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Molecular structures of some tertiary phosphine betaines in their crystalline adducts

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Abstract

Direct reaction of Ph_3P and $Ph_2P(CH_2)_2PPh_2$ with acrylic acid in AcOEt–acetone yielded the tertiary phosphine betaine triphenylphosphoniopropionate, $Ph_3P^+(CH_2)_2CO_2^-$ (L^1), and the novel double betaine ethylenebis(diphenylphosphoniopropionate) $^-O_2C(CH_2)_2Ph_2P^+(CH_2)_2Ph_2P^+(CH_2)_2CO_2^-$ (L^2), respectively. Reaction of Ph_3P with fumaric acid in AcOEt/acetone did not afford the corresponding betaine derivative $Ph_3P^+CH(CO_2H)CH_2CO_2^-$, but decarboxylates to L^1 in situ. Four adducts of L^1, L^2 and $Ph_3P^+(CH_2)_3CO_2^-$ (L^3) have been prepared and characterized by single-crystal X-ray analysis. In $L^1{\cdot}2H_2O$, **1**, two betaine molecules are joined by donor hydrogen bonds from solvated H_2O molecules to form ten-membered rings which are further linked by hydrogen bonds to form chains extending parallel to [1 0 0]. In $(HL^1)_2{\cdot}(O_2CCH{=}CHCO_2){\cdot}HO_2CCH{=}CHCO_2H{\cdot}2H_2O$, **2**, the fumaric acid molecules, fumarate anions and water molecules are interlinked by hydrogen bonds to form layers with an interlayer separation of $1/c^* = 10.713(4)$ Å; the HL^1 cations are sandwiched between adjacent layers and connected to them through hydrogen bonding. In $L^2{\cdot}(CH_3)_2CO{\cdot}5H_2O$, **3**, two independent L^2 molecules adopt different orientations and are cross-linked by hydrogen bonds with the water molecules to form layers with an interlayer spacing of $1/a^* = 10.341(1)$ Å; the $(CH_3)_2CO$ molecules are sandwiched between adjacent layers. In $[(HL^3)_2(NO_3)]NO_3$, **4**, two independent HL^3 cations are joined by one of the NO_3^- group to form a dimeric cation.

Keywords: Tertiary phosphine betaine; Triphenylphosphoniopropionate; Triphenylphosphoniobutyrate; Ethylenebis (diphenylphosphoniopropionate); Crystal structure

1. Introduction

Tertiary amine betaine compounds are zwitterionic molecules bearing a naked carboxylate group and a positively charged quaternary ammonium moiety R_3N^+. As a consequence of this dipolar structure, betaines and their derivatives usually have high melting points, high solubility in aqueous solution and insolubility in non-polar solvents [1]. However, the solubility of betaine derivatives in non-polar solvents can be altered through suitable modification of the R groups on the nitrogen atom, and the resulting products may be used as surfactants and phase transfer catalysts [2]. The structures of several tertiary amine betaines have been characterized in their hydrochloride or hydrated forms [3–5].

Tetraorganophosphonium salts are known to behave as phase-transfer catalysts and have the ability to alter the surface tension of water [6]. They have also been widely used in organic synthesis. For

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example, vinylphosphonium salts are valuable synthetic reagents used in the synthesis of heterocyclic compounds, cycloadditions and Michael additions [7–10].

In contrast to tertiary amine betaines, to our knowledge tertiary phosphine betaine derivatives, although first reported long ago in 1894 [11], have not been structurally characterized by single crystal X-ray analysis until now. In the present paper, we report the direct reaction of Ph_3P and $Ph_2P(CH_2)_2PPh_2$ (dppe) with acrylic acid in AcOEt–acetone to give the corresponding acid-free betaine compounds, and of Ph_3P with fumaric acid which led to the formation of $Ph_3P^+(CH_2)_2CO_2^-$. Four adducts containing neutral or protonated forms of these betaine compounds have been prepared and fully characterized by single crystal X-ray analysis.

2. Experimental

2.1. Preparation

$Ph_3P^+(CH_2)_3CO_2HCl$ was prepared by a reported method [12] and the solvents and other chemicals were used as purchased. Solid [^{31}P]NMR spectrum was measured on a Bruker ASX-300 solid state FT-NMR spectrometer using 85% H_3PO_4 as the reference standard.

2.1.1. Synthesis of $[Ph_3P(CH_2)_2CO_2]\cdot 2\,H_2O$ 1

Ph_3P (26.2 g, 100 mmol) was dissolved in AcOEt–acetone (100 cm^3, v/v, 4:1), and then acrylic acid (7.0 cm^3, 100 mmol) was added with stirring at room temperature. A white crystalline precipitate began to form after 0.5 h. The slurry was stirred for 24 h at ambient temperature. The precipitate obtained was washed with ether and recrystallized in ethanol to yield $Ph_3P^+(CH_2)_2CO_2^-$ (22 g, 66%), solid [^{31}P]NMR δ_{11} = 14.86, δ_{22} = 22.84 and δ_{33} = 26.71 ppm. Colorless prismatic crystals of **1** suitable for X-ray work were crystallized from EtOH–H_2O.

2.1.2. Synthesis of $[Ph_3P^+(CH_2)_2CO_2H]_2(O_2CCHCHCO_2)\cdot HO_2CCHCHCO_2H\cdot 2H_2O$, 2

Ph_3P (5.3 g, 20 mmol) was dissolved in AcOEt–acetone (20 cm^3, v/v, 4:1), and then fumaric acid (2.3 g, 20 mmol) was added. The resulting solution was stirred at room temperature for 24 h. The precipitate obtained was washed with ether, then recrystallized in EtOH–H_2O to afford colorless prismatic crystals of **2** (2.2 g, 47%).

2.1.3. Synthesis of $[Ph_2P(CH_2)(CH_2)_2CO_2]_2\cdot 5H_2O\cdot(CH_3)_2CO$, 3

$Ph_2P(CH_2)_2PPh_2$ (8.0 g, 20 mmol) was dissolved in AcOEt–acetone (40 cm^3, v/v, 4:1), and then acrylic acid (2.8 cm^3, 40 mmol) was added. The resulting solution was stirred at room temperature for 24 h. The precipitate obtained was washed using ether and recrystallized in ethanol to give $[^-O_2C(CH_2)_2Ph_2P^+(CH_2)_2Ph_2P^+(CH_2)_2CO_2^-]$ (3.5 g, 32%). Colorless prismatic crystals of **3** were crystallized from H_2O–acetone.

2.1.4. Synthesis of $[\{Ph_3P^+(CH_2)_3CO_2H\}_2\cdot NO_3](NO_3)$, 4

This compound was obtained from the reaction of $[Ph_3P^+(CH_2)_3CO_2H]Cl$ with $AgNO_3$ in an aqueous medium. The white precipitate (AgCl) formed was filtered out and colorless prismatic crystals of **4** suitable for X-ray analysis were deposited from evaporation of the filtrate.

