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Dedicated to the 90th Anniversary of Corresponding Member
of the Russian Academy of Sciences A.N. Pudovik

Synthesis and Properties of Phosphabetaine Structures: IV.[1] 3-(Triphenylphosphonio)propanoate in Reactions with Dipolar Electrophilic Reagents

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Abstract—Reactions of 3-(triphenylphosphonio)propanoate with heterocumulenes, such as phenyl isocyanate and dicyclohexylcarbodiimide, we studied under the assumption that they proceed by nucleophilic addition and 1,4-dipolar cycloaddition schemes. Quantum-chemical calculations show that the σ^5-phosphorane cycloadduct of the betaine with isocyanate is thermodynamically preferred over its isomeric zwitter-ionic adduct. However, the experimental evidence suggests that the reaction with phenyl isocyanate involves nucleophilic addition of the betaine to isocyanate followed by hydrolysis to firm finally a complex of the starting betaine with diphenylurea. The structure of the complex was established by X-ray diffraction analysis. The revealed above controversy is explained by a high protophilicity of betaine structures, which is also confirmed by the results of the reaction of the betaine with carbodiimide.

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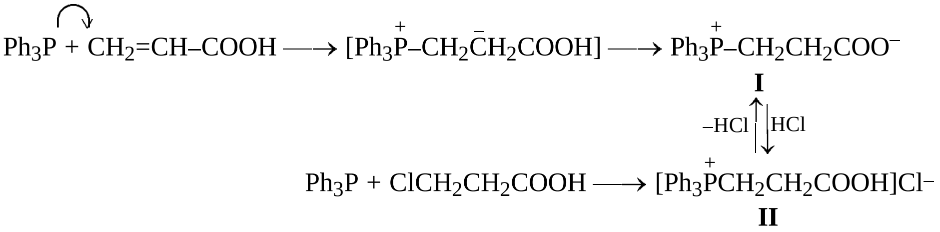
Previously we performed a systematic research into the synthesis, structure, and reactivity of phosphabetaine **I** obtained from triphenylphosphine and acrylic acid [2, 3]. We also found that quaternization of triphenylphosphine under the action of chloropropanoic acid gives rise to phosphonium salt **II** whose reversible dehydrochlorination, too, leads to phosphabetaine **I**.



$$\mathrm{Ph_3P + CH_2{=}CH{-}COOH \longrightarrow [Ph_3\overset{+}{P}{-}CH_2\overset{-}{C}H_2COOH] \longrightarrow Ph_3\overset{+}{P}{-}CH_2CH_2COO^-}\ \ \mathbf{I}$$

$$\mathbf{I}\ \underset{\mathrm{HCl}}{\overset{-\mathrm{HCl}}{\rightleftarrows}}\ \mathbf{II}$$

$$\mathrm{Ph_3P + ClCH_2CH_2COOH \longrightarrow [Ph_3\overset{+}{P}CH_2CH_2COOH]Cl^-}\ \ \mathbf{II}$$

Therewith, it was found that proton-donor reagents and solvents play an important role in stabilization of phosphabetaine structures. It is suggested that proton donors act to stabilize the separated charges in structures like **I**.

We also found that phosphabetaine **I** readily reacts with electrophilic reagents, in particular, it is alkylated with alkyl halides to form phosphonium salts **III**.

$$\mathbf{I} + \mathrm{RHlg} \longrightarrow \mathrm{[Ph_3\overset{+}{P}CH_2CH_2COOR]Hlg^-}\ \ \mathbf{III}$$

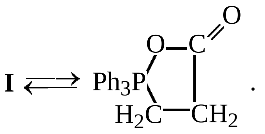
The structure of phosphabetaine **I** and its derived

For communication III, see [1].

phosphonium salts **III** was proved by elemental analysis, ^{1}H and ^{31}P NMR and IR spectroscopy, and X-ray diffraction analysis [2, 3].

