plane of one ring and C(10) and O(2) on opposite sides of the plane of the other ring.

The determination of the structure of this dimer molecule provided additional evidence (Dunkelblum, Hart & Suzuki, 1977) for reaction mechanisms which involve intermediates containing a *trans* C=C bond.

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The Cyclohexylammonium Salt of Ethyl Hydrogen Phosphate

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Abstract. $C_6H_{14}N^+.C_2H_6O_4P^-$, monoclinic, $A2/a$, $Z = 8$, $a = 18{\cdot}289$ (6), $b = 6{\cdot}026$ (3), $c = 23{\cdot}181$ (8) Å, $\beta = 96{\cdot}86$ (4)°, $V = 2536{\cdot}47$ Å^3, $\rho_{\text{calc}} = 1{\cdot}17$ Mg m^{-3}, μ(Cu $K\alpha$) = $0{\cdot}893$ mm^{-1}. The length of the P—O(ester) bond is 1·579 (5) Å, the P—O(H) bond is 1·559 (4) Å. The hydrogen bond involving the O—H group is relatively short with an O···O distance of 2·542 (6) Å.

Introduction. Kirby & Varvoglis (1967) have shown that there is a linear free-energy relationship between the rate constant for hydrolysis and the pK_a of the leaving group for both mono- and dianions of phosphate esters, ROPO(OH)$_2$. This study is part of a series of structure determinations of monoanions of such esters to determine whether the length of the P—O(ester) bond is correlated with the hydrolysis rate.

Data were collected on a Picker diffractometer with filtered Cu $K\alpha$ radiation, operating in the ω–2θ scan mode with a scan width of $\Delta 2\theta = (2{\cdot}0 + 0{\cdot}285 \tan\theta)°$ and a scan rate of 1° min^{-1}. Background was measured for 40 s at either end of the scan. 2261 independent reflexions were measured below $2\theta = 115°$. Of these, 1525 had intensity significantly above background.

The structure was solved by standard heavy-atom methods after the P atom had been located in a Patterson synthesis. Refinement by full-matrix least squares resulted in a final R value of 0·0803; $R_w = 0{\cdot}0959$. The weighting function used in the final stages of refinement was $w = 1{\cdot}00/[\sigma^2(F) + 0{\cdot}006F^2]$. All H atoms save those on the terminal methyl group were located in a difference synthesis. These have been included in the refinement subject to the constraint that they remain 1·08 Å from the C or N to which they are attached. The H attached to O has not been refined. The terminal methyl group and the quaternary ammonium group were refined as rigid groups.

The refinement was carried out using the *SHELX* (Sheldrick, 1976) system of programs. Scattering factors and anomalous-dispersion terms were taken

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Table 1. *Atomic positions* ($\times 10^4$) *for the cyclohexylammonium salt of ethyl hydrogen phosphate*

	x	*y*	*z*
P(1)	3875 (1)	1880 (2)	2192 (1)
O(1)	3545 (2)	3326 (8)	1655 (2)
O(2)	4178 (2)	3395 (7)	2677 (2)
O(3)	3250 (2)	423 (7)	2302 (2)
O(4)	4504 (2)	450 (9)	1984 (2)
C(1)	3984 (5)	5046 (17)	1435 (4)
C(2)	3572 (7)	6274 (19)	988 (5)
C(3)	1658 (3)	2255 (12)	1407 (3)
C(4)	1781 (6)	154 (20)	1073 (4)
C(5)	1635 (8)	678 (28)	420 (5)
C(6)	884 (7)	1571 (31)	267 (5)
C(7)	770 (6)	3633 (25)	609 (4)
C(8)	916 (4)	3149 (18)	1262 (3)
N(1)	1789 (2)	1686 (8)	2038 (2)

from *International Tables for X-ray Crystallography* (1974). Positional parameters for all of the atoms are given in Table 1.*

