present structure, denoted XINAM, is part of a series of structure determinations of phosphorinane and ephedrine salts, performed in order to discover significantly different structural features, as an aid in a resolution protocol. For a more general introduction and reference to related literature we refer to the first paper of this series, INAM (Kok, Wynberg, Smits, Beurskens & Parthasarathi, 1987) and the fourth, CLINAP (Kok, Wynberg, Parthasarathi, Smits & Beurskens, 1987). The present compound, XINAM, is one of a pair of diastereoisomers. The second, denoted XINAP, is presented in the following paper (Kok, Wynberg, García-Granda, Beurskens & Smits, 1988).

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). AK 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). SG-G, on leave from Physical Chemistry Department, University of Oviedo, Spain, gratefully acknowledges the Spanish Ministerio de Educacion y Ciencia (MEC) for a postdoctoral grant and the University of Oviedo for leave of absence.

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Structure of the Diastereoisomeric Salt of (–)-4-*o*-Chlorophenyl-2-hydroxy-2-oxo-1,3,2-dioxaphosphorinane-5-spirocyclohexane and (1*S*,2*R*)-(+)-α-[(1-Methylamino)ethyl]benzyl Alcohol Monohydrate

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Abstract. $C_{24}H_{33}ClNO_5P.H_2O$, $M_r = 499·97$, orthorhombic, $P2_12_12_1$, $a = 7·927$ (6), $b = 17·744$ (1), $c = 18·697$ (2) Å, $V = 2627·7$ (4) Å^3, $Z = 4$, $D_x = 1·26$ g cm^{-3}, Cu $K\alpha$ radiation, $\lambda = 1·54184$ Å, $\mu = 21·88$ cm^{-1}, $F(000) = 1064$, $R = 0·042$, $wR = 0·042$ for 3130 observed reflections and 400 variables. The structure was solved by automatic application of the vector-search orientation function and the *DIRDIF* structure expansion procedure. The structure contains phosphorinane anions, ephedrine cations and water molecules, which are linked in a three-dimensional network by N—H···O and O—H···O hydrogen bonds. The phosphorinane ring is in the chair conformation. The ephedrine is in the usual extended form. The structure of a diastereoisomer is reported by García-Granda, Beurskens, Smits, Kok & Wynberg [*Acta Cryst.* (1988), C**44**, 2233–2235].

Experimental. The title compound was prepared from (–)-phosphorinane and (+)-ephedrine. The colourless crystals were recrystallized twice from ethanol before use. Melting point 490·8 K, solubility at 298 K in 100% ethanol: 16·9 g/100 g solution.

Nearly all X-ray experiments and calculations were performed as described in a foregoing paper on a related compound (INAM; Kok, Wynberg, Smits, Beurskens & Parthasarathi, 1987) and need not be repeated here. Relevant differences are: approximate

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Table 1. *Atomic parameters (with e.s.d.'s in parentheses)*

