Table 4. *Hydrogen-bond distances* (Å) *and angles* (°)

D—H$\cdots A$	$D\cdots A$	H$\cdots A$	$\angle D$—H$\cdots A$
N(1)—H(1)$\cdots$O(4)^{ii}	2·74	1·80	159·6
N(3)—H(2)$\cdots$O(W)^{i}	2·85	2·07	169·9
N(6)—H(4)$\cdots$O(W)^{iv}	3·10	2·32	161·1
N(6)—H(5)$\cdots$O(4)^{ii}	3·14	2·40	134·5
O(W)—H(6)$\cdots$O(4)^{iii}	2·77	1·79	169·4
O(W)—H(7)$\cdots$S(2)	3·49	2·66	170·3

Symmetry code
(i) $x, \; 1-y, \; \frac{1}{2}+z$ (iii) $\frac{3}{2}-x, \; \frac{1}{2}-y, \; 1-z$
(ii) $x, \; 1-y, \; \frac{1}{2}+z-1$ (iv) $\frac{1}{2}+x, \; \frac{1}{2}-y, \; \frac{1}{2}+z$

N(1)$\cdots$O(2) or N(3)$\cdots$O(2) interactions, and that they occur in dimeric form (see also Banerjee *et al.*, 1977). However, in this structure as expected we have a different type of hydrogen-bonding pattern (Table 4), mainly attributable to the amino substitution at C(6). H atoms at N(6), N(1) and N(3) enter into strong hydrogen-bonded interactions with symmetry-related O(W) and O(4) atoms. O(W) has a nearly tetrahedral coordination: while it acts as an acceptor for two strong hydrogen bonds from symmetry-related N(3) and N(6) atoms, it also acts as a donor to O(4) and S(2) atoms. The O(W)$\cdots$S(2) interaction is 3·49 Å, with an H$\cdots$S distance of 2·66 Å and O(W)—H$\cdots$S angle of 170·3°, which shows that it is a linear but weak hydrogen bond. This is according to the general observation that in crystal structures of thio-analogues of nucleic acid constituents, S is expected to form weaker hydrogen bonds than the corresponding O analogues (Lin *et al.*, 1971). There is an unusually short intermolecular S$\cdots$S distance of 3·27 Å between molecules related by the diad axis. This suggests that the van der Waals radius of S should be assumed to be near 1·65 Å, instead of a value of 1·85 Å (Pauling, 1960). Evidence from several S-containing compounds suggests that S should have a lower value; however, 1·65 Å is probably an extreme limit. In the structure of 6-mercaptopurine monohydrate (Sletten *et al.*, 1969) there is an S$\cdots$S contact of 3·365 Å.

One of us (SS) thanks the University Grants Commission for financial assistance.

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DL-Diethyl α-Anilinobenzylphosphonate

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(*Received* 4 *April* 1978; *accepted* 24 *May* 1978)

Abstract. $C_{17}H_{22}NO_3P$, FW 319·34, triclinic, $P\bar{1}$, a = 8·824 (4), b = 10·053 (5), c = 9·959 (4) Å, α = 94·13 (2), β = 92·10 (3), γ = 94·97 (3)°, Z = 2, U = 877·01 Å^3, D_c = 1·205, D_m = 1·204 g cm^{-3}, Mo $K\alpha$ radiation (λ = 0·7107 Å, μ = 1·43 cm^{-1}). The structure was solved by *MULTAN* and refined to R = 0·066. Both D and L forms appear in the structure and form centrosymmetric hydrogen-bonded dimers, with N—H$\cdots$O(phosphoryl) = 2·990 Å. The mean value for P—O is 1·566 (4) Å and that for O—Et is 1·455 (9) Å. The phosphoryl P=O bond length is 1·465 (4) Å; C—P is 1·821 (6) Å.

Introduction. Certain derivatives of α-anilinobenzylphosphonic acid have been prepared (Jagodić, 1960; Jagodić & Herak, 1970; Jagodić & Tušek, 1972). Some have been applied as extractants (Jagodić & Grdenić, 1964; Tamhina, Herak & Jagodić, 1973) and reagents for the spectrophotometric determination of metals (Tamhina, Herak & Jagodić, 1975). The IR spectra of neutral esters, monoesters, sodium salts of monoesters, and a free α-anilinobenzylphosphonic acid and its disodium salt have been studied (Jagodić, 1977). Synthesis and basic hydrolysis of diesters of α-anilinobenzylphosphonic acid as well as a conformational study of these compounds using ^{1}H NMR spectroscopy were also reported (Jagodić, 1976).

