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Synthesis and Properties of Phosphabetaine Structures: II.[1] Synthesis and Molecular Structure of 3-(Triphenylphosphonio)propanoate and Its Alkylation Products

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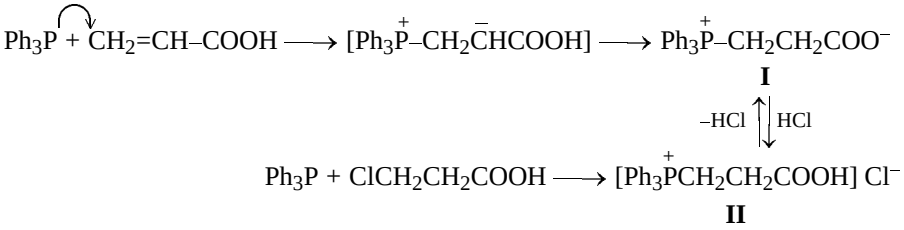
Abstract — The structure of 3-(triphenylphosphonio)propanoate was studied, and the ability of proton-donor reagents to stabilize the betaine structure was demonstrated. The phosphobetaines are alkylated by alkyl halides to form (alkoxycarbonyl)alkyltriphenylphosphonium halides and acylated by acetyl bromides. Some features of the latter reactions were revealed.

Earlier were reported the structure and reactivity of phosphabetaine **I** prepared by reaction of triphenylphosphine wiyh acrylic acid or by dehydrochlorination of salt **II** formed by quaternization of triphenylphosphine with 3-chloropropanoic acid [1]. Therewith we revealed an essential role proton-donor solvents play in stabilization of phosphabetaine structures: Satisfactory results could only be achieved when a proton-donor molecule was present to stabilize strongly separated charges in **I** and other dipolar structures [2].



In the present work we performed an X-ray diffraction study of 3-(triphenylphosphonio)propanoate (**I**) (Fig. 1) and thus obtained evidence for the above assumption, as well as firmly established the chemical structure of this compound and showed that its crystal contains water molecules. The principal geometric parameters of betaine **I** are listed in Table 1.

In the asymmetric part of the crystal cell there is one independent molecule of betaine **I** and one water molecule disordered over two sites (O^9 and O^{9a}). The coordination of the phosphorus atom is typical of a four-coordinate phosphonium center, and its bond lengths and angles fit values found in phosphonium salts [3]. The $P^1C^1C^2C^3$ fragment has a *transoid* conformation [torsion angle φ 173.0(6)°], and the conformation of the $C^1C^2C^3O^2$ fragment is close to *eclipsed* [φ 29(1)°]. The CO bond lengths in **I** are equal within error, and their values are intermediate between those characteristic of double and single CO bond lengths (Table 1).

Unfortunately, because of the disorder of water molecules in the crystal of **I**, hydrogen atoms at O^9 were revealed with larger errors, while the second hydrogen atom at O^{9a} could not be revealed at all,

[1] For communication I, see [1].

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Table 1. Bond lengths (*d*, Å) and bond (ω, deg) and torsion angles (φ, deg) in **I, Va**, and **Vb**