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

	x	y	z	U_{eq} (Å^2 × 100)
P(2)	0·35419 (14)	0·25537 (5)	0·35257 (5)	3·72 (3)
Cl(1)	−0·06861 (16)	0·03254 (7)	0·27928 (8)	6·88 (5)
O(1)	0·3215 (4)	0·30158 (13)	0·28100 (15)	4·72 (10)
O(3)	0·3672 (3)	0·17019 (13)	0·32483 (13)	3·72 (8)
O(10)	0·9211 (4)	0·34389 (20)	0·41761 (19)	5·92 (12)
O(21)	0·5231 (4)	0·27609 (17)	0·38046 (16)	5·12 (11)
O(22)	0·2058 (3)	0·26167 (15)	0·40158 (15)	4·71 (10)
O(30)	0·3069 (6)	0·2773 (3)	0·69201 (27)	11·56 (22)
N(2)	0·6269 (4)	0·34707 (18)	0·50052 (19)	3·88 (11)
C(1)	0·9253 (5)	0·38406 (23)	0·48321 (23)	3·83 (13)
C(2)	0·7432 (5)	0·41296 (23)	0·49555 (25)	4·27 (14)
C(3)	0·6873 (7)	0·4665 (3)	0·4378 (4)	6·53 (20)
C(4)	0·2369 (5)	0·14285 (19)	0·27665 (21)	3·25 (11)
C(5)	0·2371 (5)	0·19132 (20)	0·20779 (20)	3·63 (12)
C(6)	0·1955 (6)	0·27150 (21)	0·23209 (26)	4·55 (14)
C(11)	1·0478 (5)	0·44892 (21)	0·48418 (24)	4·18 (14)
C(12)	1·0896 (7)	0·4816 (3)	0·54863 (28)	5·90 (19)
C(13)	1·1967 (7)	0·5428 (3)	0·5522 (4)	7·32 (22)
C(14)	1·2678 (7)	0·5703 (3)	0·4900 (5)	7·78 (26)
C(15)	1·2270 (7)	0·5393 (3)	0·4265 (4)	7·23 (23)
C(16)	1·1184 (6)	0·4768 (3)	0·42237 (26)	5·48 (17)
C(20)	0·4541 (6)	0·3653 (3)	0·5290 (3)	5·30 (18)
C(41)	0·2703 (5)	0·05973 (20)	0·26866 (22)	3·77 (13)
C(42)	0·1418 (6)	0·00651 (22)	0·26895 (22)	4·66 (14)
C(43)	0·1779 (8)	−0·07055 (26)	0·2642 (3)	6·99 (21)
C(44)	0·3403 (9)	−0·09406 (26)	0·2571 (3)	7·57 (22)
C(45)	0·4693 (8)	−0·04341 (27)	0·25620 (27)	6·15 (19)
C(46)	0·4341 (6)	0·03291 (24)	0·26281 (24)	4·55 (14)
C(51)	0·4068 (6)	0·18758 (27)	0·16868 (23)	4·51 (15)
C(52)	0·4063 (8)	0·2307 (3)	0·09769 (27)	6·22 (19)
C(53)	0·2686 (9)	0·2016 (4)	0·0487 (3)	7·41 (23)
C(54)	0·0994 (8)	0·2067 (3)	0·0853 (3)	6·73 (22)
C(55)	0·0972 (7)	0·16491 (27)	0·15738 (25)	5·03 (16)
H(10)	1·005 (6)	0·327 (3)	0·413 (3)	7·00†
H(21)	0·613 (6)	0·3208 (23)	0·4561 (25)	6·00†
H(22)	0·665 (6)	0·3113 (25)	0·5345 (24)	6·00†
H(301)	0·214 (6)	0·2628 (27)	0·6590 (26)	7·00†
H(302)	0·252	0·3085	0·7335	7·00†‡

† U_{iso}, not varied.
‡ Fixed position.

Table 2. *Selected bond lengths* (Å) *and angles* (°)

P(2)—O(3)	1·601 (2)	C(1)—C(2)	1·548 (6)
P(2)—O(1)	1·591 (3)	C(11)—C(12)	1·378 (6)
P(2)—O(21)	1·482 (3)	C(55)—C(54)	1·538 (7)
P(2)—O(22)	1·494 (3)	C(12)—C(13)	1·379 (7)
O(3)—C(4)	1·453 (4)	C(43)—C(42)	1·400 (6)
O(1)—C(6)	1·455 (5)	C(43)—C(44)	1·359 (8)
Cl(1)—C(42)	1·739 (5)	C(2)—C(3)	1·505 (7)
N(2)—C(2)	1·491 (5)	C(41)—C(42)	1·388 (5)
N(2)—C(20)	1·503 (6)	C(41)—C(4)	1·506 (5)
C(5)—C(55)	1·528 (6)	C(45)—C(44)	1·360 (7)
C(5)—C(6)	1·529 (5)	C(13)—C(14)	1·381 (9)
C(5)—C(4)	1·548 (5)	C(14)—C(15)	1·347 (9)
C(5)—C(51)	1·531 (6)	C(54)—C(53)	1·507 (8)
C(46)—C(41)	1·385 (6)	C(53)—C(52)	1·514 (8)
C(46)—C(45)	1·388 (6)	C(51)—C(52)	1·532 (6)
C(16)—C(11)	1·376 (6)	N(2)—H(22)	0·95 (5)
C(16)—C(15)	1·407 (7)	N(2)—H(21)	0·96 (5)
C(1)—C(11)	1·505 (6)	O(10)—H(10)	0·73 (5)
C(1)—O(10)	1·419 (5)	O(30)—H(301)	1·00 (5)