Discussion. The conformations of the phosphate ester and the cyclohexylammonium ion are displayed in Fig. 1. The crystal structure and hydrogen-bonding scheme are shown in Fig. 2. There are four H atoms in each formula unit capable of forming hydrogen bonds. Since the ester oxygen, O(1), is less basic than O(2) and O(3), it does not function as an acceptor for hydrogen bonds. O(3) is acceptor for two hydrogen bonds, one from the N of the same asymmetric unit and one from the screw-related N. The dimensions are: N···O(3) 2·776 (6), H(12)···O(3) 1·70 (1), N′···O(3) 2·727 (6), H(11′)···O(3) 1·65 (1) Å. O(2) accepts one hydrogen bond from N′ and one from O(4). The dimensions are: N′···O(2) 2·789 (6), H(13′)···O(2) 1·71 (1), O(4)···O(2) 2·542 (6), H(O4)···O(2) 1·63 (1) Å. This network of hydrogen bonds links the structure in continuous ribbons parallel to the *a* axis. Since only van der Waals forces act between the chains, it is not unexpected that thermal parameters are large for the terminal methyl group and for C(6) and C(7) of the cyclohexyl ring.

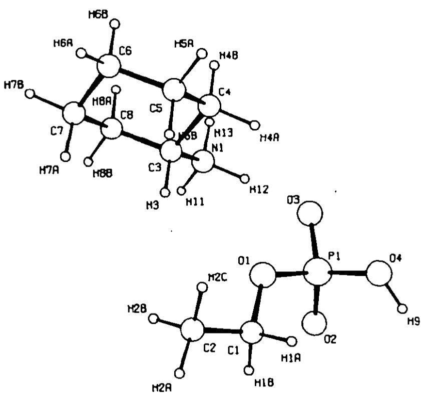

Fig. 1. The conformations of the phosphate ester and the cyclohexylammonium ion.

Bond lengths and angles are shown in Table 2. The P—O(ester) bond distance of 1·579 (5) Å is considerably shorter than the single-bond length of 1·64 Å (Cruickshank, 1964). Relevant torsion angles are O(4)—P(1)—O(1)—C(1) −67·4 (5), O(3)—P(1)—O(1)—C(1) 176·8 (5), O(2)—P(1)—O(1)—C(1) 51·8 (5)°. Thus the conformation about the P(1)—O(1) bond places the orbitals on O near the optimum orientation for overlap with the *d* orbitals on P.

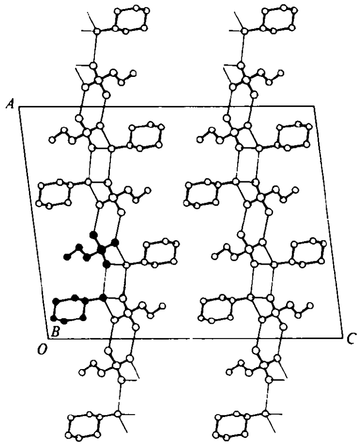

Fig. 2. The crystal structure and hydrogen-bonding scheme.

Table 2. *Bond lengths* (Å) *and angles* (°) *in the cyclohexylammonium salt of ethyl hydrogen phosphate*

P—O(1)	1·579 (5)	O(1)P(1)O(2)	109·0 (3)
P—O(2)	1·501 (4)	O(1)P(1)O(3)	103·4 (2)
P—O(3)	1·488 (4)	O(1)P(1)O(4)	106·7 (3)
P—O(4)	1·559 (4)	O(2)P(1)O(3)	116·9 (3)
		O(2)P(1)O(4)	110·3 (2)
		O(3)P(1)O(4)	109·7 (3)
O(4)—H(9)	0·93*	H(9)O(4)P(1)	113·7*
C(1)—O(1)	1·441 (9)	P(1)O(1)C(1)	120·0 (5)
C(2)—C(1)	1·415 (13)	O(1)C(1)C(2)	111·5 (8)
N(1)—C(3)	1·494 (8)	N(1)C(3)C(4)	107·0 (6)
C(3)—C(4)	1·515 (11)	N(1)C(3)C(8)	110·2 (5)
C(4)—C(5)	1·538 (15)	C(3)C(4)C(5)	108·2 (1·0)
C(5)—C(6)	1·479 (19)	C(4)C(5)C(6)	111·0 (1·0)
C(6)—C(7)	1·502 (19)	C(5)C(6)C(7)	110·9 (1·0)
C(7)—C(8)	1·533 (12)	C(6)C(7)C(8)	110·2 (1·0)
C(8)—C(3)	1·460 (10)	C(7)C(8)C(3)	110·2 (7)
		C(4)C(3)C(8)	112·4 (7)

