form. A table of torsion angles, showing the configuration of the ions, is presented and compared with other structures in paper IV.

All distances and angles are in the expected range. The shortest fourth-neighbour intramolecular contacts are C(42)···C(52): 3·285 (6), C(46)···C(51): 3·337 (6) and P(2)···C(51): 3·693 (4) Å. The shortest intermolecular contacts, excluding H atoms and apart from the contacts involved in hydrogen bonds, of which the longest is 2·822 (2) Å, are between O(21), O(22) and C(1), C(20) and range from 3·182 (3) to 3·372 (3) Å. The shortest contact between the phenyl rings of the separate moieties is 3·452 (6) Å between C(52) and C(12′) at x, $1+y$, $1+z$.

It is clear that this compound is a salt. The acidic H atom is attached to the N atom. The P—O(21) and P—O(22) bond lengths are almost the same.

This investigation was supported (in part) by the Netherlands Foundation of Technical Research (STW) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO). AMGK and HW gladly acknowledge close cooperation and fruitful discussions with Dr W. ten Hoeve (University of Groningen), Dr J. H. Noordik (University of Nijmegen) and with Dr A. Bruggink and co-workers of Océ-Andeno (Venlo, The Netherlands).

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Structure of the Diastereoisomeric Salt of (+)-2-Hydroxy-5,5-dimethyl-2-oxo-4-phenyl-1,3,2-dioxaphosphorinane and (1*S*,2*R*)-(+)-α-[(1-Methylamino)ethyl]benzyl Alcohol

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Abstract. $C_{21}H_{30}NO_5P$, $M_r = 407·445$, monoclinic, $P2_1$, $a = 14·0037$ (6), $b = 8·0948$ (7), $c = 9·7090$ (7) Å, $\beta = 98·904$ (5)°, $V = 1087·3$ Å^3, $Z = 2$, $D_x = 1·244$ Mg m^{-3}, Cu $K\alpha$ radiation (graphite-crystal monochromator, $\lambda = 1·54178$ Å), μ(Cu $K\alpha$) = 1·360 mm^{-1}, $F(000) = 436$, $T = 290$ K, final conventional R factor = 0·039, $wR = 0·049$ for 2782 ‘observed’ reflections and 342 variables. The structure contains phosphorinane cations and ephedrine anions which are linked in a three-dimensional network by N—H···O and O—H···O hydrogen bonds. The phosphorinane ring is in the usual chair conformation. The ephedrine is in the usual extended form.

Introduction. The present compound, denoted INAP, is the second of a series of crystal structure investigations on phosporinane ephedrine salts. The other compounds (INAM, CLINAM, CLINAP) are presented in the preceeding and two following papers. These structural investigations are part of a study on crystallization

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properties of diastereoisomers. INAP and INAM (Kok, Wynberg, Smits, Beurskens & Parthasarathi, 1987; paper I) form a pair of diastereoisomers. The title compound has been prepared from (+)-phosphorinane and (+)-ephedrine (see Fig. 1). The crystal was recrystallized twice from ethanol before use. The melting point, 508·5 K, and the enthalpy of fusion, ΔH^f, 51·21 kJ mol^{-1}, are measured with DSC. The solubility of the *p*-salt at 298 K in 100% and 50% ethanol is 8·3 and 31·6 (g/100 g solution) respectively. A comparison of structural results will be presented in the last paper of this series (Kok, Wynberg, Parthasarathi, Smits & Beurskens, 1987; paper IV).

Experimental. Nearly all X-ray experiments and calculations were performed as described in paper I and will not be repeated here. The differences are: size of irregularly shaped crystal 0·15 × 0·30 × 0·35 mm, 5368 reflections measured, 2918 unique ($R_{\text{int}} = 0·013$) of which 2782 observed; h −7→16, k −8→9, l 0→11; drift: 1·00–1·08; absorption correction range: 0·87–1·00; *DIFABS* range: 0·87–1·13; Bijvoet coefficient: 0·996 (2). The structure was solved using *DIRDIF* (Beurskens *et al.*, 1983), which gave all non-hydrogen atoms, with a PO_4 fragment from the best *MULTAN* solution as input (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980).