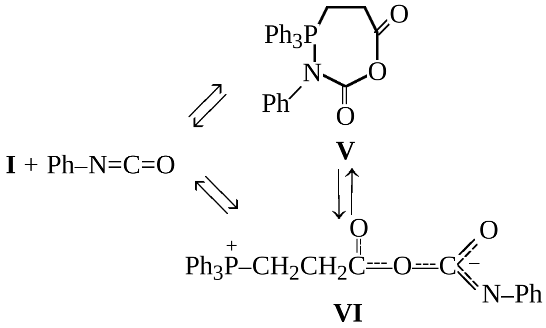
In the present work we continued a theoretical and an experimental study of phosphabetaine structures like **I** and their reaction products with electrophilic reagents. To extend the range of chemical reactions involving phosphabetaines, we reacted triphenylphosphoniopropanoate **I** with heterocumulenes, specifically phenyl isocyanate and dicyclohexylcarbodiimide.

It is well known that phosphabetaine structures formed as unstable intermediates in reactions σ^3-phosphorus derivatives with unsaturated reagents are most commonly stabilized via ring closure to form σ^5-phosphacyclanes (phosphoranes) [4]. We assumed that similar transformation of betaines **I** would result in the equilibrium betaine **I** $\rightleftarrows$ σ^5-oxaphospholane **IV**.



IV

However, in the ^{31}P NMR spectra of solutions of betaine **I** we failed to detect even traces of a phosphorane structure. We suggested that this result is associated with the instability of the strained oxaphospholane ring, and the potential phosphorane may appear if it contains a larger size ring. Such situation might be expected in reactions of betaines **I** with heterocumulenes, typical 1,3-dipolarophiles. For example, the reaction with phenyl isocyanate might be expected to involve [5 + 2]-cycloaddition to form azaphosphepane **V** or nucleophilic addition of betaine **I** by the isocyanate group to form zwitter-ionic intermediate **VI** and its subsequent closure into seven-membered cyclic phosphorane **V**.



Evidence for these suggestions was provided by the quantum-chemical calculations (Table 1) of the relative thermodynamic stability of phosphabetaines and their isomeric phosphoranes, performed by various semiempirical methods available in the HyperChem 5.0 package. All calculations showed that phosphorane structures are thermodynamically preferred over betaines (Table 1). However, experimentally, the reactions of phosphabetaine **I** with phenyl isocyanate and dicyclohexylcarbodiimide gave unexpected results. The reactions were performed at 70–90°C in a 1 : 1 chloroform–tiluene mixture; reaction completion was established by the disappearance of the N=C=O (2050 cm^{-1}) and N=C=N (2130 cm^{-1}) absorption bands in the IR spectra of the reaction mixtures.

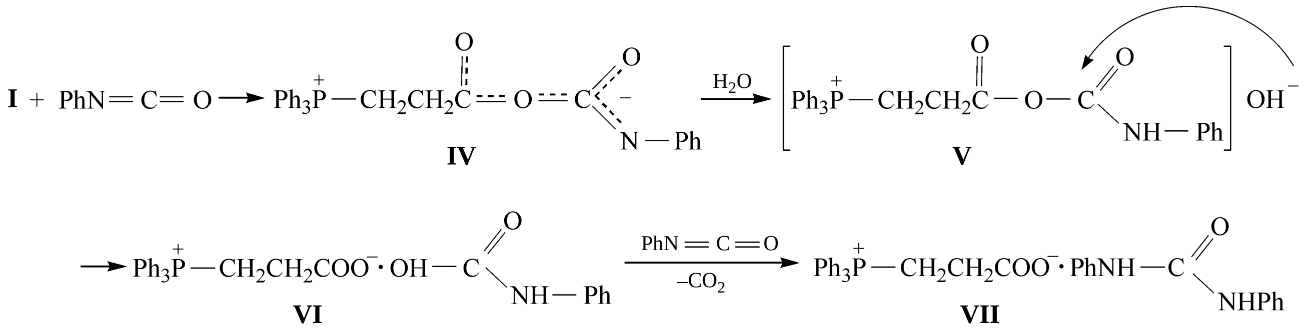
According to ^{1}H NMR, IR, and X-ray diffraction data, the vigorous reaction of phosphabetaine **I** with phenyl isocyanate results in exclusive formation of a crystalline product **VII**, rather than expected adducts **V** or **VI**. The product is a complex of betaine **I** with diphenylurea, in which the urea molecule plays the

