

(Cremer & Pople, 1975*b*). Luger & Buschmann (1983) had previously reported slight anomalies in the COC and OCC bond lengths for 103 and 148 K data when compared with theoretical calculations. The experimental data collected at 5 K reported above no longer show this discrepancy. Puckering parameters (Cremer & Pople, 1975*a*) are $q_2 = 34.3$ (2) pm (5 K) and 34.0 (2) pm (120 K) and $\psi_2 = 90$ (–)°.

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Structure of Triethylammonium Phenylcarbamoyl Phosphate

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Abstract. $C_6H_{16}N^+ \cdot C_7H_7NO_5P^-$, $M_r = 318.31$, orthorhombic, *Pbca*, $a = 9.290$ (3), $b = 11.160$ (4), $c = 31.529$ (9) Å, $V = 3269$ (2) Å³, $Z = 8$, $D_m = 1.31$, $D_x = 1.293$ Mg m⁻³, Mo *K*α, $\lambda = 0.71069$ Å, $\mu = 1.83$ cm⁻¹, $F(000) = 1360$, $T = 299$ (1) K, final $R = 0.041$ for 2425 non-zero reflections. The phosphate ester bond, P—O 1.637 (2) Å, is the longest RO—P(OH)O₂⁻ distance so far observed. The phenyl ring makes a dihedral angle of 7.3 (8)° with the plane through the carbamoyl group.

Introduction. Naturally occurring phosphate esters of carboxylic acids are effective phosphoryl donors and are a source of energy for many enzymic reactions. In particular, carbamoyl phosphate (CAP) is known to play an important role in the urea cycle and is a precursor of the pyrimidine ring in pyrimidine nucleotide synthesis (Southerland, 1990). This easily hydrolysed compound (Bergmeyer, 1970) has not been investigated in the crystalline state. The structural study reported here is the first of a compound with a carbamoyl phosphate system and is also probably the first of a compound containing a carboxyl group linked to a monoesterified phosphate group. This work is a continuation of our studies on the crystal structures of biologically important esters (Weichsel & Lis, 1990).

Experimental. The title compound was prepared by the reaction of phenyl isocyanate, triethylamine and crystalline orthophosphoric acid in acetonitrile solution (Cramer & Winter, 1959). Plate-shaped crystals were obtained from ethanol solution by slow evaporation. D_m by flotation in a CHCl₃/C₂H₄Cl₂ mixture. Specimen of dimensions $0.7 \times 0.7 \times$

0.25 mm was cut from a larger crystal; preliminary examination by rotation and Weissenberg photographs. Syntex *P2*₁ diffractometer with graphite monochromator and Mo *K*α radiation were used for lattice parameters (15 reflections in the range $20 < 2\theta < 26^\circ$) and intensity measurements; ω - 2θ scans. 5198 reflections below $2\theta = 60^\circ$ ($-13 \leq h \leq 13$, $-15 \leq k \leq 0$, $0 \leq l \leq 44$), of which 3225 had $I > 3\sigma(I)$. After each group of 50 reflections, two standards were measured; variation $\pm 3\%$. The data were corrected for Lorentz and polarization effects. An absorption correction was made using *DIFABS* (Walker & Stuart, 1983); minimum and maximum absorption corrections 0.868 and 1.061. Symmetry-related reflections were averaged after *DIFABS* to give 2425 independent data with $|F| > 0$; $R_{\text{merge}} = 0.0172$. Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1986) and refined by *SHELXL76* (Sheldrick, 1976), based on F values with $w = 1/\sigma^2(F_o)$; P, N, O and C anisotropic, H isotropic. The positional parameters of the H atoms were refined with the constraints $d(C-H) = 1.08$, $d(O-H) = 0.96$ and $d(N-H) = 1.00$ Å. Final $R = 0.0410$ and $wR = 0.0394$. Maximum Δ/σ was 0.07. Residual electron density within -0.27 and 0.19 e Å⁻³. The final atomic parameters are given in Table 1.*

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54466 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0248]