Discussion. Final positional and thermal parameters are given in Table 1.* Molecular geometry data are collected in Table 2. A stereoview of the molecule, showing the molecular configuration, is given in Fig. 1. In this figure the moieties are treated as separate entities and the ephedrine moiety is given in a projection along C(1)—H(1). The crystallographic numbering scheme is identical to that in paper I.

Table 2 also gives the hydrogen bonds. The structure contains phosphorinane cations and ephedrine anions which are linked in a three-dimensional network by N—H···O and O—H···O hydrogen bonds. Fig. 2 shows the crystal packing projected along the *c* axis. This figure clearly shows the nature of the packing: bilayers, parallel to the *bc* plane, held together internally by van der Waals contacts, mainly between the phenyl rings, and externally by the hydrogen bonds mentioned earlier.

The phosphorinane ring is in the usual chair conformation. The ephedrine is in the usual extended form. A table of torsion angles, showing the configuration of the ions, is presented and compared with other structures in paper IV.

All distances and angles are in the expected range. The shortest fourth-neighbour intramolecular contacts are C(42)···C(52): 3·333 (6), C(46)···C(51): 3·374 (6) and P(2)···C(51): 3·707 (4) Å. The shortest intermolecular contacts, excluding H atoms and apart from the contacts involved in hydrogen bonds, of which the longest is 2·923 (2) Å, are between O(21), O(22) and N(2), C(1), C(20) and range from 3·145 (3) to 3·411 (3) Å. The shortest contact between the phenyl rings of the separate moieties is longer than 3·6 Å.

The binary melting point and ternary solubility diagrams, Fig. 3, result from the DSC and solubility data of the pure salts and of mixtures of salts. The measured melting points for mixtures are lower than the calculated values; this might be due to decomposition of the mixtures during warming. There is no co-crystallization according to the solubility measurements. The eutectic is at 0·54, which means that this is an example of a poor resolution.

The crystal structures of the *p*- and *n*-salts (the present compound and INAM, paper I) are the same, except for (some) signs, caused by the use of (+)- and (−)-ephedrine. The two compounds have the same melting points and solubilities.

This investigation was supported (in part) by the Netherlands Foundation of Technical Research (STW) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO). AMGK and HW gladly acknowledge close cooperation and fruitful discussions with Dr W. ten Hoeve (University of Groningen) and with Dr A. Bruggink and co-workers of Océ-Andeno (Venlo, The Netherlands).

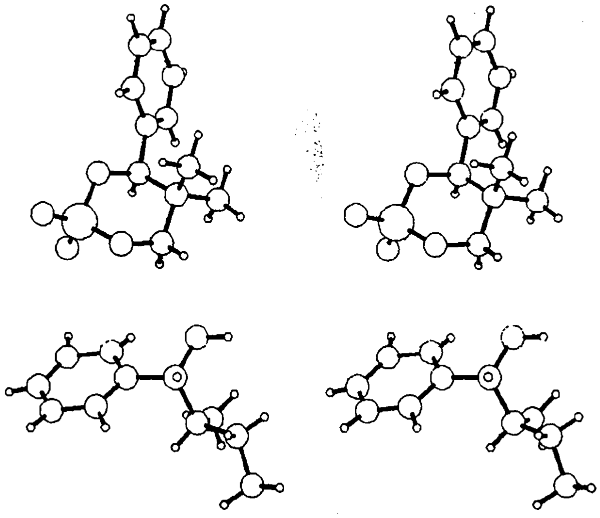

Fig. 1. Stereoview of the molecule, showing the molecular configuration. Top: (+)-dioxaphosphorinane moiety, bottom: (+)-ephedrine moiety. The ephedrine moiety is given as a projection along C(1)—H(1).