Table 1. Formation energies (kcal mol^{-1}) of betaines **I** and **VI** and their isomeric phosphoranes **IV** and **V**, as given by quantum-chemical calculations

Method	**I** $\rightleftarrows$ **IV**		**VI** $\rightleftarrows$ **V**	
	I	**IV**	**IV**	**V**
PM3	–4739	–4763	–6362	–6369
AM1	–4714	–4733	–6335	–6339
CNDO	–13727	–13748	–18799	–18835
MINDO$_3$	–4627	–4656	–6251	–6269

role of a proton donor that stabilizes the betaine structure by hydrogen bonding, like water or other proton donors in starting betaine **I** [2].

We suggest that the reaction begins with nucleophilic attack of the carboxylate anion on the isocyanate carbon atom and occurs via intermediate zwitterionic adduct **IV**. Its hydration with a molecule of crystallization water, present in the crystal of betaine **I** [2, 3], gives rise to hydroxyphosphonium salt **V** that undergoes intramolecular nucleophilic addition with the hydroxide anion at the carbonyl center, yielding a complex of the starting betaine with *N*-phenylcarbamic acid (**VI**). The subsequent conversion involves one more phenyl isocyanate molecule: Addition of carbamic acid to the latter occurs with decarboxylation and provides diphenylurea that is hydrogen-bonded with betaine **I** in final complex **VII**.



To exclude an alternative reaction mechanism in which diphenylurea forms without direct involvement of betaine **I** in the well-known reaction of phenyl isocyanate with water [5] (a molecule of water, as we showed previously [2], is present in the betaine crystal), we performed a comparative kinetic study of the reactions of phenyl isocyanate with hydrated betaine **I** and with water in the same concentration but in the absence of the betaine. As follows from the kinetic results, the first reaction is no less than 50 times as fast as the second reaction under the same conditions. This fact provides conclusive evidence to show that the phosphabetaine is involved in the reaction. The molecular structure of compound **VII** is given in Fig. 1.

The asymmetric part of the crystal cell comprises one independent betaine molecule, one diphenylurea molecule, and two disordered molecules of unidentified solvent. Since the crystals were grown from a toluene solution, we can suggest that the cell contains two rotationally disordered toluene molecules. The coordination of the phosphorus atom is normal for a four-coordinate phosphorus, and its bond lengths and angles are consistent with those found in phosphonium salts (Tables 2–4) [6] and well fit the results for betaine **I** [3]. The bond lengths and bond angles in the benzene fragments of the complex fit statistical averages [7]. The conformation of the $P^1C^1C^2C^3$ fragment is transoid [torsion angle 166.0(3)°] and that of the $C^1C^2C^3O^2$ fragment is close to eclipsing [torsion angle –25.9(5)°], which, too, nicely fits the results for betaine **I**. Such conformation of the zwitterionic fragment can be associated with intra- and intermolecular interactions in the crystal, since phosphonium salts containing no classical hydrogen bond have a different conformation [6]. It should also be noted that the C–O bond lengths in betaine **VII** are equal to each other (Table 2), which is also observed in arsenobetaine and betaine **I** [8, 2].