X-ray analysis of the above series is being carried out to provide information on molecular conformation and hydrogen bonding. In the reactions of metal-complex formation with diesters of α-anilinobenzylphosphonic acid differences in function of the two OC_2H_5 groups were observed. In order to explain such behaviour the crystal structure of the title compound was examined.

$C_{17}H_{22}NO_3P$ (Fig. 1) was first synthesized by Pudovik (1952); a modified method (Jagodić, 1960) was used here. Preliminary unit-cell dimensions and the space group were determined from oscillation and Weissenberg photographs recorded with Cu $K\alpha$ radiation. The cell dimensions given in the *Abstract* were refined from diffractometer measurements. The density was measured pycnometrically with decalin. Intensities were collected on a Philips PW 1100 computer-controlled diffractometer in the ω-scan mode [scan width = 2·0° (θ), scan speed = 0·05° (θ) s^{-1}] with graphite-monochromated Mo $K\alpha$ radiation. The intensities of 2134 observed reflexions [$I \geq 2\sigma(I)$] were measured and used in the calculation [164 reflexions had $I < 2\sigma(I)$]. The data were corrected for Lorentz and polarization effects.

The presence of the chiral centre in the molecule and statistical calculations included in *MULTAN* (Declercq, Germain, Main & Woolfson, 1973) implied the noncentrosymmetric space group $P1$. The overall temperature factor (B = 2·53 Å^2) and a scale factor were determined (Wilson, 1942) and used to compute normalized structure amplitudes (routine *NORMAL* of *MULTAN*). The structure solution in $P1$ was based on 300 reflexions with $|E| > 1{\cdot}43$. The E map corresponding to the solution with the best figure of merit revealed the positions of 23 non-hydrogen atoms. The remaining 21 non-hydrogen atoms were located from the subsequent Fourier synthesis. However, refinement failed in $P1$ (unreasonable interatomic distances and an anisotropic R of 0·09).

The two 'asymmetric units' in the cell were then seen to be related by a centre of symmetry and refinement proceeded successfully in space group $P\bar{1}$. A full-matrix least-squares procedure minimizing $\sum w||F_o| - |F_c||^2$ with $w = 1/\sigma^2_{F_o}$ was used. Heavy-atom coordinates, isotropic thermal parameters and a scale factor were refined to an R of 0·12. Anisotropic refinement and a difference Fourier synthesis were used to locate six H atoms. The H atoms of the phenyl rings were positioned geometrically but the six methyl H atoms were not located. The H atoms were included in structure factor calculations with the isotropic thermal parameters of the bonded C or N atoms; the H parameters were not refined. The final R = 0·066 and R_w = 0·072.

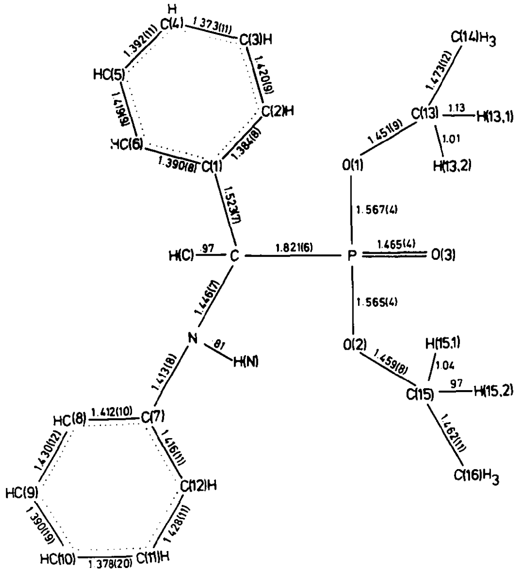

Fig. 1. Structural formula and bond lengths (Å).

Table 1. *Final positional parameters* (×10^4) *for the non-hydrogen atoms*

	x	y	z
P	−452 (2)	354 (2)	7438 (1)
O(1)	−1774 (4)	−619 (4)	6732 (4)
O(2)	−310 (4)	1419 (4)	6367 (4)
O(3)	−696 (4)	876 (4)	8817 (4)
C	1227 (6)	−573 (6)	7312 (5)
C(1)	2728 (6)	303 (5)	7490 (5)
C(2)	3315 (7)	676 (6)	8783 (6)
C(3)	4723 (8)	1480 (7)	8948 (8)
C(4)	5488 (7)	1856 (7)	7840 (8)
C(5)	4897 (8)	1481 (7)	6539 (8)
C(6)	3487 (7)	681 (7)	6361 (6)
C(7)	1891 (7)	−2722 (6)	8179 (7)
C(8)	1802 (9)	−3524 (6)	9287 (8)
C(9)	2633 (12)	−4685 (9)	9220 (12)
C(10)	3437 (12)	−5023 (10)	8088 (17)
C(11)	3499 (9)	−4232 (9)	7014 (13)
C(12)	2720 (7)	−3043 (7)	7027 (9)
C(13)	−2802 (8)	−1501 (8)	7439 (8)
C(14)	−2581 (10)	−2910 (8)	7052 (14)
C(15)	437 (8)	2757 (7)	6720 (8)
C(16)	−569 (9)	3809 (7)	6505 (11)
N	1029 (5)	−1601 (5)	8250 (5)