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters not involving hydrogen bonds have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43809 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}(Å^2 × 100)
P(2)	0·44998 (4)	0·48155	0·23923 (5)	3·96 (2)
O(1)	0·4435 (1)	0·6063 (2)	0·1117 (2)	4·95 (5)
O(21)	0·4484 (1)	0·5781 (3)	0·3690 (2)	5·61 (6)
O(22)	0·5314 (1)	0·3642 (3)	0·2414 (2)	5·69 (6)
O(3)	0·3501 (1)	0·3839 (2)	0·2054 (1)	3·93 (4)
C(4)	0·3294 (1)	0·3047 (3)	0·0693 (2)	3·87 (6)
C(5)	0·3249 (2)	0·4382 (4)	−0·0447 (2)	4·29 (7)
C(6)	0·4216 (2)	0·5281 (4)	−0·0248 (2)	4·94 (8)
C(41)	0·2390 (2)	0·2016 (3)	0·0681 (2)	4·39 (7)
C(42)	0·2258 (2)	0·0577 (4)	−0·0086 (3)	6·24 (9)
C(43)	0·1440 (3)	−0·0363 (5)	−0·0098 (5)	8·2 (1)
C(44)	0·0735 (2)	0·0096 (5)	0·0685 (4)	7·9 (1)
C(45)	0·0858 (2)	0·1506 (6)	0·1447 (4)	7·4 (1)
C(46)	0·1680 (2)	0·2471 (4)	0·1462 (3)	5·42 (9)
C(51)	0·2428 (2)	0·5603 (5)	−0·0401 (3)	5·99 (9)
C(52)	0·3137 (2)	0·3564 (5)	−0·1894 (3)	6·1 (1)
C(1)	0·2673 (2)	0·7830 (4)	0·5224 (2)	4·66 (7)
O(10)	0·2795 (1)	0·8252 (4)	0·6653 (2)	6·73 (8)
N(2)	0·4112 (1)	0·8964 (4)	0·4335 (2)	3·88 (5)
C(2)	0·3045 (1)	0·9184 (3)	0·4324 (2)	3·93 (6)
C(20)	0·4492 (2)	0·9854 (5)	0·3201 (3)	6·1 (1)
C(3)	0·2831 (2)	1·0907 (4)	0·4781 (4)	6·0 (1)
C(11)	0·1618 (2)	0·7540 (4)	0·4687 (3)	5·00 (8)
C(12)	0·1374 (3)	0·6683 (6)	0·3467 (4)	7·6 (1)
C(13)	0·0428 (3)	0·6480 (7)	0·2868 (4)	9·4 (2)
C(14)	−0·0287 (3)	0·7167 (7)	0·3488 (6)	10·2 (2)
C(15)	−0·0064 (2)	0·7977 (7)	0·4727 (6)	10·1 (2)
C(16)	0·0900 (2)	0·8171 (6)	0·5353 (4)	7·3 (1)
*H(10)	0·346 (2)	0·847 (5)	0·700 (3)	6·0
*H(21)	0·423 (2)	0·789 (5)	0·415 (3)	6·0
*H(22)	0·451 (2)	0·937 (5)	0·519 (3)	6·0

* Hydrogen atoms involved in hydrogen bridges.