It is interesting to note that such crystal structures are most commonly stabilized by proton-donor solvents [2, 8]. We failed to identify the solvent present in the crystal cell, but could reveal hydrogen bonds between the NH protons of diphenylurea and the carbonyl group (Fig. 2), as a result of which a closed hydrogen-bonded fragment is formed. The hydrogen bonds have the following parameters: $N^1–H^{22}\cdots O^{1'}$ [$1/2 - x$, $1/2 + y$, $1/2 - z$]: $N^1–H^{22}$ 0.96, $H^{22}\cdots O^{1'}$ 2.07, $N^1\cdots O^{1'}$ 2.954(5) Å, angle $N^1H^{22}O^{1'}$ 151°; $N^2–H^{29}\cdots O^{2'}$: $N^2–H^{29}$ 0.96, $H^{29}\cdots O^{2'}$ 1.75, $N^2\cdots O^{2'}$ 2.700(5) Å, angle $N^2H^{29}O^{2'}$ 167°.

The reaction of betaine **I** with dicyclohexylcarbodiimide occurs differently from the reaction with phenyl isocyanate and involves phosphabetaine P–C bond cleavage to form triphenylphosphine and salt **VIII**.

The same salt was obtained by independent synthesis from acrylic acid and carbodiimide; the reaction occurred almost immediately.

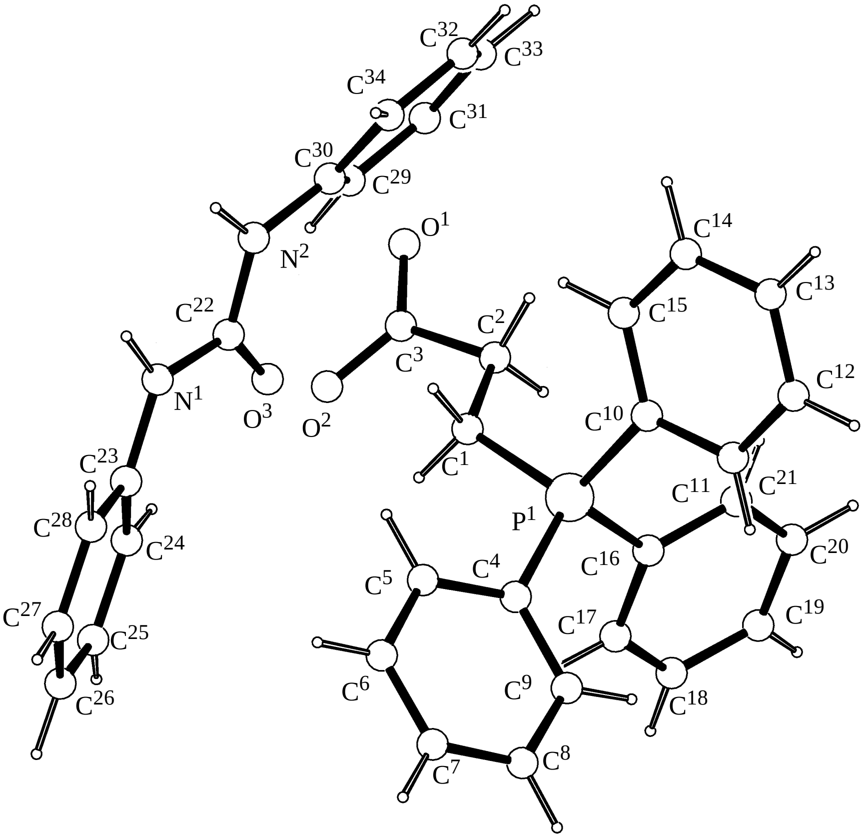


Fig. 1. Geometry of the complex of phosphabetaine **I** with diphenylurea. Disordered solvent molecules are not shown.