2.2. Crystallographic data collection and structure determination

Information concerning X-ray data collection and structure refinement is summarized in Table 1. The intensities of **1–3** were collected at 290 K in the ω-scan mode [13] on a Nicolet R3m/V diffractometer using monochromated Mo-Kα radiation (λ = 0.71073 Å). Unit-cell parameters were calculated from least-squares fitting of the 2θ angles for 25 selected strong reflections. Crystal stability was monitored by recording two check reflections at intervals of 120 data measurements, and no significant variation was detected. An empirical absorption correction based on azimuthal scan was applied to the raw intensities in data processing for compounds **1–3**.

The intensity data of complexes **4** were collected at 290 K on a Rigaku RAXIS-IIC imaging-plate diffractometer using monochromated Mo-Kα radiation (λ = 0.71073 Å) from a rotating-anode generator operating at 50 kV and 90 mA ($2\theta_{max}$ = 55°, 36 5° oscillation

Table 1
Crystallographic data for compounds **1–4**.

Formula	$C_{21}H_{23}O_4P$ (**1**)	$C_{25}H_{25}O_7P_1$ (**2**)	$C_{35}H_{48}O_{10}P_2$ (**3**)	$C_{44}H_{42}N_2O_{10}P_2$ (**4**)
M	370.4	936.8	690.7	820.7
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
Crystal size (mm)	0.30 × 0.30 × 0.36	0.28 × 0.28 × 0.30	0.38 × 0.43 × 0.50	0.15 × 0.20 × 0.40
a (Å)	9.164(3)	9.318(2)	13.811(1)	9.359(2)
b (Å)	12.834(4)	11.807(3)	12.494(2)	41.758(8)
c (Å)	16.507(4)	12.133(4)	14.589(2)	11.546(2)
α (°)	90	66.13(2)	106.10(1)	90
β (°)	98.72(3)	74.72(2)	101.14(2)	109.76(3)
γ (°)	90	86.15(2)	108.30(2)	90
U (Å^3)	1919(1)	1176(1)	1811(1)	4247(2)
Z	4	2	2	4
D_c (g cm^{-3})	1.282	1.322	1.267	1.284
F (000)	784	492	736	1720
μ (cm^{-1})	1.66	1.6	1.74	1.62
Transmission coefficients	0.87–0.89	0.92–0.97	0.90–0.99	
$2\theta_{max}$ (°)	45	50	45	55.2
No. of data collected	2520	4167	5701	4205
No. of data used, n	1575 [$F > 4\sigma(F)$]	3534[$F > 4\sigma(F)$]	4384[$F > 4\sigma(F)$]	3824[$F > 4\sigma(F)$]
No. of variables, p	236	299	425	551
R	0.061	0.063	0.061	0.072
R'	0.068	0.073	0.082	0.093
S	1.81	1.27	2.21	2.53

$R = \Sigma\Delta/\Sigma|F_o|$, $R' = [\Sigma w\Delta^2/\Sigma|F_o|^2]^{1/2}$ and $S = [w\Delta^2/(n-p)]^{1/2}$ where $w = [\sigma^2(F_o) + K|F_o|^2]^{-1}$, $\Delta = ||F_o| - |F_c||$; $10^4K = 5$, 1, 6 and 5 for compounds **1–4**, respectively.

Extinction parameter $\chi = 0.00228$, 0.00313, 0.00000 and 0.00454 for complexes **1–4**, respectively where $F_{corr} = F_c(1 + 0.002\ \chi F_c^2/\sin 2\theta)^{-1/4}$.

frames in the range 0–180°, exposure 10 min per frame) [14].

The structures of all four compounds were solved by the direct method. All non-hydrogen atoms were refined anisotropically by full-matrix least squares. The hydrogen atoms of the compounds were placed in their calculated positions with C–H = 0.96 Å, assigned fixed isotropic thermal parameters, and allowed to ride on their respective parent carbon atoms. The contributions of these hydrogen atoms were added to the structure-factor calculations, but their positions were not refined.

All calculations were carried out on a PC 486 using the SHELXTL-PLUS program package [15]. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [16]. Final atomic coordinates and equivalent isotropic thermal parameters for the four crystal structures, along with their estimated standard deviations, are presented in Tables 2–5, and selected bond lengths and angles are listed in Tables 6–9.

3. Results and discussion

3.1. Synthesis of the compounds

Direct reaction of triphenylphosphine, Ph_3P, with acrylic acid at a molar ratio of 1:1 in AcOEt–acetone mixed solvent led to the formation of the tertiary phosphine betaine triphenylphosphoniopropionate, $Ph_3P^+(CH_2)_2CO_2$, as shown in Eq. (1)

$$Ph_3P + H_2C{=}CHCO_2H \xrightarrow[25°C,\ 24h]{AcOEt-acetone} Ph_3P(CH_2)_2CO_2 \qquad (1)$$

Usually the nucleophilic addition of tertiary phosphine to an unsaturated carboxylic acid, such as propiolic acid, is carried out in concentrated

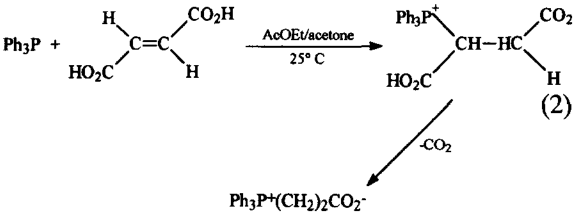
Table 2
Atomic coordinates (× 10^4) and equivalent isotropic displacement coefficients U_{eq} (Å^2 × 10^3) for compound **1**

Atom	x	y	z	U_{eq} [a]
P(1)	1473(2)	511(1)	2438(1)	40(1)
C(1)	4101(7)	972(5)	1876(4)	64(3)
C(2)	5554(8)	1331(5)	1973(5)	79(3)
C(3)	6255(8)	1570(5)	2727(6)	81(4)
C(4)	5588(8)	1465(5)	3414(5)	81(3)
C(5)	4134(7)	1111(5)	3331(4)	71(3)
C(6)	3386(6)	855(4)	2552(4)	48(2)
C(7)	2222(7)	-1061(5)	3549(4)	59(2)
C(8)	2023(8)	-1741(5)	4169(4)	70(3)
C(9)	750(9)	-1672(5)	4515(4)	70(3)
C(10)	-313(8)	-931(5)	4253(4)	64(3)
C(11)	-104(6)	-243(4)	3636(3)	50(2)
C(12)	1175(6)	-302(4)	3284(3)	41(2)
C(13)	470(6)	2271(4)	3151(4)	50(2)
C(14)	-237(7)	3216(5)	3144(4)	60(3)
C(15)	-993(7)	3596(5)	2418(5)	65(3)
C(16)	-1010(6)	3047(5)	1691(4)	59(3)
C(17)	-283(6)	2098(4)	1703(4)	51(2)
C(18)	447(5)	1699(4)	2441(3)	38(2)
C(19)	917(6)	-189(4)	1494(3)	49(2)
C(20)	-719(6)	-524(4)	1383(3)	54(2)
C(21)	-1277(9)	-982(5)	524(4)	65(3)
O(1)	-2603(6)	-839(5)	260(3)	116(3)
O(2)	-398(6)	-1443(3)	165(3)	85(2)
O(1W)	-4178(11)	790(8)	127(6)	252(6)
O(2W)	-2364(7)	2175(7)	-171(3)	201(5)

[a] U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

acidic media (HCl or HBr), or $R_3P{\cdot}HBr$ is used to replace R_3P in an organic solvent [17,18]. Unlike most tertiary amine betaines, the anhydrous form of this compound is quite stable in air. Its IR spectrum shows that the asymmetric stretching frequency of the carboxylate group is masked by the stretching frequencies of the Ph_3P moiety. The stationary solid-state [^{31}P]NMR spectrum of this compound exhibits one peak with δ_{iso} at 21.47 ppm (δ_{11} = 14.86, δ_{22} = 22.84 and δ_{33} = 26.71 ppm) which is smaller than that in $OPPh_3$ (δ = 28.99 ppm) [19].

