2$ band remains. This indicates that the first step of protonation of **3** occurs at the nitrogen atom at the $N—CH_3$ group. The band of the P=O group does not change its position (1185 cm^{-1}) due to protonation. At the same time, the band associated with the ClO_4^- anion is split (1100 and 1060 cm^{-1}). That is, in this case, unlike examples considered above, the N^+—H group of the cation forms an H-bond in the crystal with an oxygen atom of the ClO_4^- anion, $N^+—H...OClO_3^-$, rather than with the oxygen atom of the phosphoryl group. This H-bond is responsible for the band of the N^+—H vibrations at 3100 cm^{-1} in the spectrum of salt **3a**.

The spectrum of a solution of **3a** in acetonitrile contains one band associated with the ClO_4^- anion (1115 cm^{-1}), the N^+—H band occurs at 3015 cm^{-1}, and in the region of P=O vibrations, two bands, at 1190 и 1175 cm^{-1}, appear. These spectral data imply that in solution, the ion pairs of the crystal dissociate, and the cations form intermolecular H-bonds of the N^+—H...O=P type. When the solution is diluted, the intensity of the 1175 cm^{-1} band corresponding to the bonded P=O groups decreases, while that of the 1190 cm^{-1} band attributed to the free P=O groups increases, which confirms that the H-bonds in the solution are intermolecular. Thus, in dilute solutions, salt **3a** probably exists as solvent-separated ion pairs or free ions, and the cation has structure **G**:

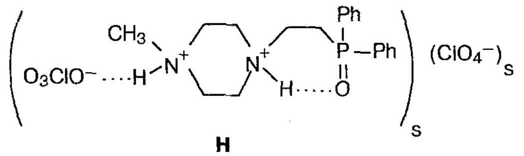


G

The data of conformational calculations and measurements of the basicity[1] also suggest that the formation of the IMHB between the hydrogen atom of the N^+—H group and the oxygen atom of the phosphoryl group attached to the other nitrogen atom of the piperazine ring in the cation of salt **3a** is impossible.

1-Methyl-4-(2-diphenylphosphorylethyl)-1,4-diazoniacyclohexane diperchlorate (3b). The addition of the second proton to compound **3** results in that in the spectrum of solid **3b**, a broadened band for the ClO_4^- anion appears at 1100 cm^{-1}, which indicates that the perchlorate anion participates in the H-bonds. In conformity with this, against the background of the broad band of the N^+—H groups, a band at ~3050 cm^{-1} is recorded that should be assigned to vibrations of the N^+—H groups involved in the H-bonds with the perchlorate anion: N^+—H...$OClO_3^-$. Vibrations of the P=O groups are manifested as a shoulder at ~1160 cm^{-1} on the broad band of perchlorate at 1100 cm^{-1}, which points to the fact that the phosphoryl groups participate in intermolecular H-bonds. Thus, two types of intermolecular hydrogen bonds exist in the diprotonated salt **3b** in the solid phase, *viz.* N^+—H...$OClO_3^-$ and N^+—H...O=P.

The H-bonds of the former type are retained in a solution of **3b** in acetonitrile. This reflects the existence of contact ion pairs in the solution and is manifested in the spectrum in that the ClO_4^- band is split into components at 1100 cm^{-1} and 1050 cm^{-1}. The intermolecular H-bonds of the latter type, N^+—H...O=P, are destroyed after dissolution of the sample, and, when the solution is diluted, similar intramolecular H-bonds are formed. They are responsible for bands at 3015 cm^{-1} (N^+—H) and at 1165 cm^{-1} (P=O) in the spectrum. In accordance with the data of conformational analysis,[1] we believe that in solutions in the range of concentrations studied, the diprotonated salt **3a** has the following structure (structure **H**):

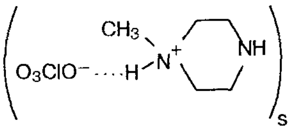


H

The fact that the hydrogen atom of the MeN^+—H group is bound to the perchlorate anion by an H-bond is also supported by the IR spectra of methylpiperazine perchlorate (**4a**).

1-Methyl-1-azonia-4-azacyclohexane perchlorate (4a). In the spectrum of solid salt **4a**, vibrations of the N^+—H groups are manifested by a broad band in the range 2400—3000 cm^{-1}, and the band corresponding to the perchlorate anion is split into two components, 1150 cm^{-1} and 1100 cm^{-1}. This indicates that intermolecular N^+—H...$OClO_3^-$ H-bonds are formed in the solid state.

In the spectrum of a solution of **4a** in acetonitrile, the broad absorption band of N^+—H at 2400—3000 cm^{-1} is retained, and the band of the perchlorate anion is no longer split but is still broadened. This means that the N^+—H...$OClO_3^-$ intermolecular H-bonds persist in the solution, in other words, that salt **4a** exists in acetonitrile solutions as contact ion pairs.



I

As has been shown previously,[1] the formation of the N^+—H...N IMHB in the cations with a piperazine ring is unfavorable.

In conclusion, it should be noted that the state of the salts of alkylamines with an N—H bond in aprotic solvents regarding the formation of H-bonds, solvation, and association has been investigated in detail previously.[7,8] The PDAC perchlorates under consideration represent a more complex and interesting example, due to the presence of phosphoryl groups that are able to form various H-bonds.