Table 2. Selected bond angles (ω, deg) in molecules **VII**

Angle	ω	Angle	ω	Angle	ω	Angle	ω
$C^1P^1C^4$	108.5(2)	$C^{22}N^1C^{23}$	126.0(3)	$C^{65}O^{62}C^{66}$	46.0(1)	$C^{16}C^{17}C^{18}$	120.1(5)
$C^1P^1C^{10}$	112.1(2)	$C^{22}N^1H^{22}$	116.6(3)	$C^{65}O^{62}C^{69a}$	31.0(7)	$C^{17}C^{18}C^{19}$	120.0(6)
$C^1P^1C^{16}$	107.7(2)	$C^{23}N^1H^{22}$	117.4(3)	$C^{66}O^{62}C^{69a}$	14.5(9)	$C^{26}C^{27}C^{28}$	119.6(5)
$C^4P^1C^{10}$	109.3(2)	$C^{22}N^2C^{29}$	125.0(4)	$P^1C^4C^9$	121.0(3)	$C^{23}C^{28}C^{27}$	121.4(5)
$C^4P^1C^{16}$	110.6(2)	$C^{22}N^2H^{29}$	117.3(4)	$C^5C^4C^9$	119.8(4)	$N^2C^{29}C^{30}$	122.7(4)
$C^{10}P^1C^{16}$	108.6(2)	$C^{29}N^2H^{29}$	117.6(4)	$C^4C^5C^6$	119.5(4)	$N^2C^{29}C^{34}$	118.4(4)
$C^{60}O^{61}C^{64}$	67.2(7)	$P^1C^1C^2$	117.6(3)	$C^5C^6C^7$	120.7(5)	$O^3C^{22}N^1$	122.7(4)
$C^{60}O^{61}C^{71}$	163.0(1)	$C^1C^2C^3$	111.4(3)	$C^6C^7C^8$	120.7(5)	$O^3C^{22}N^2$	123.5(4)
$C^{60}O^{61}C^{73}$	147.0(1)	$O^1C^3O^2$	125.4(4)	$C^7C^8C^9$	120.1(4)	$N^1C^{22}N^2$	113.8(4)
$C^{64}O^{61}C^{71}$	125.0(8)	$O^1C^3C^2$	118.3(4)	$C^4C^9C^8$	119.1(4)	$N^1C^{23}C^{24}$	123.8(4)
$C^{64}O^{61}C^{73}$	95.0(1)	$O^2C^3C^2$	116.2(4)	$P^1C^{10}C^{11}$	118.5(3)	$N^1C^{23}C^{28}$	118.3(4)
$C^{71}O^{61}C^{73}$	49.0(1)	$P^1C^4C^5$	119.2(3)	$P^1C^{10}C^{15}$	122.3(3)	$C^{24}C^{23}C^{28}$	117.9(4)
$C^{60}O^{62}C^{64}$	62.6(8)	$C^{11}C^{12}C^{13}$	120.8(5)	$C^{11}C^{10}C^{15}$	119.1(4)	$C^{23}C^{24}C^{25}$	119.7(5)
$C^{60}O^{62}C^{65}$	150.0(1)	$C^{12}C^{13}C^{14}$	119.9(5)	$C^{10}C^{11}C^{12}$	119.3(4)	$C^{30}C^{29}C^{34}$	118.9(4)
$C^{60}O^{62}C^{66}$	117.0(1)	$C^{13}C^{14}C^{15}$	121.1(5)	$C^{18}C^{19}C^{20}$	121.3(6)	$C^{29}C^{30}C^{31}$	119.1(5)
$C^{60}O^{62}C^{69a}$	129.0(1)	$C^{10}C^{15}C^{14}$	119.9(4)	$C^{19}C^{20}C^{21}$	119.8(6)	$C^{30}C^{31}C^{32}$	122.0(5)
$C^{64}O^{62}C^{65}$	89.1(9)	$P^1C^{16}C^{17}$	119.7(3)	$C^{16}C^{21}C^{20}$	119.4(5)	$C^{31}C^{32}C^{33}$	118.9(5)
$C^{64}O^{62}C^{66}$	60.0(1)	$P^1C^{16}C^{21}$	120.4(3)	$C^{24}C^{25}C^{26}$	121.8(6)	$C^{32}C^{33}C^{34}$	120.6(5)
$C^{64}O^{62}C^{69a}$	68.5(5)	$C^{17}C^{16}C^{21}$	119.5(4)	$C^{25}C^{26}C^{27}$	119.7(6)	$C^{29}C^{34}C^{33}$	120.4(5)