Scattering factors given by Cromer & Mann (1968) and (for H) by Stewart, Davidson & Simpson (1965) were used. An anomalous-dispersion correction was included for P (Cromer & Liberman, 1970).

The calculations were carried out on the Univac 1100 computer at the University Computing Centre in Zagreb with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

Positional parameters are listed in Tables 1 and 2.*

Table 2. *Positional parameters* ($\times 10^3$) *for the hydrogen atoms*

	x	y	z
H(C)	103	−104	642
H(2)	271	36	965
H(3)	519	180	995
H(4)	657	245	798
H(5)	550	179	568
H(6)	301	37	536
H(8)	114	−327	986
H(9)	264	−531	1006
H(10)	402	−592	805
H(11)	414	−451	615
H(12)	276	−241	619
H(13,1)	230	130	1150
H(13,2)	384	116	1266
H(15,1)	116	284	592
H(15,2)	80	283	766
H(N)	81	−136	901

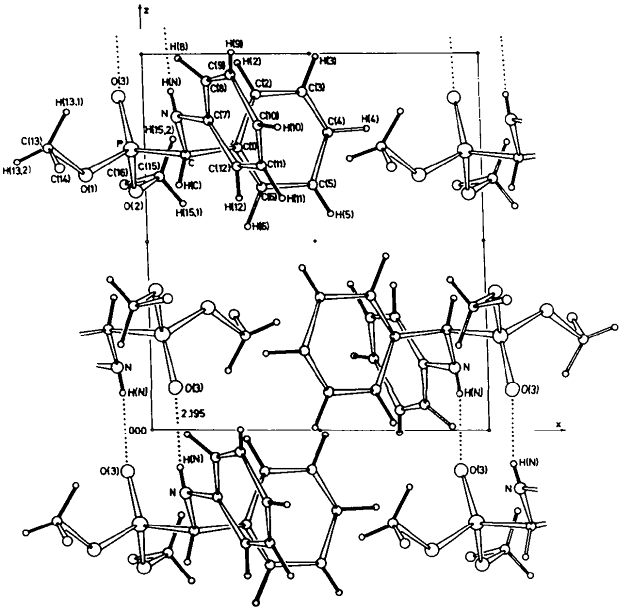

Fig. 2. A projection of the structure along [010]. N–H···O hydrogen bonds between two molecules are marked by dotted lines.

Discussion. The structural formula and bond lengths are given in Fig. 1, and the molecular packing is illustrated in Fig. 2. Bond angles are listed in Table 3.

Generally phosphonates have been classified as substituted orthophosphates. The geometry of the title compound can be described as an $(EtO)_2RP{=}O$ tetrahedron with a single mirror plane. The chiral centre (C, Fig. 1) is responsible for the existence of optically active forms but in the crystal structure there are equal numbers of D and L enantiomers. Optically active forms due to an asymmetric P tetrahedron cannot be expected in this case.

The conformation of the molecule is given by the torsion angles about the C–P bond describing the relative orientation of the C and P tetrahedra (Fig. 3). It corresponds to a staggered arrangement. The phenyl rings are perpendicular to each other with a dihedral angle of 89·9°.

The bond lengths (Fig. 1) and valency angles (Table 3) in the P tetrahedron can be compared with values given for orthophosphate esters by Corbridge (1974). Bond distances P–O(1) = 1·567 (4) and P–O(2) = 1·565 (4) Å, as well as O(1)–C(13) = 1·451 (9) and O(2)–C(15) = 1·459 (8) Å, give no evidence for the different function of the two OC_2H_5 groups in metal-

Table 3. *Bond angles* (°)