Bond	*d*			Bond	*d*		
	I	**Va**	**Vb**		**I**	**Va**	**Vb**
P^1–C^1	1.785(8)	1.815(3)	1.78(2)	O^1–C^3	1.26(1)	1.337(3)	1.34(2)
P^1–C^4	1.78(1)	1.801(3)	1.80(2)	O^2–C^{22}		1.449(4)	1.41(3)
P^1–C^{10}	1.779(8)	1.788(2)	1.84(2)	C^1–C^2	1.54(1)	1.526(4)	1.59(2)
P^1–C^{16}	1.808(8)	1.794(2)	1.80(2)	C^2–C^3	1.54(1)	1.495(4)	1.46(2)
O^2–C^3	1.19(1)	1.189(3)	1.17(2)	C^{22}–C^{23}			1.33(5)
Bond angle	ω			Bond angle	ω		
	I	**Va**	**Vb**		**I**	**Va**	**Vb**
$C^1P^1C^4$	110.7(5)	109.6(1)	110.7(8)	$O^2C^3C^2$	121.5(8)	125.3(2)	130.(2)
$C^1P^1C^{10}$	108.9(4)	109.7(1)	107.7(8)	$O^1C^3C^2$	113.3(8)	111.6(2)	111.(1)
$C^1P^1C^{16}$	109.4(4)	110.2(1)	108.5(8)	$P^1C^{16}C^{17}$	119.2(6)	119.8(2)	122.(1)
$C^4P^1C^{10}$	109.5(4)	110.0(1)	108.6(7)	$P^1C^{16}C^{21}$	118.7(6)	120.0(2)	117.(1)
$C^4P^1C^{16}$	108.0(3)	109.7(1)	110.7(7)	$P^1C^4C^5$	120.7(7)	119.1(2)	120.(1)
$C^{10}P^1C^{16}$	110.3(4)	107.7(1)	110.6(8)	$P^1C^4C^9$	119.1(8)	121.9(2)	119.(1)
$P^1C^1C^2$	113.4(6)	114.1(2)	112.(1)	$P^1C^{10}C^{11}$	116.5(7)	121.1(2)	121.(1)
$C^3O^2C^{22}$		115.9(3)	116.(2)	$P^1C^{10}C^{15}$	124.4(6)	119.9(2)	116.(1)
$C^1C^2C^3$	112.2(8)	112.4(2)	112.(1)	$O^2C^{22}C^{23}$			114.(3)
$O^2C^3O^1$	125.2(9)	123.1(3)	119.(1)				
Torsion angle	φ			Torsion angle	φ		
	I	**Va**	**Vb**		**I**	**Va**	**Vb**
$C^4P^1C^1C^2$	177.9(6)	157.9(19)	47(1)	$C^4P^1C^{16}C^{17}$	100.6(7)	160.9(2)	126(2)
$C^{10}P^1C^1C^2$	57.5(7)	81.3(2)	166(1)	$C^4P^1C^{16}C^{21}$	70.6(74)	25.9(3)	52(2)
$C^{16}P^1C^1C^2$	63.1(7)	37.1(2)	74(1)	$C^{10}P^1C^{16}C^{17}$	139.8(7)	41.3(3)	112(2)
$C^1P^1C^4C^5$	24.8(8)	175.5(2)	90(2)	$C^{10}P^1C^{16}C^{21}$	49.0(8)	145.6(2)	67(2)
$C^1P^1C^4C^9$	161.5(6)	5.7(3)	83(2)	$C^{22}O^2C^3O^1$		4.7(4)	1(2)
$C^{10}P^1C^4C^5$	144.9(7)	54.8(3)	151(1)	$C^{22}O^2C^3C^2$		177.0(2)	175(2)
$C^{10}P^1C^4C^9$	41.4(7)	126.4(3)	34(2)	$C^3O^2C^{22}C^{23}$			129(3)
$C^{16}P^1C^4C^5$	94.9(7)	63.4(3)	30(2)	$P^1C^1C^2C^3$	173.0(6)	82.3(3)	87(2)
$C^{16}P^1C^4C^9$	78.8(7)	115.4(3)	156(2)	$C^1C^2C^3O^2$	29(1)	164.9(2)	167(1)
$C^1P^1C^{10}C^{11}$	81.6(7)	23.4(3)	16(2)	$C^1C^2C^3O^1$	149.2(8)	16.8(4)	15(3)
$C^1P^1C^{10}C^{15}$	94.9(8)	157.9(2)	164(1)	$P^1C^4C^5C^6$	174.4(7)	178.6(3)	171(2)
$C^4P^1C^{10}C^{11}$	39.6(7)	97.1(2)	136(2)	$P^1C^4C^9C^8$	174.5(7)	178.6(2)	172(1)
$C^4P^1C^{10}C^{15}$	143.9(7)	81.5(3)	44(2)	$P^1C^{10}C^{11}C^{12}$	176.6(7)	179.8(2)	179(2)
$C^{16}P^1C^{10}C^{11}$	158.3(6)	143.4(2)	101(2)	$P^1C^{10}C^{15}C^{14}$	175.4(7)	179.8(3)	179(2)
$C^{16}P^1C^{10}C^{15}$	25.2(8)	37.9(3)	76(2)	$P^1C^{16}C^{17}C^{18}$	177.4(7)	171.9(2)	180(2)
$C^1P^1C^{16}C^{17}$	20.0(8)	78.4(3)	4(2)	$P^1C^{16}C^{21}C^{20}$	176.6(7)	172.8(2)	177(2)
$C^1P^1C^{16}C^{21}$	168.8(7)	94.8(2)	174(1)				

and, therefore, classical H bonds could be revealed by distances between potential H-bond donors and acceptors. Figure 2 lists the revealed H bonds and the crystal packing.

By the distances from O^{9a} to potential H-bond donors and acceptors we can suggest that this water, too, forms H bonds. Such short contacts were found between neighboring O^{9a} atoms: $O^{9a}\cdots O^{9a'}$ [*x*, 1 – *y*,

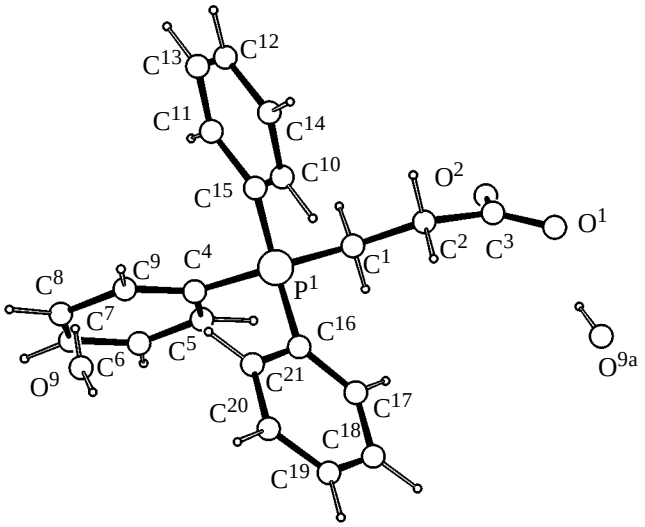


Fig. 1. Geometry of the independent part of the crystal cell of the crystal hydrate of 3-(triphenylphosphonio)-propanoate (**I**).