Table 3. Selected bond lengths (*d*, Å) in molecules **VII**

Bond	*d*	Bond	*d*
P^1–C^1	1.792(4)	C^1–C^2	1.506(6)
P^1–C^4	1.791(4)	C^2–C^3	1.519(6)
P^1–C^{10}	1.790(4)	C^4–C^5	1.380(6)
P^1–C^{16}	1.789(4)	C^4–C^9	1.382(6)
O^1–C^3	1.247(5)	C^5–C^6	1.375(7)
O^2–C^3	1.252(5)	C^6–C^7	1.356(7)
O^3–C^{22}	1.224(5)	C^7–C^8	1.349(7)
N^1–C^{22}	1.364(5)	C^8–C^9	1.398(7)
N^1–C^{23}	1.394(5)	C^{10}–C^{11}	1.404(6)
N^1–H^{22}	0.965(3)	C^{10}–C^{15}	1.388(6)
N^2–C^{22}	1.357(6)	C^{11}–C^{12}	1.385(7)
N^2–C^{29}	1.395(5)	C^{12}–C^{13}	1.365(8)
N^2–H^{29}	0.962(3)	C^{26}–C^{27}	1.380(1)
C^{13}–C^{14}	1.370(8)	C^{27}–C^{28}	1.376(8)
C^{14}–C^{15}	1.372(7)	C^{29}–C^{30}	1.401(7)
C^{16}–C^{17}	1.387(7)	C^{29}–C^{34}	1.390(7)
C^{16}–C^{21}	1.380(6)	C^{30}–C^{31}	1.375(7)
C^{17}–C^{18}	1.370(8)	C^{31}–C^{32}	1.364(8)
C^{18}–C^{19}	1.340(1)	C^{32}–C^{33}	1.384(9)
C^{19}–C^{20}	1.370(9)	C^{33}–C^{34}	1.371(7)
C^{20}–C^{21}	1.380(8)	C^{24}–C^{25}	1.375(8)
C^{23}–C^{24}	1.398(7)	C^{25}–C^{26}	1.341(9)
C^{23}–C^{28}	1.376(7)		

Table 4. Selected torsion angles (τ, deg) in molecules **VII**

Angle	τ	Angle	τ
$C^4P^1C^1C^2$	–166.8(3)	$C^{23}N^1C^{22}N^2$	–172.6(4)
$C^{10}P^1C^1C^2$	72.4(4)	$C^{22}N^1C^{23}C^{24}$	–28.6(7)
$C^{16}P^1C^1C^2$	–47.1(4)	$C^{22}N^1C^{23}C^{28}$	152.3(4)
$C^1P^1C^4C^5$	–33.9(4)	$C^{29}N^2C^{22}O^3$	–3.6(7)
$C^1P^1C^4C^9$	148.4(4)	$C^{29}N^2C^{22}N^1$	174.7(4)
$C^{10}P^1C^4C^5$	88.6(4)	$C^{22}N^2C^{29}C^{30}$	37.1(6)
$C^{10}P^1C^4C^9$	–89.1(4)	$C^{22}N^2C^{29}C^{34}$	–142.9(4)
$C^{16}P^1C^4C^5$	–151.8(4)	$P^1C^1C^2C^3$	166.0(3)
$C^{16}P^1C^4C^9$	30.4(4)	$C^1C^2C^3O^1$	156.8(4)
$C^1P^1C^{10}C^{11}$	–177.1(3)	$C^1C^2C^3O^2$	–25.9(5)
$C^1P^1C^{10}C^{15}$	3.8(4)	$P^1C^4C^5C^6$	–179.0(4)
$C^4P^1C^{10}C^{11}$	62.5(4)	$C^9C^4C^5C^6$	–1.3(7)
$C^4P^1C^{10}C^{15}$	–116.5(4)	$P^1C^4C^9C^8$	179.2(4)
$C^{16}P^1C^{10}C^{11}$	–58.2(4)	$P^1C^{10}C^{11}C^{12}$	–180.0(6)
$C^{16}P^1C^{10}C^{15}$	122.7(4)	$P^1C^{10}C^{15}C^{14}$	–179.9(5)
$C^1P^1C^{16}C^{17}$	–75.8(4)	$P^1C^{16}C^{17}C^{18}$	175.2(4)
$C^1P^1C^{16}C^{21}$	97.2(4)	$P^1C^{16}C^{21}C^{20}$	–175.4(4)
$C^4P^1C^{16}C^{17}$	42.6(4)	$N^1C^{23}C^{24}C^{25}$	–179.3(5)
$C^4P^1C^{16}C^{21}$	–144.3(4)	$N^1C^{23}C^{28}C^{27}$	179.4(5)
$C^{10}P^1C^{16}C^{17}$	162.5(4)	$N^2C^{29}C^{30}C^{31}$	178.8(4)
$C^{10}P^1C^{16}C^{21}$	–24.4(4)	$N^2C^{29}C^{34}C^{33}$	–178.5(5)
$C^{23}N^1C^{22}O^3$	5.7(7)		