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic thermal parameters

$$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$U_{eq}/U_{iso}(\text{\AA}^2)$
P	0.09663 (6)	0.01270 (5)	0.43988 (2)	0.0322 (2)
O(1)	0.18912 (16)	-0.00586 (18)	0.48013 (6)	0.0408 (5)
O(2)	-0.06151 (15)	0.00758 (17)	0.44942 (5)	0.0411 (5)
O(3)	0.14514 (19)	0.11794 (15)	0.41486 (6)	0.0431 (5)
O(4)	0.14277 (18)	-0.10985 (15)	0.41480 (6)	0.0369 (5)
O(5)	0.00030 (21)	-0.08227 (17)	0.35716 (7)	0.0527 (6)
N(1)	0.14483 (23)	-0.24787 (19)	0.36452 (7)	0.0373 (6)
N(2)	-0.06788 (24)	0.29252 (20)	0.41599 (9)	0.0487 (7)
C(1)	0.08621 (28)	-0.14136 (21)	0.37634 (8)	0.0350 (6)
C(2)	0.11042 (29)	-0.31397 (23)	0.32762 (8)	0.0388 (7)
C(3)	0.18838 (32)	-0.41839 (25)	0.32065 (10)	0.0483 (8)
C(4)	0.15762 (37)	-0.48935 (31)	0.28598 (11)	0.0676 (10)
C(5)	0.04714 (45)	-0.45757 (33)	0.25827 (12)	0.0809 (12)
C(6)	-0.02814 (43)	-0.35414 (33)	0.26503 (11)	0.0780 (12)
C(7)	0.00115 (34)	-0.28162 (29)	0.29943 (10)	0.0593 (9)
C(8)	0.0102 (4)	0.4090 (3)	0.40874 (13)	0.0617 (10)
C(9)	-0.0911 (6)	0.5149 (4)	0.40482 (19)	0.0938 (16)
C(10)	-0.1670 (5)	0.2570 (4)	0.38071 (13)	0.0780 (12)
C(11)	-0.0944 (7)	0.2477 (7)	0.33863 (17)	0.1092 (19)
C(12)	-0.1446 (4)	0.2891 (3)	0.45779 (12)	0.0636 (10)
C(13)	-0.0476 (6)	0.3047 (4)	0.49550 (15)	0.0845 (14)
H(1)	0.142 (4)	-0.007 (4)	0.5076 (6)	0.101 (14)
H(N1)	0.212 (3)	-0.285 (3)	0.3860 (8)	0.069 (10)
H(N2)	-0.002 (4)	0.221 (3)	0.4170 (13)	0.114 (15)

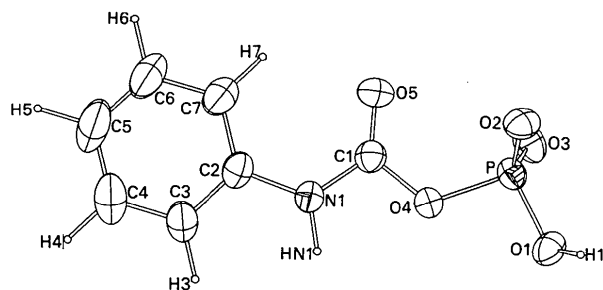


Fig. 1. Molecular geometry and numbering scheme of phenyl-carbamoyl phosphate monoanion.

Discussion. The crystals are composed of phenyl-carbamoyl phosphate monoanions and triethylammonium cations. The molecular structure and the numbering scheme for the anion are shown in Fig. 1. Selected bond lengths, bond angles and torsion angles are listed in Table 2.

The anion contains a hydrophilic phosphate group at one end and a hydrophobic phenyl ring at the other end. The plane of the phenyl ring forms an angle of 7.3 (8)° with the plane through C(1), N(1), O(4) and O(5). The P—O(4) bond which corresponds to the 'high-energy' phosphate ester bond in CAP is relatively long. Indeed, this is the longest P—O(ester) bond so far found among monoionized phosphate groups in phosphate monoesters (Starynowicz, 1986). The hydroxyl phosphate oxygen O(1) is *trans* to C(1) and is involved in the smallest O(ester)—P—O angle. The P atom is *trans* to N(1) so that H(N1) points away from the terminal phosphate O atoms. This conformation is in accordance with the