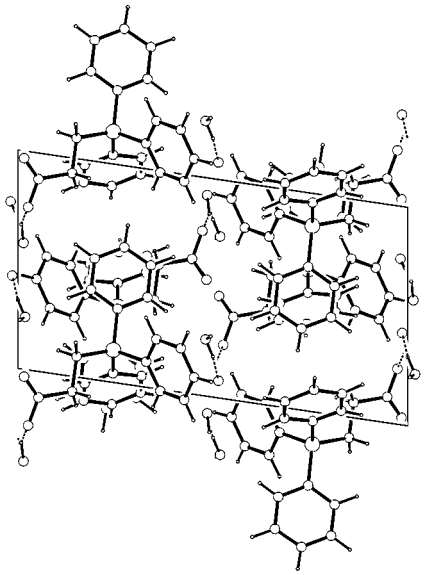
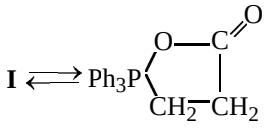


Fig. 2. Hydrogen bonds and crystal packing in the crystal hydrate of 3-(triphenylphosphonio)propanoate (**I**).

1 – *z*] 2.36(2) Å, as well as between O^{9a} and oxygen atoms of two betaine fragments closest to this water molecule: $O^{9a}\cdots O^{1''}$ [–1 + *x*, *y*, *z*] 2.94(2), $O^{9a}\cdots O^{1'''}$ [–*x*, 1 – *y*, 1 – *z*] 2.54(2), and $O^{9}\cdots O^{2''''}$ [1/2 – *x*, –1/2 + *y*, 1/2 – *z*] 2.61(1) Å. The crystal packing comprises hydrophilic and hydrophobic layers (Fig. 2).

According to [4], the same situation takes place in structurally related carboxylate arsenobetaines whose crystal lattice, too, incorporates water molecules, and the crystal packing is similar to that we suggest for **I**. These data provide convincing evidence to show that proton-donor reagents strongly stabilize phospha-betaine strictures.

Attempted isolation of "individual" phosphabetaine **I**, without proton donors in the crystal lattice, gave unexpected and interesting results. We reacted triphenylphosphine with acrylic acid in a thoroughly dried apolar aprotic solvent (benzene). It was expected that the absence of the stabilizing proton-donor molecule would render the dipolar betaine structure unstable, and it would isomerize into phosporane **III**.



III

As follows from the energies of formation of forms **I** and **III**, estimated quatum-chemically, in the gas phase the latter form is preferred [5].

Unlike the reaction in chloroform, the reaction in benzene is much slower and results, according to NMR and IR data, in exclusive formation of betaine **I** stabilized by a molecule of acrylic acid. Noteworthy, the coordinated molecule of acrylic acid is no longer capable of adding triphenylphosphine. As a result, the yield of betaine **I** (after purification) with respect to triphenylphosphine at a 1 : 1 reagent molar ratio is as low as 46% [which is very close to theory (50%)], while 37% of triphenylphosphine is recovered. This result can be explained in no other way except by involvement in reaction of two molecules of acrylic acid per one molecule of triphenylphosphine; therewith, the second molecule of acrylic acid acts as proton donor and gives up its proton for stabilizing the phosphabetaine in complex **IV**.

$$Ph_3P + 2CH_2{=}CHCOOH$$

$$\longrightarrow Ph_3\overset{+}{P}{-}CH_2CH_2COO^{-}\cdots\overset{+}{H}\cdots{}^{-}OOCCH{=}CH_2.$$

IV

The molecule of acrylic acid, incorporated in complex **IV**, is almost completely ionized and thus loses its ability to add nucleophilic reagents (triphenylphosphine inclusive) by the C=C bond. To prove the structure of compound **IV** chemically, we tried to alkylate it to obtain the known methyl ester **Va** [1]. However, complex **IV**, unlike betaine **I**, proved to be much more difficult to alkylate, and the isolable yield of the target reaction product proved to be very low; the major reaction product was methyl acrylate formed by alkylation of the acrylate anion.