Thus, our results show that phosphabetaine **I** fairly smoothly reacts with dipolar electrophilic reagents, but the reactions provide no expected phosphoranes. This result contradicts the results of quantum-chemical calculations, according to which all the four semiempirical methods point to thermodynamic preference for phosphorane structures (on average, 10–30 kcal mol^{-1}). It is reasonable to suggest from these data that the observed preference for betaine structures is explained with their additional stabilization with proton-donor reagents. In this connection we performed additional quantum-chemical calculations of the hydration energies of carboxylate phosphabetaines with a molecule of water to find a considerable energy gain (~25 kcal mol^{-1}), which is much larger than the energy of a usual hydrogen bond. This result agrees well with the mentioned published and our own data, according to which both in solution and in crystal one betaine molecule is accompanied by one molecule of a proton-donor reagent which is impossible to remove by conventional methods of purification.

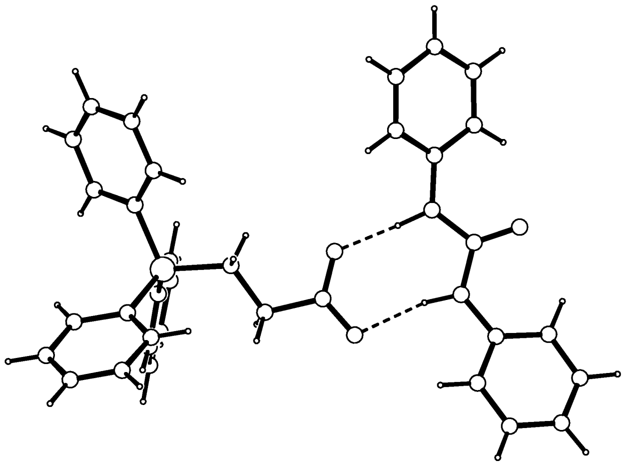


Fig. 2. Hydrogen bonds in crystal **VII** (shown be dashed lines).

EXPERIMENTAL

The IR spectra were measured on a Specord M-80 instrument at 700–3600 cm^{-1} in thin films or in mineral oil between KBr plates. The ^1H and ^{31}P NMR spectra were obtained in $CDCl_3$ on a Varian Unity-300 instrument at 300 (^1H, internal reference HMDS) and 121.64 MHz (^{31}P, external reference H_3PO_4).