Reaction of Ph_3P with fumaric acid in AcOEt–acetone did not yield the expected product Ph_3P^+ $CH(CO_2H)CH_2CO_2^-$, but instead compound **2** was obtained. It is believed that in this reaction the compound $HO_2CCH_2(P^+Ph_3)CH_2CO_2^-$ is an intermediate which undergoes decarboxylation in situ [20,21].



The isolated product from this reaction is an adduct (**2**) of $Ph_3P^+(CH_2)_2CO_2^-$ and fumaric acid which has a "sandwich-like" structure.

Reaction of 1,2-bis(diphenylphosphino)ethane with acrylic acid in AcOEt–acetone afforded the corresponding novel double betaine $^-O_2C(CH_2)_2Ph_2P^+(CH_2)_2Ph_2P^+(CH_2)_2CO_2^-$ as shown in Eq. (3).

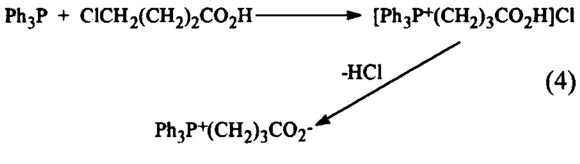
$$\mathrm{Ph_2P(CH_2)_2PPh_2 + H_2C{=}CHCO_2H} \xrightarrow[25^\circ\mathrm{C}]{\mathrm{AcOEt-acetone}} \mathrm{[Ch_2Ph_2P(CH_2)_2CO_2]_2} \qquad (3)$$

Table 3
Atomic coordinates ($\times 10^5$ for *P*, $\times 10^4$ for other atoms) and equivalent isotropic displacement coefficients U_{eq} ($Å^2 \times 10^4$ for *P*, $Å^2 \times 10^3$ for other atoms) for compound **2**

Atom	*x*	*y*	*z*	U_{eq} [a]
P(1)	22224(7)	32106(6)	37890(6)	412(3)
C(1)	-223(4)	1894(4)	3923(4)	76(2)
C(2)	-1591(5)	1267(4)	4514(5)	89(2)
C(3)	-2305(4)	1123(4)	5708(5)	83(2)
C(4)	-1657(5)	1585(5)	6333(5)	110(3)
C(5)	-271(4)	2220(4)	5751(4)	85(2)
C(6)	431(3)	2390(2)	4543(3)	49(1)
C(7)	2880(3)	4454(3)	5120(3)	53(1)
C(8)	3334(3)	4490(4)	6114(3)	66(2)
C(9)	3841(4)	3442(4)	6925(3)	72(2)
C(10)	3941(4)	2367(4)	6749(3)	76(2)
C(11)	3489(4)	2308(3)	5780(3)	63(1)
C(12)	2948(3)	3351(3)	4962(3)	45(1)
C(13)	3288(3)	5468(3)	1886(3)	52(1)
C(14)	3155(4)	6690(3)	1140(3)	59(1)
C(15)	1758(4)	7186(3)	1189(3)	60(1)
C(16)	497(4)	6454(3)	1966(3)	62(1)
C(17)	610(3)	5229(3)	2727(3)	53(1)
C(18)	2023(3)	4731(2)	2694(2)	43(1)
C(19)	3432(3)	2281(3)	3100(3)	52(1)
C(20)	5059(3)	2686(3)	2549(3)	61(1)
C(21)	6029(3)	1621(3)	2502(3)	49(1)
O(1)	5605(3)	561(2)	3085(3)	83(1)
O(2)	7376(3)	1976(2)	1797(2)	70(1)
Fumaric acid and anions				
O(4)	6872(3)	-4479(2)	830(3)	90(1)
C(23)	8126(3)	-4207(3)	166(3)	51(1)
O(3)	8580(2)	-3095(2)	-674(2)	66(1)
C(22)	9291(3)	-5141(3)	272(3)	50(1)
C(24)	5627(3)	-41(2)	160(3)	45(1)
C(25)	6893(3)	-796(2)	-176(3)	45(1)
O(5)	8089(2)	-676(2)	47(3)	67(1)
O(6)	6657(2)	-1500(2)	-666(2)	62(1)
H_2O solvate molecule				
O(1W)	9042(2)	233(2)	1527(2)	66(1)

[a] U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

The hydrochloride of $Ph_3P^+(CH_2)_3CO_2^-$ was prepared according to the literature method (Eq. (4)) [12]. Reaction of equimolar quantities of Ph_3P and γ-chlorobutyric acid at 140°C for ca. 20 h led to the formation of $[Ph_3P(CH_2)_3CO_2H]Cl$, and further reaction of this compound with $AgNO_3$ afforded $[\{Ph_3P(CH_2)_3CO_2H\}_2(NO_3)]NO_3$ (**3**). The acid-free betaine $Ph_3P^+(CH_2)_3CO_2^-$ can be easily obtained by passing an aqueous solution of $[Ph_3P(CH_2)_3CO_2H]Cl$ through an anion-exchange (OH^- form) column (Eq. (4)).



$$Ph_3P + ClCH_2(CH_2)_2CO_2H \longrightarrow [Ph_3P^+(CH_2)_3CO_2H]Cl \xrightarrow{-HCl} Ph_3P^+(CH_2)_3CO_2^- \quad (4)$$

3.2. *Crystal structures of compounds* **1–4**

3.2.1. *Crystal structure of $Ph_3P(CH_2)_2CO_2{\cdot}2H_2O$* (**1**)

As illustrated in Fig. 1, in the inner salt $Ph_3P^+(CH_2)_2CO_2^-$ the phosphorus atom is coordinated

Table 4
Atomic coordinates (× 10^5 for *P*, × 10^4 for other atoms) and equivalent isotropic displacement coefficients U_{eq} (Å^2 × 10^4 for *P*, Å^2 × 10^3 for other atoms) for compound **3**