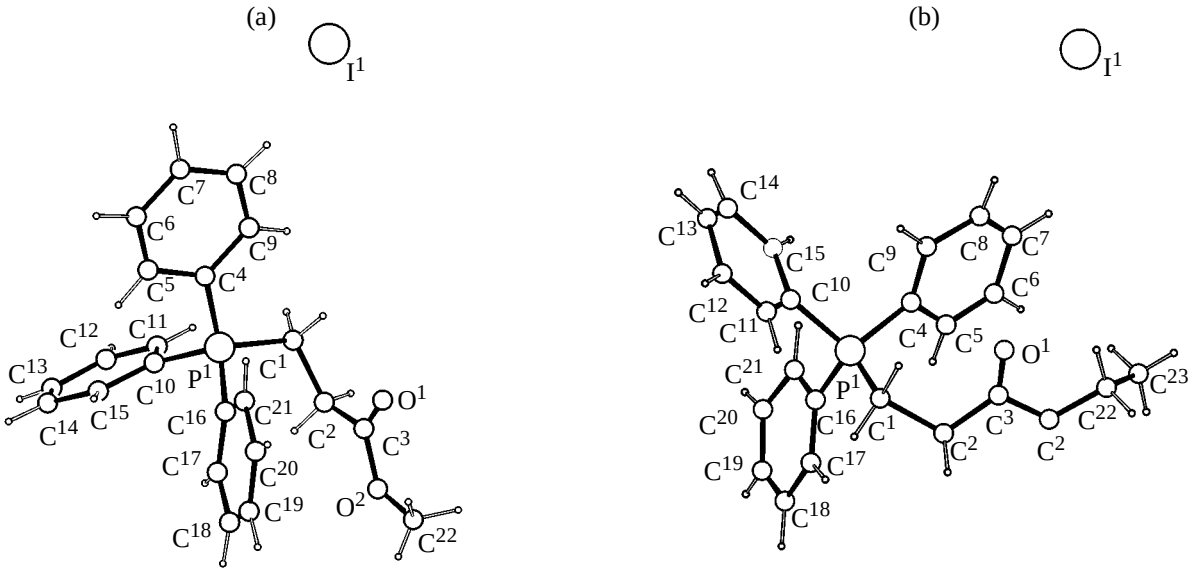


Fig. 3. Molecular structures of (a) (2-methoxycarbonyl)triphenylphosphonium iodide and (b) (2-ethoxycarbonyl)triphenylphosphonium iodide (**Vb**).

$$\underset{\mathbf{V}}{Ph_3\overset{+}{P}–CH_2CH_2COO^{-}\cdots\overset{+}{H}\cdots{}^{-}OOCCH=CH_2} + MeI$$

$$\longrightarrow \underset{\mathbf{Va}}{[Ph_3\overset{+}{P}–CH_2CH_2COOMe]I^{-}} + MeOOCCH=CH_2.$$

The latter result provides convincing evidence not only for the structure of complex **IV**, but also for the previously mentioned extremely high protophilicity of betaine structures which actively coordinate various proton donors, as well as for our conclusion about a considerable (or even complete) proton transfer from acrylic acid, resulting in deactivation of the C=C bond.

Earlier we showed [1] that phosphabetaine **I** is readily alkylated with methyl and ethyl iodide. The compositions and structures of the resulting phosphonium salts were proved by ^{1}H and ^{31}P NMR and IR spectroscopy. In the present work we extended the range of alkylating agents. It was found that phosphabetaine **I** is readily alkylated with other alkylating agents to give phosphonium salts **Va**–**Vh** (Table 2).

$$\mathbf{I} + RHlg \longrightarrow \underset{\mathbf{Va}–\mathbf{Vh}}{[Ph_3\overset{+}{P}–CH_2CH_2COOR]Hlg^{-}},$$

For R and Hlg, see Table 2.

The reactions were performed with various alkyl halides. As would be expected, iodides proved to be the most reactive. With methylene bromide, only one bromine atom was substituted, irrespective of reagent ratio.

The composition and structure of phosphonium salts **Va**–**Vh** were proved by elemental analysis, ^{1}H and ^{31}P NMR and IR spectroscopy, as well as X-ray diffraction (for **Va** and **Vb**; see Fig. 3).

The alkylation is readily observable in the IR spectra by an appreciable (~100–150 cm^{-1}) blue shift of the carbonyl absorption band. If the ν(CO) band of the parent betaine is in the range characteristic of carboxylate ions (1600 cm^{-1}), then, as the COO^{-} ion converts to COOR with alkylation progress, this band shifts to 1700–1740 cm^{-1} (Table 2).

Note that posphonium salts, unlike the betaine itself, are no longer capable of incorporating proton-donor agents into the crystal lattice, implying that this property is a distinguishing feature of betaine struc-

Table 2. Phosphonium salts **Va**–**Vh**

Comp. no.	R	Hlg	mp, °C	IR spectrum, ν(C=O), cm^{-1}
Va	Me	I	166–167	1720
Vb	Et	I	99–101	1720
Vc	CH_2Br	Br	134–136	1715
Vd	Pr	I	[a]	1720
Ve	*i*-Pr	Cl	[a]	1725
Vf	Bu	I	[a]	1735
Vg	*i*-Bu	I	[a]	1740
Vh	*i*-Am	I	[a]	1730

[a] Oily liquid.