* H(9) not refined.

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* Lists of structure factors, anisotropic thermal parameters and H-atom atomic coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34570 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

P—O(ester) bonds involving ethyl groups display a wide variety of lengths and conformations. In dipotassium ethyl phosphate, McDonald & Cruickshank (1971) report a bond distance of 1·564 Å and a torsion angle of 25°. In the Mg salt of the diethyl ester, Ezra & Collin (1973) report bond distances of 1·548 and 1·577 Å with torsion angles of 77·6 and 87·4° respectively. In view of the relatively high thermal motion in these compounds, detailed discussion of molecular geometry is not warranted.

In the study of hydrolysis rate *vs* pK_a (Kirby & Varvoglis, 1967), the most reactive compound studied was 2,4-dinitrophenyl phosphate (pK_a 4·07) and the least reactive compound was ethyl phosphate. The relatively high bond order of the P—O(ester) bond indicated by the length of 1·579 (5) Å is consistent with the slow hydrolysis rate of ethyl phosphate.

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Mandélate de Phényl-1 Ethylamine

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Abstract. $C_8H_{11}N^+.C_8H_7O_3^-$, orthorhombic, $P2_12_12_1$, $a = 25{\cdot}602$ (7), $b = 6{\cdot}874$ (2), $c = 8{\cdot}401$ (3) Å, $Z = 4$. The structure was solved by direct methods. Full-matrix least-squares refinement converged at $R_w = 0{\cdot}049$ for all the 1609 observed reflexions. The molecules are linked by hydrogen bonds in columns parallel to the 2_1 axis in the [010] direction.

Introduction. L'étude du sel de l'acide mandélique et de la phényl-1 éthylamine, décrit dans cet article, s'inscrit dans le cadre d'une étude des sels diastéréoisomères utilisés dans le dédoublement des racémiques. Cette étude porte en particulier sur les conditions de la syncristallisation partielle ou totale dans deux sels diastéréoisomères (Leclercq & Jacques, 1975).

Les mesures d'intensité ont été effectuées, sur diffractomètre Philips PW 1100 en utilisant la radiation $K\alpha$ du cuivre et en déduisant un font continu théorique résultant d'une série unique de mesures effectuées en fonction de l'angle θ.

Les positions des atomes de carbone, d'azote et d'oxygène ont été déterminées à l'aide du programme *MULTAN* (Germain, Main & Woolfson, 1971); celles

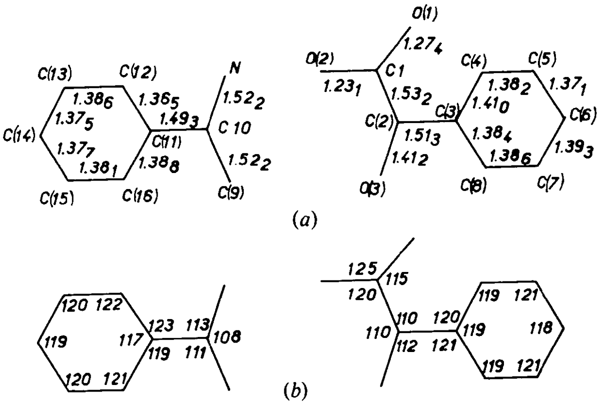

Fig. 1. Longueurs de liaisons (Å) (σ = 0,006 Å) et angles de valence (°) (σ = 0,7°).

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