Atom	*x*	*y*	*z*	U_{eq}[a]
P(1)	748(9)	14 787(8)	44 357(6)	342(4)
C(1)	-822(5)	3104(4)	3972(4)	69(3)
C(2)	-1757(5)	3537(5)	3728(4)	85(3)
C(3)	-2953(5)	3031(4)	3799(3)	64(2)
C(4)	-3240(4)	2081(4)	4118(4)	63(2)
C(5)	-2318(4)	1635(4)	4365(3)	52(2)
C(6)	-1104(3)	2127(3)	4273(3)	39(2)
C(7)	1649(4)	3135(4)	6278(3)	51(2)
C(8)	2813(5)	4039(4)	6948(3)	64(2)
C(9)	3869(5)	4415(4)	6630(4)	70(2)
C(10)	3800(4)	3902(4)	5654(4)	65(2)
C(11)	2658(4)	3001(4)	4968(3)	50(2)
C(12)	1583(3)	2616(3)	5288(3)	37(2)
C(13)	-484(3)	308(3)	4929(3)	35(2)
C(14)	229(4)	841(3)	3223(3)	41(2)
C(15)	-1048(4)	-125(3)	2485(3)	49(2)
C(16)	-1180(4)	-252(4)	1400(3)	46(2)
O(1)	-345(3)	495(3)	1222(2)	68(2)
O(2)	-2173(3)	-1095(3)	763(2)	69(2)
P(2)	6971(10)	65 653(8)	-4783(7)	376(4)
C(17)	3146(4)	6660(4)	-589(4)	67(2)
C(18)	4284(5)	7161(5)	-772(4)	88(3)
C(19)	4562(5)	8211(5)	-975(4)	82(3)
C(20)	3721(5)	8751(5)	-983(5)	90(3)
C(21)	2570(5)	8267(4)	-809(4)	71(3)
C(22)	2254(4)	7202(3)	-613(3)	43(2)
C(23)	-452(4)	4975(3)	-2429(3)	49(2)
C(24)	-1329(4)	4503(4)	-3372(3)	60(2)
C(25)	-2227(4)	4978(4)	-3583(3)	64(2)
C(26)	-2290(4)	5911(4)	-2858(3)	58(2)
C(27)	-1419(4)	6389(4)	-1908(3)	51(2)
C(28)	-492(3)	5936(3)	-1684(3)	38(2)
C(29)	687(4)	5370(3)	-9(3)	43(2)
C(30)	372(4)	7725(3)	342(3)	47(2)
C(31)	1199(4)	8239(4)	1434(3)	53(2)
C(32)	530(4)	7795(4)	2148(3)	46(2)
O(3)	1132(3)	8340(3)	3062(2)	68(2)
O(4)	-554(3)	6933(3)	1779(2)	57(1)
$(CH_3)_2CO$ solvate molecule				
O(5)	3767(5)	11 174(4)	6166(4)	144(3)
C(33)	4759(6)	11 650(5)	6848(5)	93(3)
C(34)	4850(7)	11 347(8)	7754(5)	146(5)
C(35)	5906(7)	12 449(7)	6800(6)	138(6)
H_2O solvate molecules				
O(1W)	2158(3)	1085(3)	1116(2)	75(2)
O(2W)	3789(3)	2155(3)	3064(3)	85(2)
O(3W)	-4324(5)	4646(5)	-1074(4)	152(3)
O(4W)	3420(4)	10 335(4)	3947(3)	107(2)
O(5W)	-3077(3)	6642(3)	811(3)	102(2)

[a] U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

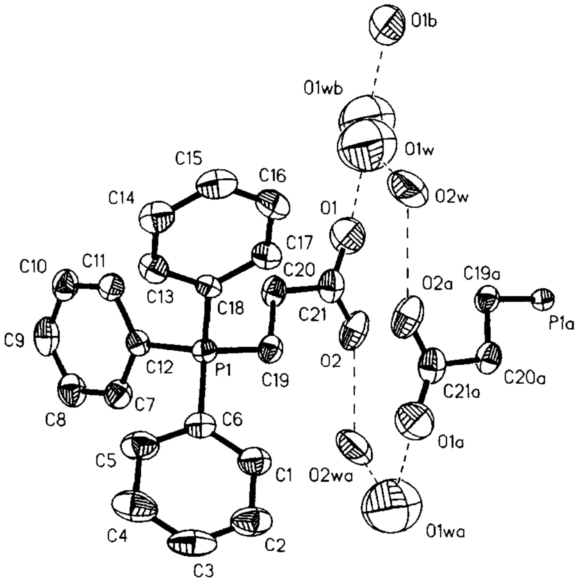


Fig. 1. ORTEP drawing of the molecule structure and atom numbering scheme of $[Ph_3P(CH_2)_2CO_2]\cdot 2H_2O$ **1**. Hydrogen atoms are omitted for clarity, and hydrogen bonds are indicated by broken lines. The thermal ellipsoids are drawn at the 35% probability level. Symmetry codes: (a) $-x, -y, -z$; b) $-1-x, -y, -z$.

in a normal tetrahedral environment with P–C bonds ranging from 1.789(6) to 1.805(5) Å and angles around the phosphorus atom from 107.2(2) to 110.9(3)°. The phenyl groups are arranged in a propeller-like fashion with dihedral angles of 60.5, 65.6 and 79.5° between them. Although it is anticipated that an aryl group attaching to phosphorus will have a shorter P–C bond length due to overlap between the phosphorus 3d orbitals and the π-oribitals of the phenyl ring (for example, the average P–C bond length of 1.831 Å [22] in Ph_3P is somewhat shorter than 1.868 Å in $(cyclohexyl)_3P$ [19]), the four P–C bond lengths in **1** are not significantly different within experimental error. In the betaine molecule the propionate moiety stretches away from the bulky Ph_3P group to achieve a more stable conformation, thereby ruling out the possible alternative lactone-like structure in which the phosphorus atom is five-coordinated [19] and the ylid structure [23].

The carboxylate group of **1** has nearly identical C–O bond lengths [C–O = 1.22 (1) and 1.24(1) Å] and C–C–O angles [115.7(6) and 118.5(6)°], and the O–C–O angle is 125.7(6)°. These values are comparable to those found in $Me_3NCH_2CO_2\cdot H_2O$ [C–O = 1.251(4) and 1.239(3) Å; C–C–O = 112.6(2) and 120.0(2)°; O–C–O = 127.2(2)°] [4].

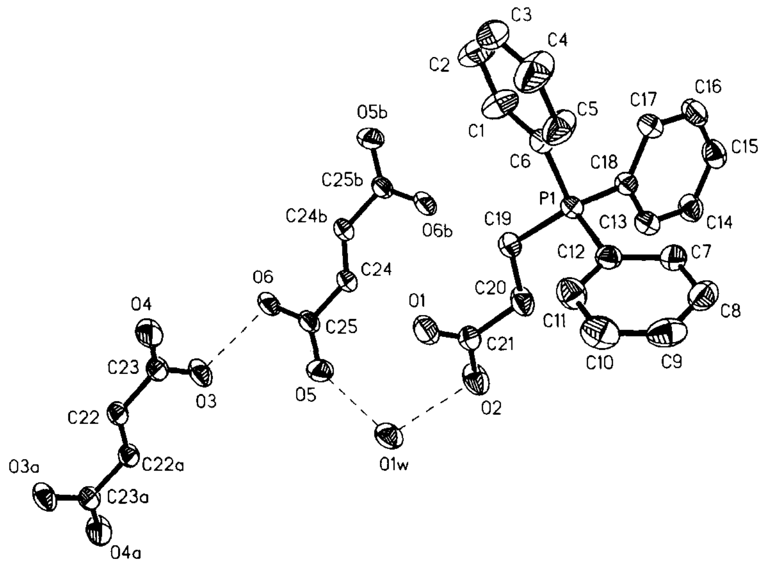


Fig. 2. ORTEP drawing of the molecule structure and atom numbering scheme of $[Ph_3P^+(CH_2)_2CO_2H]_2(O_2CCH{=}CHCO_2)\cdot HO_2CCH{=}CHCO_2\cdot H2H_2O$, **2**. Hydrogen atoms are omitted for clarity, and hydrogen bonds are indicated by broken lines. The thermal ellipsoids are drawn at the 35% probability level. Symmetry codes: (a) $2-x, -1-y, -z$; (b) $1-x, -y, -z$.