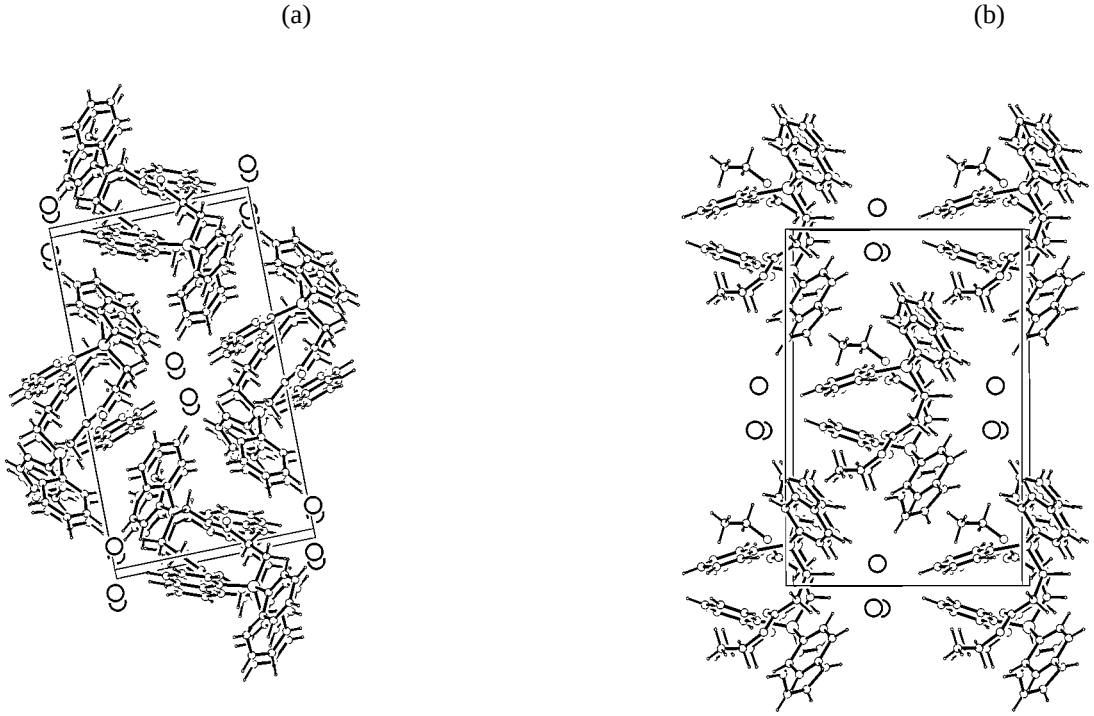


Fig. 4. Crystal packing of (a) (2-methoxycarbonyl)triphenylphosphonium iodide (**Va**) and (b) (2-ethoxycarbonyl)triphenylphosphonium iodide (**Vb**).

tures, and, as already mentioned, most likely serves to stabilize strongly separated charges.

This is clearly evident from X-ray diffraction data (Fig. 3) which are fully supportive of the above conclusions concerning the structure of the alkylation products. Figure 3 shows the geometries of the corresponding methyl and ethyl esters **Va** and **Vb**.

In iodides **Va** and **Vb** (Table 1), like in phosphabetaine **I**, the phosphorus atom has usual geometry. As follows from the values of torsion angles (Table 1), the conformation of the $P^1C^1C^2C^3$ fragment both in **Va** and in **Vb**, unlike phosphobetaine **I**, is *orthogonal*, while the $C^1C^2C^3O^2$ fragment has the same (*eclipsed*) conformation as in **I**. The CO bond lengths are characteristic of double and single CO bonds (Table 1). The structural similarity of compounds **Va** and **Vb** shows up in their crystal packings: Iodide anions reside in channels parallel to one of the crystallographic axes (Fig. 4).

We also reacted phosphabetaine **I** with acetyl bromide. According to ^{1}H NMR and X-ray diffraction data, phosphabetaine **I** contains one stabilizing water molecule per one betaine molecule. Taking into account that this water can independently react with acetyl bromide, in our experiments we used more than double excess of acetyl bromide, assuming that one its molecule would bind water, while the second would acylate phosphabetaine **I**. The acetic acid formed was neutralized with potassium carbonate.

$$\mathbf{I} + \mathrm{AcBr} \longrightarrow [Ph_3\overset{+}{P}\text{–}CH_2CH_2\overset{O}{\overset{\|}{C}}OAc]\ Br^-$$

VI

The liquid reaction product **VI** was studied by spectral methods. Its IR spectrum shows no carbonyl stretching absorption bands of the starting compounds [1600 (**I**) and 1800 cm^{-1} (acetyl bromide] and acquires a new, single band at 1700 cm^{-1}, which is likely to belong to the anhydride group of the acylation product. The ^{1}H NMR spectrum of compound **VI**, too, is fully supportive of the proposed stucture of the acylation product, displaying well-defined signals of all proton groups: CH_3CO [1.95 ppm, s (3H)], PCH_2CH_2 [2.62 ppm, m (2H) and 3.58 ppm, m (2H)], and C_6H_5 [7.6–7.9 ppm, m (15H)].

EXPERIMENTAL

The IR spectra were measured on a Specord M-80 spectrometer at 700–3600 cm^{-1} in thin films or in mineral oil between KBr plates. The ^{1}H and ^{31}P NMR

spectra were obtained in $CDCl_3$ on a Varian Unity-300 spectrometer at 300 MHz (^1H), internal reference HMDS, and at 121.64 MHz (^{31}P), external reference H_3PO_4.

X-ray diffraction analysis of compounds **I**, **Va**, and **Vb** was performed on an Enraf–Nonius CAD-4 diffractometer at 20°C (MoK_α radiation, λ 0.71073 Å).

Crystals of compound **I**, $C_{21}H_{19}O_2P \cdot H_2O$, yellow, prismatic, monoclinic. At 20°C, *a* 9.125(4), *b* 12.754(4), *c* 16.38(1) Å; β 98.42(6)°, *V* 1886(2) Å^3, *Z* 4, d_{calc} 1.125 g/cm^3, space group $P2_1/n$.

Crystals of compound **Va**, $C_{22}H_{22}O_2P^+ \cdot I^-$, yellow, rhombic, monoclinic. At 20°C, *a* 11.001(2), *b* 17.949(3), *c* 11.093(3) Å; β 109.47(2)°, *V* 2065.0(8) Å^3, *Z* 4, d_{calc} 1.53 g/cm^3, space group $P2_1/c$.

Crystals of ester **Vb**, $C_{23}H_{24}O_2P^+ \cdot I^-$, yellow, rhombic, monoclinic. At 20°C, *a* 11.131(3), *b* 17.396(5), *c* 12.023(3) Å; β 97.59(2)°, *V* 2306(1) Å^3, *Z* 4, d_{calc} 1.41 g/cm^3, space group *Cc*.