Table 2. Selected distances (Å), bond angles (°), torsion angles (°) and hydrogen-bond geometries (Å, °)

P—O(1)	1.546 (2)	C(4)—C(5)	1.394 (5)
P—O(2)	1.501 (2)	C(5)—C(6)	1.366 (5)
P—O(3)	1.485 (2)	C(6)—C(7)	1.380 (5)
P—O(4)	1.637 (2)	C(7)—C(2)	1.397 (4)
O(4)—C(1)	1.368 (3)	N(2)—C(8)	1.506 (4)
O(5)—C(1)	1.199 (3)	N(2)—C(10)	1.497 (5)
C(1)—N(1)	1.360 (3)	N(2)—C(12)	1.499 (5)
C(2)—N(1)	1.414 (3)	C(8)—C(9)	1.515 (5)
C(2)—C(3)	1.390 (4)	C(10)—C(11)	1.492 (7)
C(3)—C(4)	1.380 (5)	C(12)—C(13)	1.502 (6)
O(1)—P—O(2)	112.0 (1)	C(2)—C(3)—C(4)	119.9 (3)
O(1)—P—O(3)	111.9 (1)	C(3)—C(4)—C(5)	120.2 (4)
O(1)—P—O(4)	98.0 (1)	C(4)—C(5)—C(6)	119.6 (4)
O(2)—P—O(3)	115.7 (1)	C(5)—C(6)—C(7)	121.1 (4)
O(2)—P—O(4)	108.7 (1)	C(2)—C(7)—C(6)	119.4 (3)
O(3)—P—O(4)	108.9 (1)	C(9)—C(8)—N(2)	112.7 (3)
P—O(4)—C(1)	122.9 (2)	C(11)—C(10)—N(2)	113.7 (4)
O(4)—C(1)—O(5)	124.2 (3)	C(13)—C(12)—N(2)	114.1 (3)
O(4)—C(1)—N(1)	108.3 (3)	C(1)—N(1)—C(2)	126.2 (3)
O(5)—C(1)—N(1)	127.5 (3)	C(8)—N(2)—C(10)	114.3 (3)
C(3)—C(2)—C(7)	119.7 (3)	C(8)—N(2)—C(12)	112.6 (3)
C(3)—C(2)—N(1)	116.7 (2)	C(10)—N(2)—C(12)	110.8 (3)
C(7)—C(2)—N(1)	123.6 (3)		
P—O(4)—C(1)—O(5)	1.2 (4)	O(4)—C(1)—N(1)—C(2)	177.1 (3)
P—O(4)—C(1)—N(1)	-179.1 (3)	O(5)—C(1)—N(1)—C(2)	-3.3 (4)
O(1)—P—O(4)—C(1)	177.8 (3)	O(5)—C(1)—N(1)—H(N1)	-177 (3)
O(2)—P—O(4)—C(1)	61.2 (3)	C(1)—N(1)—C(2)—C(3)	177.1 (4)
O(3)—P—O(4)—C(1)	-65.7 (4)	C(1)—N(1)—C(2)—C(7)	-5.0 (5)
X—H...O	X...O	H...O	∠X—H...O
O(1)—H(1)...O(2)	2.518 (2)	1.55 (2)	178 (3)
N(1)—H(N1)...O(3 ^b)	2.927 (3)	1.94 (3)	165 (3)
N(2)—H(N2)...O(3)	2.777 (3)	1.78 (3)	167 (3)

Symmetry code: (i) $-x, -y, 1-z$; (ii) $0.5-x, y-0.5, z$.