Table 5

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients U_{eq} ($\text{Å}^2 \times 10^3$) for compound **4**

Atom	x	y	z	U_{eq}[a]
P(1)	2860(1)	7006(1)	1693(1)	45(1)
C(1)	3533(6)	7617(1)	1049(7)	65(3)
C(2)	4329(7)	7905(1)	1252(7)	78(3)
C(3)	5448(7)	7951(1)	2392(7)	75(3)
C(4)	5787(7)	7719(1)	3295(7)	78(3)
C(5)	5013(6)	7430(1)	3064(6)	59(2)
C(6)	3882(5)	7380(1)	1920(6)	52(2)
C(7)	1390(6)	6771(1)	3246(6)	71(3)
C(8)	337(7)	6797(1)	3841(7)	74(3)
C(9)	-566(7)	7061(2)	3683(7)	81(4)
C(10)	-426(7)	7311(1)	2973(8)	86(4)
C(11)	617(6)	7292(1)	2378(6)	64(3)
C(12)	1548(5)	7020(1)	2504(6)	50(2)
C(13)	2517(6)	6980(1)	-806(5)	55(2)
C(14)	1759(7)	6896(1)	-2018(6)	65(3)
C(15)	336(7)	6773(1)	-2362(7)	74(3)
C(16)	-352(7)	6731(1)	-1473(6)	72(3)
C(17)	370(5)	6811(1)	-238(6)	54(2)
C(18)	1850(5)	6939(1)	84(5)	49(2)
C(19)	4210(5)	6686(1)	2274(5)	50(2)
C(20)	5390(5)	6668(1)	1646(5)	57(2)
C(21)	6483(5)	6394(1)	2086(5)	55(2)
C(22)	7606(5)	6372(1)	1421(6)	54(2)
O(1)	8480(5)	6112(1)	1769(4)	81(2)
O(2)	7714(4)	6559(1)	689(5)	79(2)
P(2)	1148(1)	4435(1)	3662(1)	45(1)
C(23)	-1251(5)	4016(1)	3373(6)	61(2)
C(24)	-2385(6)	3877(1)	3703(7)	66(3)
C(25)	-2551(6)	3960(1)	4848(7)	75(3)
C(26)	-1561(7)	4176(1)	5620(7)	75(3)
C(27)	-430(6)	4315(1)	5240(6)	64(3)
C(28)	-290(5)	4238(1)	4143(5)	47(2)
C(29)	-1233(6)	4770(1)	2021(6)	63(3)
C(30)	-1838(8)	5017(2)	1198(7)	89(3)
C(31)	-958(9)	5258(1)	1034(7)	87(3)
C(32)	607(9)	5251(1)	1667(7)	94(4)
C(33)	1249(7)	5008(1)	2451(6)	71(3)
C(34)	308(5)	4766(1)	2678(5)	48(2)
C(35)	3695(6)	4353(1)	5682(6)	61(2)
C(36)	4815(8)	4442(2)	6777(8)	94(4)
C(37)	4836(9)	4753(2)	7189(8)	102(4)
C(38)	3783(9)	4972(2)	6510(7)	88(4)
C(39)	2672(6)	4885(1)	5431(7)	75(3)
C(40)	2634(5)	4570(1)	5014(5)	49(2)
C(41)	1880(5)	4159(1)	2831(5)	48(2)
C(42)	3131(5)	4295(1)	2378(5)	55(2)
C(43)	3655(5)	4049(1)	1656(5)	56(2)
C(44)	4829(5)	4176(1)	1135(6)	63(3)
O(3)	5223(5)	4451(1)	1196(5)	91(2)
O(4)	5422(5)	3948(1)	655(4)	83(2)

Table 5 Continued

Atom	x	y	z	U_{eq}[a]
NO_3^- anions				
N(1)	6861(5)	8430(1)	232(5)	56(2)
O(5)	7967(4)	8588(1)	226(4)	73(2)
O(6)	6815(5)	8139(1)	50(5)	90(2)
O(7)	5770(4)	8565(1)	432(5)	84(2)
N(2)	-1464(6)	4010(1)	-525(7)	61(3)
O(8)	-2272(17)	3970(3)	-1544(20)	105(8)
O(9)	-1918(15)	4105(3)	303(16)	133(8)
O(10)	-39(14)	4015(3)	-220(16)	70(6)
O(8')	-1391(21)	3900(3)	-1583(18)	111(9)
O(9')	-2889(22)	4028(4)	-665(19)	159(11)
O(10')	-398(30)	4069(5)	246(20)	183(14)

[a] U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms O(8)–O(10) and O(8()–O(10() belong to a two-fold disordered NO_3^- group and each has a site occupancy of 1/2.

On the other hand, two symmetry-related $Ph_3P^+(CH_2)_2CO_2^-$ molecules are linked by donor hydrogen bonds from a pair of solvated water molecules to form a ten-membered ring (Fig. 1). It is worthy of note that the carboxylate group forms hydrogen bonds with bridging water molecules through the anti lone pairs rather than the syn pairs [O···O–C angles 131.6(5) and 148.5(6)°]. This hydrogen bonding pattern contrasts with that in carboxylic acid dimers which achieve a cyclic structure through syn–syn hydrogen bonding and without the participation of bridging water molecules.

Furthermore, the present dimeric structures are linked through hydrogen bonds between the lattice water molecules [O···O = 2.539(8) Å] to form chains which extend parallel to [1 0 0].