Table 2. *Selected distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(1)–C(2)	1·542 (3)	P(2)–O(3)	1·596 (2)
C(1)–C(11)	1·507 (3)	C(4)–C(5)	1·542 (3)
N(2)–C(20)	1·482 (3)	C(5)–C(6)	1·524 (3)
P(2)–O(22)	1·482 (2)	C(1)–O(10)	1·413 (3)
C(4)–C(41)	1·515 (3)	N(2)–C(2)	1·503 (3)
C(5)–C(52)	1·539 (3)	P(2)–O(21)	1·486 (2)
O(1)–C(6)	1·458 (3)	O(3)–C(4)	1·456 (2)
C(2)–C(3)	1·507 (4)	C(5)–C(51)	1·521 (4)
P(2)–O(1)	1·589 (2)		
C(1)–H(1)	0·93 (4)	C(4)–H(4)	1·01 (3)
N(2)–H(22)	0·99 (3)	O(10)–H(10)	0·95 (3)
C(6)–H(62)	1·03 (4)	N(2)–H(21)	0·91 (4)
C(2)–H(2)	0·97 (3)	C(6)–H(61)	0·99 (4)
C(2)–C(1)–C(11)	108·3 (2)	O(10)–C(1)–C(2)	112·6 (2)
O(10)–C(1)–C(11)	109·9 (2)	P(2)–O(1)–C(6)	114·3 (2)
C(1)–C(2)–N(2)	109·5 (2)	C(1)–C(2)–C(3)	113·0 (2)
N(2)–C(2)–C(3)	110·5 (2)	C(2)–N(2)–C(20)	114·1 (2)
O(1)–P(2)–O(21)	108·6 (1)	O(1)–P(2)–O(22)	111·7 (1)
O(1)–P(2)–O(3)	102·2 (1)	O(21)–P(2)–O(22)	116·0 (1)
O(21)–P(2)–O(3)	107·9 (1)	O(22)–P(2)–O(3)	109·5 (1)
P(2)–O(3)–C(4)	116·7 (1)	O(3)–C(4)–C(41)	107·4 (2)
O(3)–C(4)–C(5)	108·8 (2)	C(5)–C(4)–C(41)	116·0 (2)
C(4)–C(5)–C(51)	112·4 (2)	C(4)–C(5)–C(52)	109·9 (2)
C(4)–C(5)–C(6)	107·9 (2)	C(51)–C(5)–C(52)	109·6 (2)
C(6)–C(5)–C(51)	110·3 (2)	C(6)–C(5)–C(52)	106·5 (2)
O(1)–C(6)–C(5)	112·3 (2)		
C(2)–N(2)–H(21)	109 (2)	C(2)–N(2)–H(22)	114 (2)
C(20)–N(2)–H(21)	103 (2)	C(20)–N(2)–H(22)	104 (2)
H(21)–N(2)–H(22)	113 (3)	C(1)–O(10)–H(10)	111 (2)

Possible hydrogen bonds.
Primed atoms: $1-x$, $0\cdot5+y$, $1-z$. *D*: donor atom; *A*: acceptor atom

D H *A*	Angle	*D*–H	H–*A*	*D*–*A*
N(2)–H(21)···O(21)	176·1°	0·906 Å	1·816 Å	2·721 Å
N(2)–H(22)···O(21′)	154·8	0·985	1·999	2·923
O(10)–H(10)···O(22′)	172·9	0·951	1·734	2·681

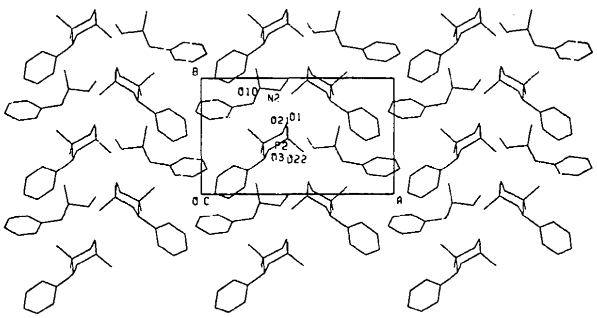
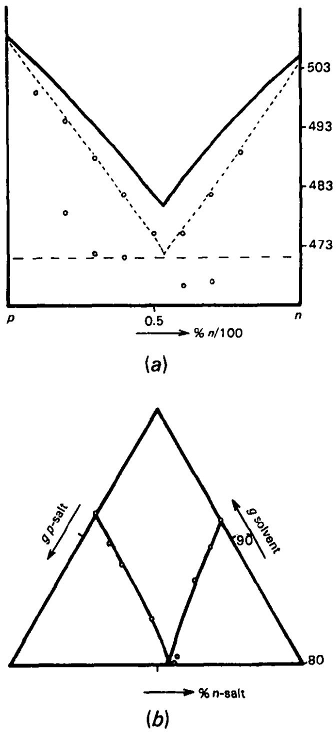


Fig. 2. Projection of the structure along the *c* axis.



(*a*)

(*b*)

Fig. 3. (*a*) Melting-point diagram for *p*- and *n*-salts derived from (+)-dioxaphosphorinane and (+)- and (−)-ephedrine. (— calculated, ○ measured). (*b*) Solubility diagram for the same salts in ethanol. Quantities of the *p*-salt and the solvent are in grams and of the *n*-salt in % at 298 K.

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