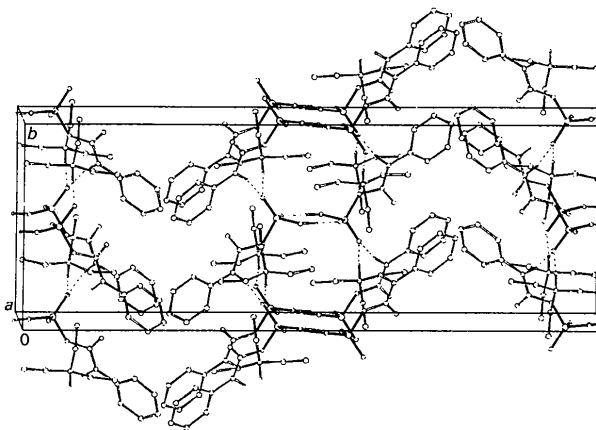


Fig. 2. The packing arrangement. Dashed lines show hydrogen bonds.

results of studies on the hydrolysis of CAP and its *N*-derivatives (Allen, Richelson & Jones, 1966), where the authors suggested that the decomposition of CAP monoanions bearing an aromatic group on the N atom proceeds by P—O(ester) bond cleavage and that the H atom of the amide N does not participate in the reaction.

The crystal packing and the hydrogen-bonding scheme are shown in Fig. 2. Hydrogen-bonding parameters are listed in Table 2. The anions form pairs related by a centre of inversion and linked through hydrogen bonds between phosphate O atoms. These pairs are linked by hydrogen bonds between amide N and terminal phosphate oxygen O(3) into infinite chains parallel to *b*. The O(3) atom also participates in a hydrogen bond with the N atom of the triethylammonium cation. The exterior surfaces of the chains are defined by the hydrophobic phenyl and ethyl groups whereas the hydrophilic groups occupy the interiors of the chains.

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Structure of Methyl 4-Methylthio-2-oxo-3-phenyl-2,3-dihydro-1,3-thiazole-5-carboxylate

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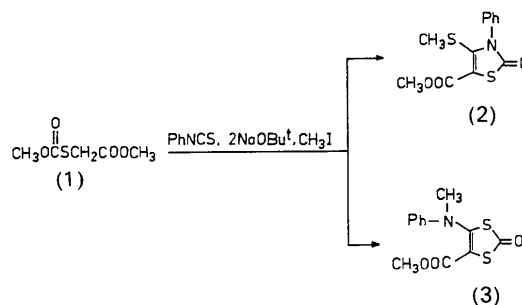
Abstract. $C_{12}H_{11}NO_3S_2$, $M_r = 281.4$, triclinic, $P\bar{1}$, $a = 9.492$ (2), $b = 11.110$ (3), $c = 6.854$ (2) Å, $\alpha = 75.68$ (1), $\beta = 79.54$ (1), $\gamma = 68.43$ (1)°, $V = 648.0$ (3) Å³, $Z = 2$, $D_m = 1.42$, $D_x = 1.44$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.354$ mm⁻¹, $F(000) = 292$, room temperature, final $R = 0.038$, $wR = 0.032$ for 2186 reflections. The structure was solved by the heavy-atom method. Bond distances and angles are within the expected ranges. The thiazoline ring is almost exactly planar and twisted to the benzene ring by 99.4°.

Introduction. Recently we have been able to show that CH-acidic thio- and dithiocarbonates react with heterocumulenes giving the products of heterocyclization (Augustin & Dölling, 1990). In the case of the reaction of the thiocarbonate (1) with phenyl isothiocyanate, two cyclization directions might be possible. The products expected according to the two pathways should be the 1,3-thiazolin-2-one (2) or the 1,3-dithiol-2-one (3). In order to come to a decision between these two alternatives an X-ray analysis of the reaction product has been performed. As a result the reaction product has been identified as the title compound (2).

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Experimental. The title compound (2) was prepared by treatment of methyl methoxycarbonylthioglycolate (1) with phenyl isothiocyanate and sodium *tert*-butoxylate followed by alkylation according to a recently published procedure (Augustin, Dölling & Rudolf, 1989). Pale-yellow clear crystals (m.p. 396–397 K) were obtained by recrystallization from methanol. The density was measured by flotation in aqueous KI solution. All X-ray data were collected on a Stoe STADI-4 diffractometer for a crystal with dimensions 0.4 × 0.3 × 0.1 mm using graphite-monochromated Mo *K*α radiation. The unit-cell dimensions were obtained from least-squares refinement of the setting angles of 25 reflections in the 2θ range 12–25°. Intensity data measurement: ω–2θ scan, 2θ_{max} = 50°, *hkl* range from –10, –12, 0