3.2.2. *Crystal structure of* $[Ph_3P(CH_2)_2CO_2H]_2(O_2CHCCHCO_2)\cdot HO_2CHCCHCO_2H\cdot 2H_2O$ (**2**)

Compound **2** comprises $[Ph_3P^+(CH_2)_2CO_2H]$ cations, fumarate anions, fumaric acid molecules and water molecules packed together in the crystal lattice (Fig. 2). The coordination geometry about the phosphorus atom is very close to that in **1** with P–C bond lengths ranging from 1.782(2) to 1.804(3) Å and C–P–C angles from 107.4(1) to 110.2(1)°. The C–O bond lengths of the carboxylate groups [C(21)–O(1) = 1.194(3) and C(21)–O(2) = 1.303(3) Å; C(23)–O(3) =

Table 6
Selected bond lengths (Å) and angles (°) for compound **1**

P(1)–C(6)	1.789 (6)	P(1)–C(12)	1.798 (5)
P(1)–C(18)	1.792 (5)	P(1)–C(19)	1.805 (5)
C(19)–C(20)	1.544 (8)	C(20)–C(21)	1.549 (8)
C(21)–O(1)	1.24 (1)	C(21)–O(2)	1.22 (1)
C(6)–P(1)–C(12)	108.9(3)	C(6)–P(1)–C(18)	107.2(2)
C(12)–P(1)–C(18)	110.5(3)	C(6)–P(1)–C(19)	110.9(3)
C(12)–P(1)–C(19)	109.0(2)	C(18)–P(1)–C(19)	110.3(2)
C(19)–C(20)–C(21)	113.1(5)	C(20)–C(21)–O(1)	115.7(6)
C(20)–C(21)–O(2)	118.5(6)	O(1)–C(21)–O(2)	125.7(6)
Hydrogen bonding			
O(1)···O(1w)	2.520(8)	O(1w)···O(2w)	2.519(8)
O(2w)···O(2a)	2.694(8)	O(1w)···O(1wb)	2.539(8)
O(1w)···O(1)–C(21)	131.6(5)	O(1wb)···O(1w)···O(1)	71.0(6)
O(2w)···O(1w)···O(1)	102.8(4)	O(1w)···O(2w)···O(2a)	113.5(5)
O(2w)···O(2a)···C(21a)	148.5(6)		

Symmetry codes: (a) $-x, -y, -z$; (b) $-1-x, -y, -z$.

Table 7
Selected bond lengths (Å) and angles (°) for compound **2**

$[Ph_3P(CH_2)_2CO_2H]^+$ cation			
P(1)–C(6)	1.805(3)	P(1)–C(12)	1.796(4)
P(1)–C(18)	1.782(2)	P(1)–C(19)	1.804(3)
C(19)–C(20)	1.510(4)	C(20)–C(21)	1.509(4)
C(21)–O(1)	1.194(3)	C(21)–O(2)	1.303(3)
C(6)–P(1)–C(12)	108.2(1)	C(6)–P(1)–C(18)	110.2(1)
C(12)–P(1)–C(18)	108.2(1)	C(6)–P(1)–C(19)	107.4(1)
C(12)–P(1)–C(19)	109.1(2)	C(18)–P(1)–C(19)	113.7(1)
C(19)–C(20)–C(21)	112.0(3)	C(20)–C(21)–O(1)	122.9(2)
C(20)–C(21)–O(2)	113.3(2)	O(1)–C(21)–O(2)	123.8(3)
$[HO_2CCH_2=CH_2CO_2H]$ molecule			
O(4)–C(23)	1.209(3)	C(23)–O(3)	1.307(3)
C(23)–C(22)	1.486(4)	C(22)–C(22a)	1.308(5)
O(4)–C(23)–O(3)	124.1(3)	O(4)–C(23)–C(22)	121.3(2)
O(3)–C(23)–C(22)	114.6(2)	C(23)–C(22)–C(22a)	123.6(3)
$[O_2CCH_2=CH_2CO_2]^{2+}$ anion			
C(25)–O(5)	1.243(4)	C(25)–O(6)	1.260(5)
C(24)–C(25)	1.500(4)	C(24)–C(24b)	1.311(6)
C(25)–C(24)–C(24b)	124.1(4)	C(24)–C(25)–O(5)	117.7(3)
C(24)–C(25)–O(6)	117.1(3)	O(5)–C(25)–O(6)	125.2(3)
Hydrogen bonding			
O(3)···O(6)	2.513(2)	O(5)···O(1w)	2.773(2)
O(5)···O(1wc)	2.785(2)	O(2)···O(1w)	2.570(3)
O(6)···O(3)–C(23)	113.5(3)	O(1w)···O(2)–C(21)	115.4(2)
O(3)···O(6)–C(25)	113.9(3)	O(1w)···O(5)···O(1wc)	89.2(3)

Symmetry code: (a) $2-x,\ -1-y,\ -z$; (b) $1-x,\ -y,\ -z$.

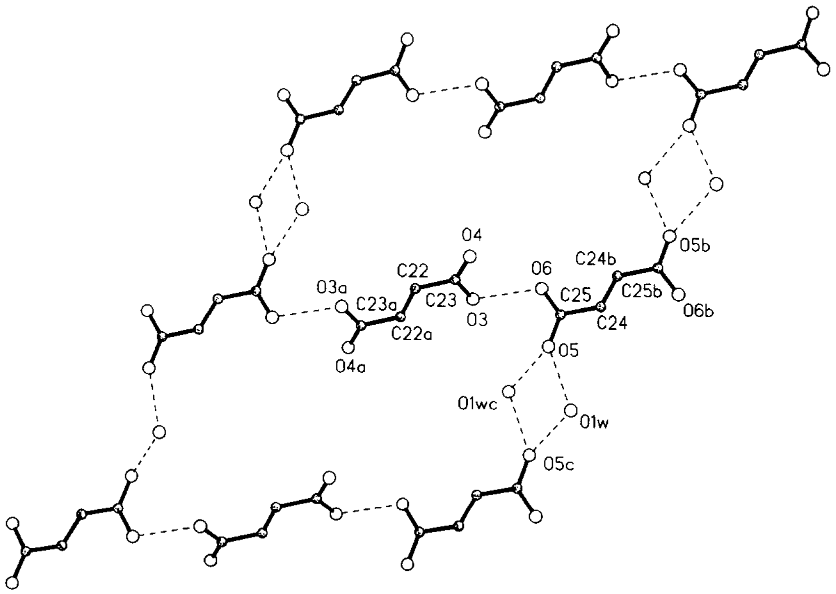


Fig. 3. Perspective view of a layer formed by fumaric acid molecules, fumarate anions and water molecules in **2**. Hydrogen atoms are omitted for clarity, and hydrogen bonds are indicated by broken lines. Symmetry codes: (a) $2-x,\ -1-y,\ -z$; (b) $1-x,\ -y,\ -z$; (c) $2-x,\ -y,\ -z$.