In fact, stabilization of a cation with an N^+—H bond in solvents, incapable of solvation with the formation of H-bonds, can be achieved by a number of ways. In dilute solutions, the cation is "solvated" by a molecule of the amine itself (the N^+—H...N intermolecular bond or BHB^+ complexes). In the case of diamines of an appropriate structure, the N^+—H...N IMHB completing a six- or seven-membered chelate ring is formed.[9] We suppose that this type of stabilization occurs in the monoprotonated cations of 1,5-diazacyclooctane or PDAC based on the same ring having two diphenylphosphorylmethyl pendants, where the IMHB of the N^+—H...O=P type with closure of the five-membered ring would be unfavorable.[1] In more concentrated solutions, salts of amines with N—H bonds exist as contact ion pairs (an H-bond with the anion). We observed this in the study of perchlorates **4a** and **3b**. In the case of salts of aminophosphoryl compounds, the presence of the phosphoryl group, which is highly prone to form H-bonds results in the competition between the above-listed ways of the stabilization of the cation and the possibility of stabilization owing to intra- and intermo-

Table 2. The data of elemental analysis of the salts and the solvents in which the reactions of the preparation of PDAC perchlorates and some model amines were carried out

Salt	Solvent	Found / Calculated (%) C	H	N	Molecular formula
1a*	$MeNO_2$	60.8 60.7	6.2 6.2	4.2 4.2	$C_{34}H_{40}N_2O_2P_2$ $HClO_4$
1b	MeCN	53.1 52.9	5.8 5.4	3.9 3.6	$C_{34}H_{40}N_{22}O_2P_2$ $2HClO_4$
2a**	MeOH	60.0 59.8	5.9 5.8	4.6 4.4	$C_{32}H_{36}N_2O_2P_2$ $HClO_4$
3a	$MeNO_2$	53.4 53.2	6.2 6.1	6.5 6.5	$C_{19}H_{25}N_2OP$ $HClO_4$
3b	MeCN; $MeNO_2$	43.4 43.1	5.6 5.1	5.9 5.3	$C_{19}H_{25}N_2OP$ $2HClO_4$
4a	MeCN	30.2 29.9	6.7 6.5	14.0 14.0	$C_5H_{12}N_2$ $HClO_4$
5a	MeCN	53.6 53.8	6.4 6.2	3.5 3.5	$C_{18}H_{24}NOP$ $HClO_4$

* The ^{31}P {H} NMR (MeCN), δ: 33.2.
**The ^{31}P {H} NMR ($CHCl_3$), δ: 31.0.

lecular H-bonds of the N^+—H...O=P type. Consequently, in the case of "self-solvation" of the cation owing to IMHB, the salt exists in the solution as solvent-separated ion pairs (for example, compounds **1a**, **1b**, **2a**, **3b**). When the IMHB are weaker, an equilibrium between cations with the IMHB, free cations, and three-membered ion units (intermolecular H-bonds of the same type) exists in solutions in the same region of concentrations (salt **5a**). If the formation of the IMHB is unfavorable (salt **3a**), the former type of cations is excluded from this equilibrium.

Experimental

The ^{31}P {H} NMR spectra were recorded on a Bruker-WP-200-SY spectrometer (using 85% H_3PO_4 as the external standard). The IR spectra were run on a UR-20 instrument (KBr pellets or 0.2—0.05 mol L^{-1} solutions in chloroform or acetonitrile, d = 0.12 and 0.22 (CaF_2)).

Dried and freshly distilled solvents were used.

The starting PDAC **1—3** and amines **4** and **5** were prepared and purified in a way similar to what had been done in the previous work.[1] Perchloric acid dihydrate was prepared by distillation of 57 % acid of the "chemically pure" grade.

Perchlorates and diperchlorates of the amines and diamines studied were prepared by the reactions of the appropriate amounts of corresponding bases with $HClO_4$ dihydrate in acetonitrile or another solvent. The solvent was slowly evaporated at 20 °C, and the precipitated crystals were separated, washed with ether or recrystallized from acetonitrile or nitromethane, and dried *in vacuo* at 20 °C over P_2O_5. The data of elemental analysis and the solvents used for the synthesis are listed in Table 2.

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References

1. S. V. Matveev, A. G. Matveeva, E. I. Matrosov, B. K. Shcherbakov, Yu. M. Polikarpov, and M. I. Kabachnik, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 2007 [*Russ. Chem. Bull.*, 1994, **43**, 1895 (Engl. Transl.)].
2. L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Methuen & Co. Ltd., Bungay, London; John Wiley & Sons, Inc., New York.
3. G. V. Bodrin, A. G. Matveeva, M. I. Terekhova, E. I. Matrosov, E. S. Petrov, Yu. M. Polikarpov, and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 912 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 810 (Engl. Transl.)].
4. G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond*, San Francisco — London, 1960.
5. E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, *Conformational Analysis*, J. Wiley & Sons, Inc., NewYork/ London/ Sydney, 1965.
6. E. I. Matrosov, V. A. Gilyarov, V. Yu. Kovtun, and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1971, 1162 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1971, **20**, 1076 (Engl. Transl.)].
7. I. M. Kolthoff, *Pure and Appl.Chem.*, 1971, **25**, 305.
8. P. L. Huyskens, *Pure and Appl.Chem.*, 1987, **59**, 1103.
9. J. F. Coetzee and G. R. Padmanabhan, *J. Am. Chem. Soc.*, 1965, **87**, 5005.
10. Yu. V. Karyakin and N. I. Angelov, *Chistye khimicheskie veshchestva* [*Pure Chemical Compounds*], Khimiya, Moscow — Leningrad, 1974, 198 (in Russian).

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