Crystals of compound **VII**, $C_{21}H_{19}O_2P_1 \cdot C_{13}H_{12} \cdot N_2O$, mp 55°C, monoclinic. At 20°C, *a* 10.441(4), *b* 13.315(3), *c* 26.53(1) Å; β 90.15(3)°, *V* 3689(2) $Å^3$,

Z 4, d_{calc} 1.25 g cm^{-3}, space group $P2_1/n$. The unit cell parameters and the intensities of 8016 reflections, 4382 of which with $I \geq 3\sigma$, were measured on an Enraf–Nonius CAD-4 automatic four-circle diffractometer (λCuK_α radiation, graphite monochromator, $\omega/2\theta$ scanning, $\theta \leq 74°$). No intensity decay of three control reflections was observed during measurements. Absorption, in view of its weakness (μCu 9.70 cm^{-1}) was not included. The structure was solved by the direct method using the SIR program [7] and refined isotropically. The difference electron density series showed numerous peaks that were interpreted as two disordered solvent molecules. Attempts to establish the type of disorder and identify the solvent molecules failed. Presumably, these are two toluene molecules. The structure was further refined anisotropically, apart from the disordered solvent molecules that were refined isotropically. All hydrogen atoms were then refined from difference electron density series, apart from H atoms in the disordered molecules, whose contribution in structure amplitudes was included with fixed positional and isotropic thermal parameters in the final refinement stage. Final divergence factors: R 0.074 and R_W 0.084 on 3610 unique reflections with $F^2 \geq 3\alpha$. All calculations were performed on an AlphaStation-200 computer using the MolEN program package [9]. Drawings and analysis of intermolecular contacts in crystal were performed using the PLATON program [10].

The syntheses of 3-(triphenylphosphonio)propanoate (**I**) and its alkylation products are described in [1, 2].

Reaction of phosphabetaine I with phenyl isocyanate. Compound **I**, 0.78 g, in 3 ml of chloroform was added to a solution of 0.3484 g of phenyl isocyanate in 3 ml of toluene. The reaction mixture was thoroughly stirred and heated for 4 h at 85°C. The solvent was removed in a vacuum. The ^{31}P NMR spectrum of the reaction mixture contained a single signal at δ_P 25 ppm. Dry ether was added to the mixture, the precipitate that formed was filtered off, washed with diethyl ether, and dried in a vacuum to obtain colorless crystals. Yield 69%, mp 55°C, δ_P 25 ppm. According to the ^{1}H NMR spectrum, the crystalline material contained one molecule of compound **VII** and two molecules of toluene. The proton signals of the α-methylene group on phosphorus are a multiplet centered at 3.5 ppm ($^2J_{PH}$ 16, $^3J_{HH}$ 6 Hz. The β-methylene protons absorb at 2.72 ppm ($^2J_{PH}$ 16, $^3J_{HH}$ 6 Hz). The multiplets of phenyl protons appear at 7.16–7.78 ppm, the NH singlet, at 10.01 ppm, and toluene CH_3 protons, at 2.4 ppm.

Reaction of phosphabetaine I with dicyclohexylcarbodiimide. Betaine **I**, 54 g, in 5 ml of chloroform was added to a solution of 0.41 g of dicyclohexylcarbodiimide in 5 ml of toluene. The reaction mixture was thoroughly stirred and heated for 1 h at 90°C. The precipitate that formed was filtered off to obtain colorless crystals insoluble in water, toluene, acetonitrile, chloroform, and acetone. Yield 72%, mp 226°C. IR spectrum, cm^{-1}: 3300 (NH), 1600 (COO$^-$). The ^{31}P NMR spectrum contained a single signal at δ_P –7 ppm which corresponds to the chemical shift of triphenylphosphine.

Independent synthesis. A solution of 0.61 g of acrylic acid was added dropwise with continuous stirring to a solution of 1.54 g of dicyclohexylcarbodiimide in 5 ml of toluene. The reaction occurred almost instantaneously with a strong heat release. As a result, colorless crystals insoluble in toluene were obtained. Moreover, the product is insoluble in water, acetonitrile, chloroform, and acetone. Yield 76%, mp 227°C. IR spectrum, cm^{-1}: 3300 (NH), 1600 (COO$^-$).

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