The unit cell parameters and the intensities of 4258 (**I**), 4562 (**Va**), and 4268 (**Vb**) reflections, 1285 (**I**), 3102 (**Va**), and 1218 (**Vb**) of which [$I > 3\sigma(I)$] were measured by ω/2θ scanning at a variable scan rate (1–16.4 deg/min on θ). No intensity decay of three reference reflections was observed. With structure **I**, absorption was not included (μMo 1.46 cm^{-1}), and with structures **Va** and **Vb** was included empirically (μMo 16.21 and 14.54 cm^{-1}, respectively).

The structures were solved by the SIR program [6] and refined first isotropically and then anisotropically. The hydration water in structure **I** is disordered over two positions with occupancies of 0.6 (O^9) and 0.4 (O^{9a}). Hydrogen atoms were revealed by difference synthesis, except for one H atom on O^{9a} in structure **I**. In structures **I** and **Vb**, hydrogen atoms were not refined, and their contributions in structure amplitudes were included with fixed positional and isotropic thermal parameters. In structure **Va**, hydrogen atoms were refined isotropically. The final divergence factors were as follows: structure **I**: *R* 0.070 and R_W 0.072, on 1140 unique reflections with $F_2 \geq 3\sigma$; structure **Va**: *R* 0.024 and R_W 0.031, on 3110 unique reflections with $F_2 \geq 3\sigma$; and structure **Vb**: *R* 0.069 and R_W 0.079, on 1166 unique reflections with $F_2 \geq 3\sigma$. All calculations were performed using the MolEN program package [7] on AlphaStation 200. Molecular drawings and analysis of intermolecular contacts, including H bonds in crystals, were perfomed using the PLATON program [8]. The atomic coordinates in structures **I**, **Va**, and **Vb** are listed in Tables 3–5, respectively.

Table 3. Atomic coordinates in structure **I**, equivalent isotropic thermal parameters of non-hydrogen atoms $B = 4/3\sum_{i=1}^{3}\sum_{j=1}^{3}(a_i a_j)B(i,j)$ (Å^2), and isotropic thermal parameters of hydrogen atoms B_{iso} (Å^2)[a]

Atom	*x*	*y*	*z*	*B*
P^1	0.8513(3)	0.0517(2)	0.7552(2)	2.52(5)
O^2	1.0333(8)	0.1444(5)	0.9839(4)	6.4(2)
O^9	0.740(1)	0.295(1)	0.5187(6)	8.7(4)
O^{9a}	1.421(2)	0.073(1)	0.986(1)	5.2(4)
O^1	1.2543(9)	0.0871(7)	0.9735(5)	8.9(3)
C^1	0.906(1)	0.0179(6)	0.8492(5)	3.4(2)
C^2	1.069(1)	0.0537(7)	0.8610(5)	4.0(2)
C^3	1.119(1)	0.1015(7)	0.9470(6)	4.8(3)
C^4	0.660(1)	0.0862(6)	0.7444(6)	3.2(2)
C^5	0.590(1)	0.0965(7)	0.8123(6)	4.3(3)
C^6	0.445(1)	0.1322(7)	0.8031(7)	5.3(3)
C^7	0.374(1)	0.1574(7)	0.7270(7)	5.7(3)
C^8	0.438(1)	0.1489(7)	0.6589(7)	5.9(3)
C^9	0.587(1)	0.1124(7)	0.6676(7)	4.5(3)
C^{10}	0.8830(9)	0.0293(6)	0.6710(5)	2.2(2)
C^{11}	0.773(1)	0.1050(7)	0.6446(6)	3.8(2)
C^{12}	0.798(1)	0.1735(7)	0.5820(6)	4.5(3)
C^{13}	0.922(1)	0.1691(7)	0.5477(6)	4.6(3)
C^{14}	1.031(1)	0.0950(7)	0.5736(5)	4.4(3)
C^{15}	1.007(1)	0.0261(6)	0.6346(5)	3.2(2)
C^{16}	0.9577(8)	0.1714(6)	0.7559(5)	2.3(2)
C^{17}	1.024(1)	0.2104(6)	0.8288(5)	3.4(2)
C^{18}	1.103(1)	0.3055(7)	0.8312(6)	4.2(2)
C^{19}	1.101(1)	0.3597(6)	0.7593(6)	4.3(3)
C^{20}	1.028(1)	0.3240(7)	0.6848(6)	4.2(2)
C^{21}	0.952(1)	0.2279(7)	0.6834(5)	3.5(2)
H^5	0.6423	0.0763	0.8696	6
H^6	0.3936	0.1397	0.8513	6
H^7	0.2715	0.1852	0.7179	7
H^8	0.3856	0.1650	0.6009	8
H^9	0.6380	0.1047	0.6205	5
H^{11}	0.6814	0.1082	0.6710	5
H^{12}	0.7211	0.2272	0.5639	6
H^{13}	0.9311	0.2198	0.5043	5
H^{14}	1.1191	0.0982	0.5497	5
H^{15}	1.0848	0.0286	0.6527	4
H^{17}	1.0185	0.1711	0.8806	4
H^{18}	1.1585	0.3325	0.8838	5
H^{19}	1.1549	0.4259	0.7613	5
H^{20}	1.0302	0.3649	0.6331	5
H^{21}	0.8960	0.2002	0.6306	5
H^{111}	0.8429	0.0791	0.8515	4
H^{112}	0.8906	0.0254	0.8959	4
H^{211}	1.1299	0.0065	0.8508	5
H^{212}	1.0813	0.1037	0.8173	5
H^{911}	0.8143	0.3416	0.500	6
H^{912}	0.7234	0.2429	0.505	6
H^{91a}	1.3370	0.0244	0.991	6

[a] Hydrogen atoms were not refined.

