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Academician M. I. Kabachnik, V. A. Gilyarov, M. M. Yusupov

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Abstract

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On the Study of Conjugation in Systems with a Tetrahedral Phosphorus Atom. Phosphaazacyanines

Consideration of conjugation in noncoplanar systems with a tetrahedral phosphorus atom has shown that in many cases interactions of this kind belong to the weak (low-frequency) type ([1]); they do not appreciably affect the optical properties of substances, but are manifested quite clearly in chemical properties ([2]) and can be detected by radio-spectroscopic methods ([3]). The chemical indications of weak conjugation in noncoplanar systems are of the same character as in coplanar systems, but are less strongly expressed. In other cases, however, organophosphorus conjugated systems behave quite like coplanar purely organic ones, and conjugation in them is clearly detected both by optical and by chemical criteria ([4]).

Among systems of the first type there apparently belongs the triad

$$-\mathrm{N}=\overset{|}{\mathrm{P}}-\mathrm{N}=$$

in polymeric phosphoronitriles—cyclic or linear, for example in tri- and tetraphosphonitrile chlorides. A quantum-chemical consideration of these molecules has not given an unambiguous result. According to Craig and co-workers ([5]), they are benzene-like, i.e., possess complete ring conjugation. According to Dewar et al. ([6]), on the contrary, the molecular $d_\pi - p_\pi$ π-orbitals include only the triads $\mathrm{P}=\mathrm{N}-\mathrm{P}$, and thus conjugation is interrupted at each phosphorus atom. According to structural data, the conformation of these molecules is not planar but only slightly bent, which is consistent with both views. According to spectral data (UV), conjugation is absent ([7]); however, the ring groupings are sufficiently stable and are retained in various substitution reactions. The totality of all the data makes it possible to assign phosphonitriles to systems with weak conjugation.

To the second type undoubtedly belong phosphamidine systems

$$\begin{array}{lll} \mathrm{RO}\backslash & \mathrm{N}-\mathrm{R} & \\ \quad \mathrm{P}= & & \rightleftharpoons \\ \mathrm{RO}/ & \mathrm{NH}-\mathrm{R}' & \end{array} \qquad \begin{array}{ll} \mathrm{RO}\backslash & \mathrm{NH}-\mathrm{R} \\ \quad \mathrm{P} & \\ \mathrm{RO}/ & \mathrm{N}-\mathrm{R}' \end{array}$$

These are typical tautomeric and doubly reacting substances ([8]), and their behavior practically does not differ from that of ordinary conjugated triad systems: amidine (aminopyridine), lactim–lactam, and others. Hence followed the conclusion concerning the mesomeric structure of the anion of phosphamidines:

$$\begin{array}{lll} \mathrm{RO}\backslash & \mathrm{N-R} & \\ \mathrm{P}= & & \longleftrightarrow \\ \mathrm{RO}/ & \bar{\mathrm{N}}-\mathrm{R}' & \end{array} \qquad \begin{array}{ll} \mathrm{RO}\backslash & \bar{\mathrm{N}}-\mathrm{R} \\ \mathrm{P} & \\ \mathrm{RO}/ & \mathrm{N}-\mathrm{R}' \end{array}$$

similar to the mesomeric structure of anions of organophosphorus thionthiols and amides. The spectra of salts, for example of monothio acids of phosphorus, unquestionably testify to the mesomeric structure of the anions.

Thus, one and the same group of atoms in polyphosphonitriles and in phosphamidine anions behaves either as capable only of weak conjugation, or as fully conjugated. The difference in the structure of NPN groups in substances of both types cannot be reduced to a difference in symmetry,

since, as in phosphamidine anions, both nitrogen atoms bonded to phosphorus are equivalent. A difference may be seen in that the first system is neutral, whereas the second carries a negative charge. In this connection, it seemed important to obtain and study the properties of systems of the same type but carrying a positive charge. Such systems should include the phosphorus analogs of azacyanines.

$$\text{A C–N=P(OR)}_2\text{–N=C B} \rightleftharpoons \text{A C=N–P(OR)}_2\text{=N–C B}$$

If these systems belong to the class of conjugated systems, then the ionic charge should be distributed between the terminal nitrogen atoms, and the single and multiple bonds should be equalized to some extent*; the absorption region for such a system should be shifted toward longer wavelengths, into the visible part of the spectrum. If, however, the phosphorus atom is a barrier interrupting conjugation, then in the limiting case two isomers should exist: in one, the ammonium nitrogen is in ring A, and in the other–in ring B. In the case of weak (low-frequency) interactions, the formation of a single substance should be expected, but spectrally the conjugation may not be observed.