O(3)—P(2)—O(1)	103·0 (1)	N(2)—C(2)—C(3)	111·0 (4)
O(3)—P(2)—O(21)	106·9 (2)	C(1)—C(2)—C(3)	112·1 (4)
O(1)—P(2)—O(21)	108·4 (2)	C(46)—C(41)—C(42)	116·9 (4)
O(3)—P(2)—O(22)	108·7 (2)	C(46)—C(41)—C(4)	120·6 (3)
O(1)—P(2)—O(22)	110·4 (2)	C(42)—C(41)—C(4)	122·5 (4)
O(21)—P(2)—O(22)	118·4 (2)	C(46)—C(45)—C(44)	119·5 (5)
P(2)—O(3)—C(4)	118·0 (2)	C(12)—C(13)—C(14)	119·2 (6)
P(2)—O(1)—C(6)	116·8 (2)	Cl(1)—C(42)—C(43)	117·5 (4)
C(2)—N(2)—C(20)	114·5 (3)	Cl(1)—C(42)—C(41)	121·5 (3)
C(55)—C(5)—C(6)	108·2 (3)	C(43)—C(42)—C(41)	121·0 (4)
C(55)—C(5)—C(4)	110·0 (3)	C(13)—C(14)—C(15)	120·0 (6)
C(6)—C(5)—C(4)	105·6 (3)	O(3)—C(4)—C(5)	109·2 (3)
C(55)—C(5)—C(51)	109·1 (3)	O(3)—C(4)—C(41)	105·3 (3)
C(6)—C(5)—C(51)	111·8 (3)	C(5)—C(4)—C(41)	117·5 (3)
C(4)—C(5)—C(51)	112·0 (3)	C(55)—C(54)—C(53)	112·3 (5)
C(41)—C(46)—C(45)	122·0 (5)	C(54)—C(53)—C(52)	110·2 (5)
C(11)—C(16)—C(15)	119·1 (5)	C(43)—C(44)—C(45)	120·6 (5)
C(11)—C(1)—O(10)	114·2 (4)	C(5)—C(51)—C(52)	113·0 (4)
C(11)—C(1)—C(2)	110·2 (3)	C(53)—C(52)—C(51)	110·8 (4)
O(10)—C(1)—C(2)	105·8 (3)	C(16)—C(15)—C(14)	121·1 (6)
C(16)—C(11)—C(1)	121·8 (4)	C(2)—N(2)—H(22)	112 (3)
C(16)—C(11)—C(12)	119·1 (4)	C(20)—N(2)—H(21)	108 (3)
C(1)—C(11)—C(12)	119·2 (4)	H(301)—O(30)—H(302)	107 (3)
C(5)—C(55)—C(54)	112·6 (4)	C(20)—N(2)—H(22)	101 (3)
C(11)—C(12)—C(13)	121·5 (5)	H(22)—N(2)—H(21)	107 (4)
C(42)—C(43)—C(44)	120·0 (5)	C(2)—N(2)—H(21)	113 (3)
O(1)—C(6)—C(5)	112·3 (3)	C(1)—O(10)—H(10)	106 (5)
N(2)—C(2)—C(1)	109·0 (3)		

Hydrogen bonds

(1—2···3)	(1–2)	(2–3)	(1–3)	(1–2–3)
N(2)—H(21)···O(21)	0·96 (5)	1·77 (5)	2·702 (5)	162 (5)
N(2)—H(22)···O(22^{i})	0·95 (4)	1·79 (4)	2·732 (4)	171 (4)
O(10)—H(10)···O(22^{ii})	0·73 (5)	1·98 (5)	2·702 (4)	167 (6)
O(30)—H(301)···O(21^{iii})	1·00 (5)	1·81 (5)	2·788 (6)	165 (4)

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

crystal size 0·23 × 0·25 × 0·06 mm, θ range for cell dimensions: 20–36°, 10 703 reflections measured, $\theta < 70°$, *hkl* limits (−8, −21, −22) and (9, 21, 22), drift: 1·00–1·04, absorption correction range: 0·79 to 1·00, $R_{int} = 0·040$, for 4990 unique reflections, 3130 observed with $I > 3\sigma(I)$.

The structure was solved by application of vector-search rotation functions, using the *ORIENT* option of the *DIRDIF* system (Beurskens, Beurskens, Strumpel & Nordman, 1987), to the PO_4 group of the related compound INAM. The orientation, position, and expansion to the complete structure were achieved in one run. DIFABS range: 0·91–1·26. The positional parameters of all atoms except H(302), and the anisotropic thermal parameters of the non-hydrogen atoms were refined. The H atoms had fixed isotropic temperature factors. The hydrogen atom H(302), which belongs to the water molecule, did not refine very well and was kept fixed at the Fourier peak position: this H does not participate in the hydrogen-bonding scheme. Weights: $w = 1/[\sigma^2(F_o) + 0·00040F_o^2]$. $R = 0·042$, $wR = 0·042$ and $S = 1·1936$ for the 3130 observed reflections and 400 variables. Final maximum shift-over-e.s.d. ratio: 0·07 for the non-hydrogen and 0·09 for the H atoms. The final difference Fourier map showed no peaks higher nor deeper than ±0·3 e Å^{-3}. The absolute configuration was checked with the *BIJVOET* program: $B = 0·840$ (6) for 363 pairs.