Table 8
Selected bond lengths (Å) and angles (°) for **3**

P(1)–C(6)	1.789(5)	P(1)–C(12)	1.787(3)
P(1)–C(13)	1.800(4)	P(1)–C(14)	1.795(4)
C(13)–C(13A)	1.549(9)	C(14)–C(15)	1.521(4)
C(15)–C(16)	1.520(6)	C(16)–O(1)	1.233(6)
C(16)–O(2)	1.250(4)	P(2)–C(22)	1.783(4)
P(2)–C(28)	1.789(3)	P(2)–C(29)	1.805(5)
P(2)–C(30)	1.795(5)	C(29)–C(29A)	1.564(8)
C(30)–C(31)	1.521(5)	C(31)–C(32)	1.529(7)
C(32)–O(3)	1.251(4)	C(32)–O(4)	1.253(4)
C(6)–P(1)–C(12)	110.0(2)	C(6)–P(1)–C(13)	109.0(2)
C(12)–P(1)–C(13)	109.5(2)	C(6)–P(1)–C(14)	107.3(2)
C(12)–P(1)–C(14)	111.1(2)	C(13)–P(1)–C(14)	109.9(2)
P(1)–C(13)–C(13A)	111.7(4)	C(14)–C(15)–C(16)	113.8(3)
C(15)–C(16)–O(1)	118.4(3)	C(15)–C(16)–O(2)	115.8(4)
O(1)–C(16)–O(2)	125.7(4)	C(22)–P(2)–C(28)	108.8(2)
C(22)–P(2)–C(29)	107.6(2)	C(28)–P(2)–C(29)	109.1(2)
C(22)–P(2)–C(30)	109.6(2)	C(28)–P(2)–C(30)	109.2(2)
C(29)–P(2)–C(30)	112.5(2)	P(2)–C(29)–C(29A)	112.3(4)
C(30)–C(31)–C(32)	115.5(3)	C(31)–C(32)–O(3)	115.8(3)
C(31)–C(32)–O(4)	118.4(3)	O(3)–C(32)–O(4)	125.8(4)
Hydrogen bonding			
O(4w)···O(3)	2.747(4)	O(2w)···O(1w)	2.760(4)
O(1w)···O(1)	2.771(4)	O(1w)···O(2c)	2.748(4)
O(2c)···O(5wb)	2.716(4)	O(5wb)···O(4b)	2.818(5)
O(5w)···O(3w)	2.874(5)		
O(4w)···O(3)–C(32)	128.0(2)	O(2w)···O(1w)···O(1)	106.9(2)
O(1)···O(1w)···O2c)	109.5(2)	O(1w)···O(2c)···O(5wb)	113.1(2)
O(3w)···O(5w)···O(4)	114.1(2)	O(3wb)····O(5wb)···O(2c)	117.6(2)

Symmetry codes: (a) – x, – y, 1 – z; (b) – x, 1 – y, – z; (c) – x, – y, – z.

1.209(3) and C(23)–O(4) = 1.307(3) Å; C(25)–O(5) = 1.243(4) and C(25)–O(6) = 1.260(5) Å] unambiguously indicate that the betaine molecule exists in the protonated form and one of the fumaric acid molecules as a dianion.

As anticipated, the fumaric acid molecule and fumarate anion which occupy $\bar{1}$ sites each has a planar configuration with mean atomic deviation from the least-squares plane of 0.034 and 0.025 Å, respectively. The dihedral angle between the fumaric acid molecule [comprising atoms C(22), C(23), O(3) and O(4)] and fumarate anion [comprising atoms C(24), C(25), O(5) and O(6)] is 110.2(2)°. The C–O bond lengths and O–C–O angle for these two species are comparable to those in $[Ph_3P^+(CH_2)_2CO_2H]$ and $Ph_3P^+(CH_2)_2CO_2^-$, respectively, which implies that the carboxylate groups in $Ph_3P^+(CH_2)_2CO_2^-$ and the fumarate anion have similar electronic properties.

As depicted in Fig. 3, the fumaric acid molecules and fumarate anions are arranged alternately to form chains through hydrogen bonding [O(3)···O(6) = 2.513(2) Å; O(6)···O(3)–C(23) = 113.5(3)° and O(3)···O(6)–C(25) = 113.9(3)°], and such chains are further joined by donor hydrogen bonds from the lattice water molecules to the fumarate anions [O(5)···O(1w) = 2.773(2) and O(5)···O(1wc) = 2.785(2) Å; O(1w)···O(5)···O(1wc) = 89.2(3)°; the dihedral angle between planes C(25)O(5)O(6) and O(5)O(1w)O(1wc)O(5c) is 39.2°] to form negatively charged layers which lie parallel to the (0 0 1) plane. The distance between adjacent layers is $1/c^*$ = 10.713(4) Å.

The $[Ph_3P(CH_2)_2CO_2H]^+$ cations are sandwiched between the layers, each forming a hydrogen bond with a lattice water molecule belonging to one layer [O(2)···O(1w) = 2.570(3) Å, O(1w)···O(2)–C(21) = 115.4(2)°]. The torsion angle O(1w)···O(2)–C(21)–C(20) at – 175.4° indicates that the water molecule is nearly coplanar with the carboxylate group of the $[Ph_3P(CH_2)_2CO_2H]^+$ cation.

Table 9
Selected bond lengths (Å) and angles (°) for **4**

P(1)–C(6)	1.804 (4)	P(1)–C(12)	1.783(7)
P(1)–C(18)	1.800 (5)	P(1)–C(19)	1.806(4)
C(19)–C(20)	1.508 (9)	C(20)–C(21)	1.507(6)
C(21)–C(22)	1.494 (9)	C(22)–O(1)	1.340(6)
C(22)–O(2)	1.175 (8)	P(2)–C(28)	1.807(6)
P(2)–C(34)	1.795 (4)	P(2)–C(40)	1.800(5)
P(2)–C(41)	1.783 (5)	C(41)–C(42)	1.540(8)
C(42)–C(43)	1.509 (8)	C(43)–C(44)	1.512(9)
C(44)–O(3)	1.198 (6)	C(44)–O(4)	1.315(8)
C(6)–P(1)–C(12)	108.7(2)	C(6)–P(1)–C(18)	110.7(3)
C(12)–P(1)–C(18)	109.2(2)	C(6)–P(1)–C(19)	108.8(2)
C(12)–P(1)–C(19)	110.5(2)	C(18)–P(1)–C(19)	108.9(2)
P(1)–C(19)–C(20)	113.2(4)	C(19)–C(20)–C(21)	114.1(5)
C(20)–C(21)–C(22)	113.3(5)	C(21)–C(22)–O(1)	111.2(5)
C(21)–C(22)–O(2)	124.9(5)	O(1)–C(22)–O(2)	124.0(6)
C(28)–P(2)–C(34)	109.5(2)	C(28)–P(2)–C(40)	108.3(3)
C(34)–P(2)–C(40)	110.5(2)	C(28)–P(2)–C(41)	109.6(2)
C(34)–P(2)–C(41)	108.7(3)	C(40)–P(2)–C(41)	110.3(2)
P(2)–C(41)–C(42)	114.7(3)	C(41)–C(42)–C(43)	111.0(4)
C(42)–C(43)–C(44)	113.3(4)	C(43)–C(44)–O(3)	124.4(6)
C(43)–C(44)–O(4)	112.5(4)	O(3)–C(44)–O(4)	123.1(7)

3.2.3. Crystal structure of $[CH_2Ph_2P(CH_2)_2CO_2]_2\cdot(CH_3)_2CO\cdot5H_2O$ (3)

Compound 3 consists of a packing of $[Ph_2P(CH_2)(CH_2)_2CO_2]_2$ molecules, lattice water molecules and acetone molecules. There are two $[CH_2Ph_2P(CH_2)_2CO_2]$ moieties from two distinct but nearly identical betaine molecules (A and B) in the asymmetric unit (Fig. 4). Two of the phenyl groups on different phosphorus atoms and the $P(CH_2)_2P$ chain lie in a plane (mean atomic deviation