The synthesis of structures Ia, with the ammonium nitrogen in the benzothiazole ring, and Ib, with the ammonium nitrogen in the pyridine ring, was carried out according to the scheme:

$$\text{(II)} + \text{(III)} \longrightarrow \text{(Ia)}$$

$$\text{(V)} + \text{(IV)} \longrightarrow \text{(Ib)}$$

Phosphaazacyanine (Ia) was obtained by the reaction of O,O-diethyl-(1-ethyl-2-pyridonimido)phosphite (II) with 2-azido-3-ethylbenzothiazolium fluoroborate (III) [10]. Phosphaazacyanine (Ib) was synthesized by the interaction of O,O-diethyl-(3-ethyl-2-benzothiazolonimido)phosphite (IV) with 2-azido-1-ethylpyridinium fluoroborate (V) [10]. The α-pyridonimidophosphite (II) required for the synthesis of phosphaazacyanine (Ia) was obtained by the following transformations:

$$\text{2-aminopyridine} \xrightarrow{C_2H_5J} \text{(VI)} \xrightarrow{KOH} \text{(VII)} \xrightarrow{(C_2H_5O)_2PN(C_2H_5)_2} \text{(II)}$$

* The degree of equalization, of course, depends on the nature of rings A and B. When $A = B$, the charge is distributed equally. On the influence of the basicity of rings A and B on the charge distribution in cyanine dyes, see [9].

Iodoethylate of α-aminopyridine (VI), obtained under the conditions described by Chichibabin [11] for iodomethylate of α-aminopyridine, is converted on heating under the action of alkali into 1-ethyl-2-pyridonimine (VII); from the latter, by reamidation [12] with O,O-diethyl-N-diethylamidophosphite, substance (II) was synthesized. It possesses all the properties of trivalent phosphorus compounds—it adds sulfur with formation of O,O-diethyl-(1-ethyl-2-pyridonimido)-thiophosphate (VIII); it reacts with phenyl azide with evolution of nitrogen and formation of O,O-diethyl-N-(1-ethyl-2-pyridonimido)-N′-phenylimidophosphate (IX), which with hydrogen chloride is converted into O-ethyl-N-(1-ethyl-2-pyridonimido)-N′-phenylamidophosphate (X). On treatment of substance (II) with an equimolar amount of hydrogen chloride, 1-ethyl-2-pyridonimine hydrochloride was isolated, which confirms the presence in (II) of an unchanged pyridonimine ring.

$$\text{(II)} \xrightarrow{C_6H_5N_3} \text{(IX)} \xrightarrow{HCl} \text{(X)},$$

$$\text{(II)} \xrightarrow{S} \text{(VIII)},$$

$$\text{(II)} \xrightarrow{HCl} \text{1-ethyl-2-pyridonimine} \cdot \text{HCl}.$$

O,O-Diethyl-(3-ethyl-2-benzothiazolonimido)-phosphite (IV), required for the synthesis of phosphaazacyanine (Ib), was obtained analogously to substance (II) by reaction of O,O-diethyl-N-diethylamidophosphite with 3-ethyl-2-benzothiazolonimine [13].

When the reaction of the pyridine imidophosphite (II) with benzothiazolyl azide (III) was carried out in chloroform at room temperature, there was formed—