Final parameters are given in Table 1.* Geometry calculations (Table 2) were performed with *PARST* (Nardelli, 1983). Fig. 1 shows the molecular con-

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* Lists of structure factors, anisotropic thermal parameters, hydrogen atoms not involved in hydrogen bonds, selected torsion angles and angles between least-squares planes, and a table comparing torsion angles of related compounds have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51243 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

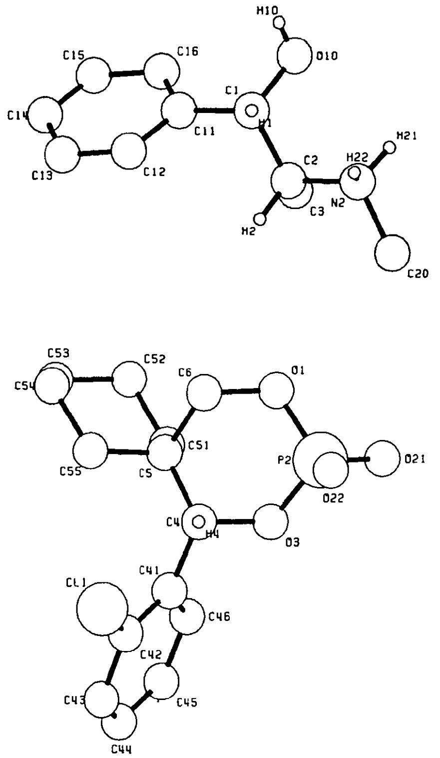

Fig. 1. Projections of the ions with crystallographic atomic numbering scheme. The ephedrine part is given as a projection along H(1)—C(1).

figuration and the crystallographic numbering. The ephedrine is given in a projection along H(1)—C(1). The molecular packing is shown in Fig. 2.

Related literature. The present compound, denoted XINAP, is the second of two crystal structure determinations of phosphorinane and ephedrine salts; the first denoted XINAM (Garcia-Granda, Beurskens, Smits, Kok & Wynberg, 1988). These two compounds form a pair of diastereoisomers. In previous work we have reported a series of related compounds [INAM, INAP, CLINAM and CLINAP with summary; see Kok, Wynberg, Parthasarathi, Smits & Beurskens (1987)].

The present X-ray analysis revealed the presence of a water molecule in the crystal structure of XINAP. Comparison of XINAM and XINAP reveals that notwithstanding some similarities in the crystal packing (see Fig. 2 for both structures) the hydrogen-bonding schemes are rather different. XINAM, which crystallizes without water molecules, has a ten times smaller solubility in ethanol. Further studies are needed to investigate the effect of small amounts of water in the solvent. It is clear that it will be very hard to predict differences in solubilities of diastereoisomers by molecular interaction studies: one should always be aware of possible (differences in) presence of water or solvent molecules in the crystals.

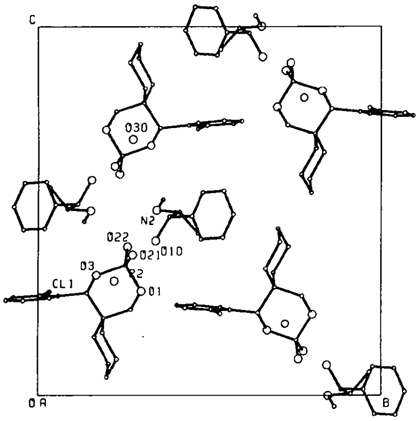

Fig. 2. Molecular packing viewed along the *a* axis.

A table showing the structural differences, through the values of characteristic torsion angles, for a number of phosphorinane–ephedrine compounds has been deposited.

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). AK 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). SG-G, on leave from Physical Chemistry Department, University of Oviedo, Spain, gratefully acknowledges the Spanish Ministerio de Educacion y Ciencia (MEC) for a postdoctoral grant and the University of Oviedo for leave of absence.

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