Table 4. Atomic coordinates in structure **Va**, equivalent isotropic thermal parameters of non-hydrogen atoms $B = 4/3\sum_{i=1}^{3}\sum_{j=1}^{3}(a_i a_j)B(i,j)$ (Å^2), and isotropic thermal parameters of hydrogen atoms B_{iso} (Å^2)

Atom	*x*	*y*	*z*	*B*
I^1	0.22952(2)	0.06019(1)	0.01945(2)	3.982(4)
P^1	0.22844(6)	0.13417(4)	0.34216(6)	2.48(1)
O^1	0.2675(2)	0.0648(1)	0.4131(2)	4.15(5)
O^2	0.1142(2)	0.0742(1)	0.5016(2)	4.51(5)
C^1	0.1427(3)	0.0542(1)	0.2540(2)	2.93(5)
C^2	0.0752(2)	0.0071(2)	0.3273(2)	2.91(5)
C^3	0.1649(2)	0.0466(1)	0.4169(3)	2.84(6)
C^4	0.3506(2)	0.1630(1)	0.2771(2)	2.85(5)
C^5	0.4219(3)	0.2269(2)	0.3249(3)	4.16(7)
C^6	0.5177(3)	0.2494(2)	0.2792(4)	5.04(8)
C^7	0.5433(3)	0.2092(2)	0.1851(3)	5.10(8)
C^8	0.4740(3)	0.1461(2)	0.1368(3)	4.86(8)
C^9	0.3772(3)	0.1227(2)	0.1824(3)	3.58(6)
C^{10}	0.1177(2)	0.2088(1)	0.3316(2)	2.73(5)
C^{11}	0.0013(3)	0.2128(2)	0.2314(3)	3.61(6)
C^{12}	0.0833(3)	0.2713(2)	0.2257(3)	4.56(8)
C^{13}	0.0526(3)	0.3250(2)	0.3186(3)	4.75(7)
C^{14}	0.0642(3)	0.3230(2)	0.4157(3)	5.17(8)
C^{15}	0.1489(3)	0.2653(2)	0.4237(3)	4.13(7)
C^{16}	0.3019(2)	0.1111(1)	0.5081(2)	2.59(5)
C^{17}	0.2273(2)	0.1089(2)	0.5875(3)	3.42(6)
C^{18}	0.2793(3)	0.0822(2)	0.7109(3)	3.95(7)
C^{19}	0.4067(3)	0.0586(2)	0.7558(3)	4.13(7)
C^{20}	0.4813(3)	0.0623(2)	0.6783(3)	3.88(7)
C^{21}	0.4299(2)	0.0878(2)	0.5541(3)	3.09(6)
C^{22}	0.1962(4)	0.1242(2)	0.5969(3)	6.22(9)
H^5	0.413(2)	0.254(2)	0.399(3)	4.6(7)
H^6	0.566(3)	0.294(2)	0.319(3)	5.8(8)
H^7	0.611(3)	0.224(2)	0.144(4)	8(1)
H^8	0.485(3)	0.118(2)	0.076(3)	6.8(9)
H^9	0.334(2)	0.080(1)	0.152(3)	3.7(6)
H^{11}	0.018(2)	0.177(1)	0.172(3)	3.8(6)
H^{12}	0.163(2)	0.269(2)	0.156(3)	4.6(7)
H^{13}	0.109(3)	0.361(2)	0.319(3)	4.7(7)
H^{14}	0.083(3)	0.363(2)	0.476(3)	5.9(8)
H^{15}	0.227(3)	0.266(2)	0.485(3)	7(1)
H^{17}	0.133(2)	0.124(1)	0.560(2)	3.4(6)
H^{18}	0.231(3)	0.082(2)	0.767(3)	4.7(7)
H^{19}	0.439(3)	0.040(2)	0.841(3)	4.5(7)
H^{20}	0.566(3)	0.048(1)	0.710(3)	4.4(7)
H^{21}	0.479(2)	0.093(1)	0.504(2)	2.9(5)
H^{111}	0.082(3)	0.070(1)	0.167(3)	3.8(6)
H^{112}	0.204(2)	0.024(2)	0.231(2)	4.3(7)
H^{211}	0.032(2)	0.036(1)	0.369(2)	2.9(6)
H^{212}	0.014(2)	0.019(2)	0.267(2)	4.0(6)
H^{221}	0.194(4)	0.173(2)	0.561(4)	9(1)
H^{222}	0.284(3)	0.117(2)	0.614(3)	8(1)
H^{223}	0.184(5)	0.115(3)	0.668(5)	13(2)

Table 5. Atomic coordinates in structure **Vb**, equivalent isotropic thermal parameters of non-hydrogen atoms, $B = 4/3\sum_{i=1}^{3}\sum_{j=1}^{3}(a_i a_j)B(i,j)$ (Å^2), and isotropic thermal parameters of hydrogen atoms B_{iso} (Å^2)