Table 1

No.	Yield, %	M.p., °C	Empirical formula	C, % found	C, % calculated	H, % found	H, % calculated	P, % found	P, % calculated	F, % found	F, % calculated	N, % found	N, % calculated
Ia	65[1]	101–102	$C_{20}H_{28}N_4F_4O_2SBP$	47.4	47.6	5.4	5.6	–	6.1	15.2	15.0	10.9	11.1
Ib	48	101–102	$C_{20}H_{28}N_4F_4O_2SBP$	47.3	47.6	5.5	5.4	5.8	6.1	15.4		11.1	11.2
II[2]	61.6	–	$C_{11}H_{19}N_2PO_2$	54.2	54.1	7.9	8.0	12.9	12.8	–	–	–	–
IV[3]	49	–	$C_{13}H_{19}N_2PO_3$	53.3	53.8	6.4	6.6	10.1	10.7	–	–	–	–
VI	41.3	144–145.5	$C_7H_{11}N_3$	–	–	–	–	–	–	–	–	11.5	11.2
VII[4]	93	–	$C_7H_{10}N_3$	–	–	–	–	–	–	–	–	22.9	22.9
VII·HCl[5]	90	170	$C_7H_{11}N_3Cl$	53.2	53.3	7.2	7.0	–	–	–	–	–	–
VIII	85	63–64	$C_{11}H_{18}N_2PO_2$	54.8	54.9	7.1	7.0	11.1	11.3	–	–	–	–
IX	83	68.5–70	$C_{17}H_{24}N_3PO_2$	61.5	61.6	7.6	7.3	9.1	9.3	–	–	–	–
X	47	170–171	$C_{15}H_{20}N_3PO_2$	58.9	59.0	6.6	6.6	10.2	10.1	–	–	–	–
XI	70	127–128	$C_{20}H_{28}N_4F_4O_2SBP$	47.4	47.6	5.4	5.3	6.1	5.8	14.4	14.2	15.8	15.7
XII	68	98–99	$C_{15}H_{24}N_2F_4O_3BP$	45.6	45.4	5.6	7.1	7.3	7.2	18.0	17.7	–	–

[1] Calculated for triazene (XI).
[2] B.p. 112–113°/0.1 mm; n_D^{20} 1.5552; d_4^{20} 1.0841.
[3] B.p. 129–130°/0.04 mm; n_D^{20} 1.5941; d_4^{20} 1.1662.
[4] B.p. 88–89°/7–8 mm; n_D^{20} 1.5840; d_4^{20} 1.0404.
[5] Found, %: Cl 22.8, 22.8. Calculated, %: Cl 22.4.

···triazene (XI) of yellow color, which on heating in chlorobenzene at 130–140° decomposes with evolution of nitrogen and formation of phosphazacyanine

$$\left[\text{ 1-ethylpyridylidene} = \text{N} - \text{P}(OC_2H_5)_2 = \text{N} - \text{N} = \text{N} - \text{3-ethylbenzothiazolium }\right] \text{BF}_4^- \quad \text{(XI)},$$

$$[(C_2H_5O)_3\text{P} = \text{N} - \text{3-ethylbenzothiazolium}]\,\text{BF}_4^- \quad \text{(XII)}$$

(Ia)—a colorless crystalline substance. Azide (III) with triethyl phosphite forms crystalline O,O,O-triethyl-N-(3-ethylbenzothiazolinyl)-imidophosphate (XII).

The reaction of benzothiazole imidophosphite (IV) with pyridine azide (V) was carried out over several days at 5–8° (the corresponding triazene could not be

isolated). On further heating (80-90°), a colorless phosphazacyanine (Ib) was obtained with the same melting point as preparation (Ia) (in a simple and mixed sample). Their UV spectra are also identical. Thus, the phosphazacyanine preparations (Ia) and (Ib) are one and the same substance, in the cation of which the positive charge is distributed over the terminal nitrogen atoms.

At the same time, the substance is colorless, and the absorption curve in the ultraviolet can be satisfactorily represented as the result of superposition of the absorption curves of substances (II) and (XII), i.e., in spectral properties the parts of the phosphazacyanine molecule with amino and ammonium nitrogen atoms are as if independent. The totality of the properties of phosphazacyanine Ia Ib indicates the presence of weak (low-frequency) conjugation*. The constants and yields of the substances are given in Table 1.

Institute of Organoelement Compounds
Academy of Sciences of the USSR

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* Another possible explanation of the observed facts could be the assumption of phosphonium phosphorus in cation (Iv) with a fixed charge.

$$\left[\ \text{1-ethylpyridylidene} = \text{N} - \overset{+}{\text{P}}(OC_2H_5)_2 - \text{N} = \text{3-ethylbenzothiazoline}\ \right] \text{BF}_4^- \quad \text{(Iv)}$$

However, such a structure is incompatible with the stability of two alkoxy groups at a phosphorus atom bearing a positive charge. If, however, this stability is explained by delocalization of the phosphonium charge, then we return to the structures Ia Ib.

Note: Figure translations are in progress. See original paper for figures.