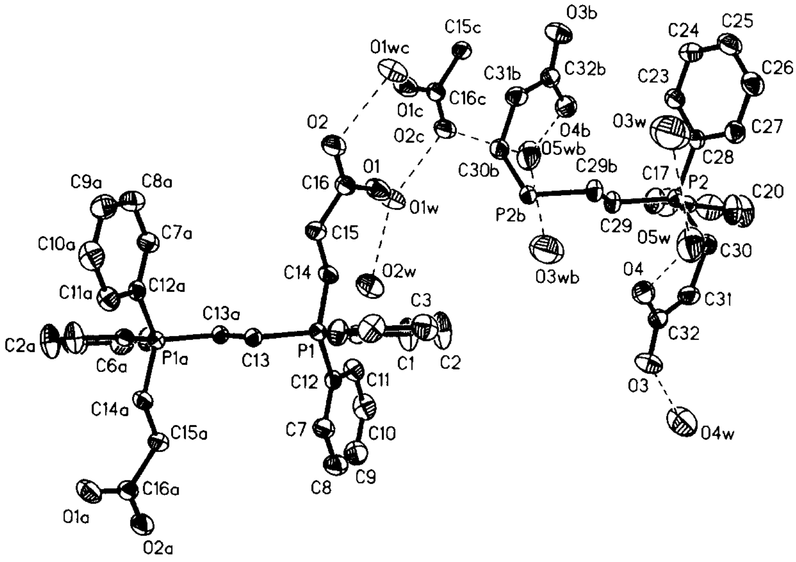


Fig. 4. ORTEP drawing of the molecule structure and atom numbering scheme of $[CH_2Ph_2P(CH_2)_2CO_2]_2$ in **3**. Hydrogen atoms are omitted for clarity, and hydrogen bonds are indicated by broken lines. The thermal ellipsoids are drawn at the 35% probability level. symmetry codes: (a) $-x$, $-y$, $1-z$; (b) $-x$, $1-y$, $-z$. (c) $-x$, $-y$, $-z$.

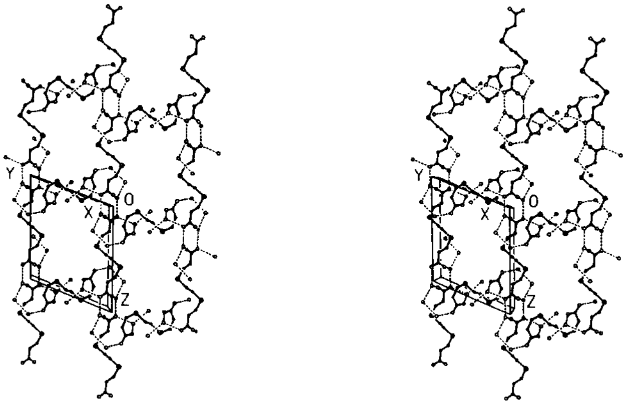


Fig. 5. Stereoview of the layer structure of compound 3. Phenyl groups and hydrogen atoms are omitted for clarity, and hydrogen bonding is indicated by broken lines. The origin of the cell lies at the right upper corner with *a* pointing toward the reader, *b* from right to left, and *c* downward.

0.044 Å from the least-squares plane), with the remaining phenyl groups protruding on both sides to reach the most stable conformation. The tetrahedral geometry about phosphorus [P–C bond lengths ranging from 1.783(4) to 1.805(5) Å and C–P–C angles from 117.3(2) to 110.0(2)°] and the geometry about the carboxylate group [C–O = 1.233(6) and 1.250(4) Å, O–C–O = 125.7° for A; C–O = 1.251(4) and 1.253(4) Å, O–C–O = 125.8° for B] are very close to those in **1**.

As shown in Fig. 5, the betaine molecules of type A are linked with the lattice water molecules to form an infinite chain parallel to [1 0 0], and such chains are joined by hydrogen bonds between the betaine molecules of type B and the lattice water molecules to form layers with an interlayer spacing of $1/a^* = 10.341(1)$ Å. The solvated acetone molecules which have weak hydrogen bonding interaction with the solvated water molecule [O(5)···O(4W) = 3.016 (2) Å] are sandwiched between the layers.

3.2.4. *Crystal structure of* $[Ph_3P(CH_2)_3CO_2H](NO_3)$ (**4**)

Compound 4 comprises a packing of two distinct but nearly identical $[Ph_3P(CH_2)_3CO_2H]^+$ cations (designated I and II) and NO_3^- anions in the crystal lattice. The tetrahedral geometry about each phosphorus atom is similar to those in **1**–**3** with P–C bond lengths ranging from 1.777(5) to 1.815(6) Å and C–P–C angles from 108.3(3) to 110.7(3)°.

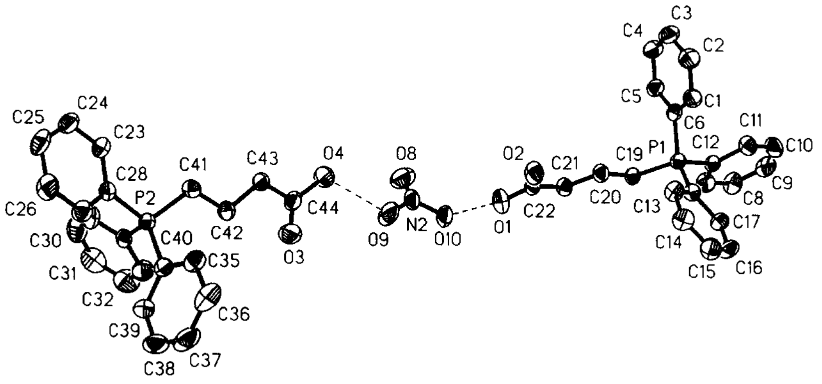


Fig. 6. ORTEP drawing of the molecule structure and atom numbering scheme of the bridged $[\{Ph_3P(CH_2)_3CO_2H\}_2(NO_3)]^+$ moiety in **4**. Hydrogen atoms are omitted for clarity, and hydrogen bonds are indicated by broken lines. The thermal ellipsoids are drawn at the 35% probability level.

However, the orientation of the phenyl groups in these two betaine cations are markedly different: the dihedral angles between the phenyl groups are 93.8, 125.3 and 84.6° in I, and 74.1, 54.5 and 90.0° in II. The geometry about the carboxylate groups [C–O = 1.180(8) and 1.336(6) Å, O–C–O = 124.7(5)° for I; C–O = 1.200(6) and 1.313(8) Å, O–C–O = 123.5(6)° for II] is comparable to those in $[Ph_3P(CH_2)_2CO_2H]^+$ of **2**. This result indicates that the induction effect of the Ph_3P^+ moiety on the carboxylate group may become less important as the number of methylene spacers between the Ph_3P^+ moiety and the carboxylate group is increased.

The independent $[Ph_3P(CH_2)_3CO_2H]^+$ cations form donor hydrogen bonds to a NO_3^- anion, which exhibits two-fold orientational disorder, to give a bridged dimeric structure (Fig. 6). The dihedral angles between the NO_3^- and the carboxylate groups are 68.0 and 110.3°, and that between the two carboxylate groups is 42.3°.

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