O(1)–P–O(2)	99·1 (2)	C(2)–C(3)–C(4)	120·2 (6)
O(1)–P–O(3)	116·3 (2)	C(3)–C(4)–C(5)	121·2 (6)
O(1)–P–C	104·6 (2)	C(4)–C(5)–C(6)	119·2 (7)
O(2)–P–O(3)	115·7 (2)	C(1)–C(6)–C(5)	119·1 (6)
O(2)–P–C	106·5 (2)	C(8)–C(7)–C(12)	123·0 (6)
O(3)–P–C	113·0 (2)	C(8)–C(7)–N	115·9 (6)
P–O(1)–C(13)	124·1 (4)	C(12)–C(7)–N	121·1 (6)
P–O(2)–C(15)	120·9 (4)	C(7)–C(8)–C(9)	116·8 (8)
P–C–C(1)	114·0 (4)	C(8)–C(9)–C(10)	121 (1)
P–C–N	105·5 (4)	C(9)–C(10)–C(11)	121·3 (9)
C(1)–C–N	115·1 (4)	C(10)–C(11)–C(12)	121 (1)
C–C(1)–C(2)	118·7 (5)	C(7)–C(12)–C(11)	117·3 (8)
C–C(1)–C(6)	119·6 (5)	O(1)–C(13)–C(14)	110·3 (7)
C(2)–C(1)–C(6)	121·8 (5)	O(2)–C(15)–C(16)	112·5 (6)
C(1)–C(2)–C(3)	118·6 (6)	C–N–C(7)	121·3 (5)

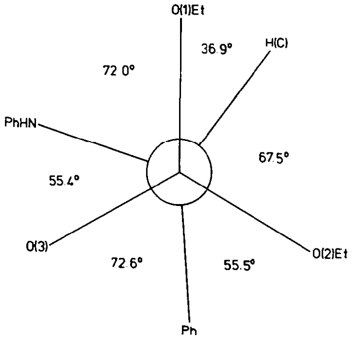

Fig. 3. Newman projection along the C–P bond showing the staggered arrangement.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33646 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

complex formation. The P—O—C angles are 124·1 (4) and 120·9 (4)°. The geometries of these OC_2H_5 groups do not show significant differences. The O—P—O angles are in the range of 99·1–116·3° (Table 3). The P—C bond value of 1·821 (6) Å is in good agreement with the value of 1·81 (2) Å in $(CH_3)_3PO$ (Wang, 1965).

Both enantiomers related by the centre of symmetry are hydrogen bonded forming dimers. Each molecule is involved as a donor and an acceptor in the hydrogen bond N—H···O(3), 2·990 Å (Fig. 2). H···O(3) is 2·195 Å and ∠N—H···O(3) is 168°.

The authors thank Dr V. Jagodić for preparing the samples, and Magistar M. Bruvo for collecting the intensities at the Department of General and Inorganic Chemistry, Faculty of Science, University of Zagreb.

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Acta Cryst. (1978). B**34**, 3113–3115

1,1-Bis(*p*-chlorophenyl)-2,2,2-trichloroethanol

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(*Received* 10 *April* 1978; *accepted* 26 *May* 1978)

Abstract. $C_{14}H_9Cl_5O$, triclinic, $P\bar{1}$, $a = 16{\cdot}779$ (10), $b = 10{\cdot}443$ (6), $c = 9{\cdot}684$ (8) Å, $\alpha = 107{\cdot}52$ (5), $\beta = 93{\cdot}06$ (6), $\gamma = 106{\cdot}99$ (5)°, $M_r = 370{\cdot}5$, $Z = 4$, $D_x = 1{\cdot}60$ g cm^{-3}, μ(Mo $K\alpha$) = 8·6 cm^{-1}, $R = 0{\cdot}069$, 2535 observed reflexions. Two independent molecules (*A*,*B*) in the asymmetric unit differ in conformation. The difference is considered to be due to the effects of hydrogen bonding (O···O 3·00 Å) between the hydroxyl groups of two symmetry-related *A* molecules. No similar associations were found for the *B* molecules.

Introduction. Dicofol was first reported to be a highly active acaricide by Wilson & Barker (1954). It is structurally related to DDT, but has limited insecticidal activity (Gunther, Blinn & Metcalf, 1956; Metcalf & Fukuto, 1968). However, it is one of the products of the biological degradation of DDT in the environment (Metcalf, 1973). It is also known as Acarin, DTMC, FW293, Kelamite, Kelthane, and Mitigan (*PANS Pesticide Index*, 1976). Needle-shaped crystals were grown from a continuously stirred solution of the compound in *n*-hexane.

2535 reflexions with $|F_o| > 2{\cdot}5\sigma(F_o)$ were considered observed out of 4035 collected from one crystal (0·44 × 0·24 × 0·12 mm) mounted on a Syntex $P\bar{1}$ four-circle diffractometer ($2\theta_{\max} = 57°$, Mo $K\alpha$