Atom	*x*	*y*	*z*	*B*
I^1	0.6265	0.062	0.0258	7.82(3)
P^1	0.9922(3)	0.1165(3)	0.1254(4)	3.51(8)
O^1	1.088(1)	0.0768(7)	0.245(1)	5.2(3)
O^2	1.097(1)	0.1299(8)	0.071(1)	6.9(3)
C^1	0.917(1)	0.031(1)	0.150(1)	3.8(3)
C^2	0.956(1)	0.0399(9)	0.076(2)	3.8(4)
C^3	1.051(1)	0.080(1)	0.142(2)	4.4(4)
C^4	1.141(1)	0.098(1)	0.139(1)	3.7(3)
C^5	1.192(1)	0.076(1)	0.035(1)	4.3(4)
C^6	1.294(1)	0.054(1)	0.051(2)	5.2(4)
C^7	1.361(1)	0.053(1)	0.164(2)	5.8(5)
C^8	1.314(1)	0.073(1)	0.260(2)	4.7(4)
C^9	1.204(1)	0.097(1)	0.254(1)	4.4(4)
C^{10}	0.966(1)	0.186(1)	0.242(1)	4.3(4)
C^{11}	0.881(1)	0.177(1)	0.307(2)	5.3(4)
C^{12}	0.860(2)	0.228(2)	0.396(2)	6.7(5)
C^{13}	0.938(2)	0.291(1)	0.413(2)	7.8(6)
C^{14}	1.017(2)	0.303(2)	0.347(3)	10.0(8)
C^{15}	1.037(2)	0.248(1)	0.257(2)	7.2(5)
C^{16}	0.941(1)	0.153(1)	0.023(1)	4.1(4)
C^{17}	0.854(1)	0.121(1)	0.094(1)	4.9(4)
C^{18}	0.814(2)	0.148(1)	0.209(2)	5.8(5)
C^{19}	0.872(2)	0.213(2)	0.247(2)	7.9(6)
C^{20}	0.954(2)	0.248(1)	0.180(2)	6.8(5)
C^{21}	0.999(2)	0.217(1)	0.066(2)	5.7(5)
C^{22}	1.185(2)	0.175(1)	0.130(3)	9.3(7)
C^{23}	1.277(3)	0.176(2)	0.074(3)	21(1)
H^5	1.1481	0.0798	0.0430	6
H^6	1.3294	0.0356	0.0214	6
H^7	1.4370	0.0347	0.1743	7
H^8	1.3587	0.0676	0.3351	7
H^9	1.1713	0.1174	0.3248	6
H^{10}	0.8279	0.1348	0.2896	7
H^{12}	0.7978	0.2203	0.4421	9
H^{13}	0.9244	0.3217	0.4813	10
H^{14}	1.0632	0.3482	0.3621	13
H^{15}	1.0980	0.2558	0.2093	9
H^{17}	0.8162	0.0784	0.0601	6
H^{18}	0.7488	0.1232	0.2566	7
H^{19}	0.8505	0.2330	0.3270	9
H^{20}	0.9849	0.2940	0.2120	8
H^{21}	1.0644	0.2408	0.0190	7
H^{112}	0.8360	0.0333	0.1122	6
H^{113}	0.9411	0.0094	0.2561	6
H^{211}	0.9785	0.0210	0.0003	5
H^{212}	0.8960	0.0750	0.0549	5

Table 5. (Contd.)

Atom	*x*	*y*	*z*	*B*
H^{222}	1.1596	0.2277	0.1328	10
H^{223}	1.2042	0.1568	0.2088	10
H^{231}	1.3315	0.2048	0.1137	18
H^{232}	1.2546	0.1936	0.0083	18
H^{233}	1.2992	0.1226	0.0676	18

[a] Hydrogen atoms were not refined.

Synthesis and alkylation of 3-(triphenylphosphonio)propanoate (**I**) have been described in [1].

Reaction of triphenylphosphine with acrylic acid in benzene. A solution of 0.55 g of acrylic acid was added dropwise with stirring to a solution of 2.02 g of triphenylphosphine in 7 ml of absolute benzene. Strong heat release was observed. The reaction mixture was allowed to stand at room temperature for 1 day. Two layers formed and were separated by decanting. The lower layer was treated with absolute diethyl ether. A precipitate formed and was filtered off, washed with diethyl ether, and dried in a vacuum to obtain crystals of compound **IV**, yield 46%, mp 82–84°C. ^{31}P NMR spectrum: δ_P 25 ppm. IR spectrum: ν(CO) 1605 cm^{-1}. The higher layer was concentrated in a vacuum. Colorless crystals formed and were reprecipitated from aqueous 2-propanol. By spectral data, the isolated compound (yield 38%, mp 78–79°C) was identified as triphenylphosphine.

Reaction of phosphabetaine I with acetyl bromide. A solution of 1.2 g of betaine **I** in 5 ml of chloroform was treated with a double excess of acetyl bromide. The reaction was fast and involved strong heat release. The postreaction mixture was treated with K_2SO_3 to remove acetic acid. The yield of compound **VI** was 45 %. ^{31}P NMR spectrum: δ_P 25.45 ppm.

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