salt-forming centres are the same. Comparison of Fig. 2 with the corresponding figure in paper I makes clear that, although different in detail, the packing is essentially the same.

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

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Abstract. $C_{21}H_{29}ClNO_5P$, $M_r = 441{\cdot}89$, monoclinic, $P2_1$, $a = 13{\cdot}8421$ (11), $b = 8{\cdot}3808$ (6), $c = 9{\cdot}8118$ (9) Å, $\beta = 99{\cdot}672$ (7)°, $V = 1122{\cdot}1$ Å^3, $Z = 2$, $D_x = 1{\cdot}308$ Mg m^{-3}. Cu $K\alpha$ radiation (graphite-crystal monochromator, $\lambda = 1{\cdot}54178$ Å), μ(Cu $K\alpha$) = $2{\cdot}464$ mm^{-1}, $F(000) = 468$, $T = 290$ K, final conventional R factor = 0·043, $wR = 0{\cdot}057$ for 3259 'observed' reflections and 348 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. Related 1,3,2-dioxaphosphorinane and ephedrine compounds are compared.

Introduction. The present compound, denoted CLINAP, is the fourth of a series of crystal structure investigations on phosporinane ephedrine salts. The other compounds (INAM, INAP, CLINAM) are presented in the three preceding papers [Kok, Wynberg, Smits, Beurskens & Parthasarathi (1987) (paper I); Smits, Beurskens, Kok & Wynberg (1987) (paper II); Smits, Beurskens, Parthasarathi, Rijk, Kok & Wynberg (1987) (paper III)]. These structural investigations are part of a study on crystallization properties of diastereoisomers. CLINAP is the chlorine derivative of the second compound INAP (paper II), with which it was found to be isomorphous and isostructural except for the chlorine atom. CLINAP and the preceding compound CLINAM (paper III) form a pair of diastereoisomers.

The synthesis of the dioxaphosphorinane, a novel chiral acidic resolving agent, has recently been described by ten Hoeve & Wynberg (1985). The crystal structure of the diastereoisomeric *p*-salt with ephedrine has been determined in order to discover significantly different structural features as an aid in a resolution protocol. Studies related to this subject have been published by Brianso (1981) and by Gould & Walkinshaw (1984).

The title compound has been prepared from (+)-phosphorinane and (+)-ephedrine (see Fig. 1). The salt was recrystallized from a mixture of ethanol and ethyl acetate before use. The melting point, 489·4 K, and the enthalpy of fusion, ΔH^f, 41·42 kJ mol^{-1}, were

0108-2701/87/071336-06$01.50

measured with DSC. The solubility of this *p*-salt at 298 K in 100% and 50% ethanol is 19·3 and 12·8 (g/100 g solution) respectively.

We emphasize that only thorough examination of both diastereomeric salts of a set (calculations, X-ray analyses, melting points, heats of fusion and solubilities, with particular attention to intra- and intermolecular interactions) will allow predictive conclusions.

As is evident from the work of Gould & Walkinshaw (1984) and Gorman, Gould, Gray, Tayler & Walkinshaw (1986) and, more specifically, from the recent work of Wood *et al.* (1986), studies like the one described in this paper may contribute to an understanding of substrate receptor interactions.

In this paper we present a comparison of structural results of the four structures.

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 0·07 × 0·21 × 0·35 mm, 8489 reflections measured, 4245 unique (R_{int} = 0·035) of which 3259 observed; h −16→16, k −10→10, l 0→11; drift: 1·00–1·14; absorption correction range: 0·73–1·00; *DIFABS* range: 0·90–1·25; Bijvoet coefficient: 0·903 (2). The structure was solved using *DIRDIF* (Beurskens *et al.*, 1983) which gave all non-hydrogen atoms, with Cl and P positions 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. The crystallographic numbering scheme is given in Fig. 2. In these figures the moieties are treated as separate entities and the ephedrine moiety is given in a projection along C(1)–H(1).

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. 3 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.

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

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

	x	y	z	U_{eq}(Å² × 100)
Cl(1)	0·31057 (8)	−0·0169 (2)	−0·0595 (1)	7·68 (4)
P(2)	0·44391 (6)	0·48155	0·24479 (8)	4·54 (2)
O(1)	0·4445 (2)	0·5994 (3)	0·1173 (2)	5·01 (8)
O(21)	0·4515 (2)	0·5770 (4)	0·3722 (3)	6·5 (1)
O(22)	0·5277 (2)	0·3602 (3)	0·2477 (3)	5·91 (9)
O(3)	0·3452 (2)	0·3952 (3)	0·2109 (2)	4·45 (7)
C(4)	0·3237 (2)	0·3158 (4)	0·0777 (3)	4·2 (1)
C(5)	0·3188 (2)	0·4443 (4)	−0·0370 (3)	4·6 (1)
C(6)	0·4183 (3)	0·5279 (5)	−0·0182 (4)	5·0 (1)
C(41)	0·2320 (2)	0·2185 (4)	0·0797 (3)	4·5 (1)
C(42)	0·2197 (3)	0·0666 (5)	0·0208 (4)	5·4 (1)
C(43)	0·1379 (3)	−0·0254 (7)	0·0285 (5)	7·3 (2)
C(44)	0·0676 (3)	0·0317 (6)	0·0938 (6)	7·4 (2)
C(45)	0·0740 (3)	0·1799 (7)	0·1513 (6)	7·6 (2)
C(46)	0·1579 (3)	0·2735 (6)	0·1456 (4)	6·0 (1)
C(51)	0·2375 (3)	0·5638 (6)	−0·0344 (5)	6·2 (1)
C(52)	0·3055 (4)	0·3632 (6)	−0·1806 (4)	6·4 (1)
C(1)	0·2676 (3)	0·7677 (5)	0·5046 (4)	5·4 (1)
O(10)	0·2836 (3)	0·7951 (6)	0·6468 (3)	9·6 (2)
N(2)	0·4128 (2)	0·8875 (4)	0·4281 (3)	4·75 (9)
C(2)	0·3047 (3)	0·9032 (5)	0·4224 (4)	4·9 (1)
C(20)	0·4519 (4)	0·9811 (8)	0·3193 (5)	7·3 (2)
C(3)	0·2802 (4)	1·0680 (7)	0·4719 (7)	7·6 (2)
C(11)	0·1595 (3)	0·7442 (5)	0·4563 (4)	5·7 (1)
C(12)	0·1280 (4)	0·6715 (7)	0·3326 (5)	8·4 (2)
C(13)	0·0309 (6)	0·652 (1)	0·2816 (7)	10·9 (3)
C(14)	−0·0360 (5)	0·706 (1)	0·352 (1)	12·4 (3)
C(15)	−0·0095 (5)	0·782 (1)	0·475 (1)	12·8 (4)
C(16)	0·0902 (4)	0·8017 (9)	0·5295 (6)	9·1 (2)
*H(10)	0·335 (3)	0·826 (5)	0·684 (4)	6·0
*H(21)	0·429 (3)	0·798 (6)	0·414 (4)	6·0
*H(22)	0·446 (3)	0·913 (5)	0·506 (5)	6·0

* Hydrogen atoms involved in hydrogen bridges.

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

Cl(1)–C(42)	1·739 (4)	P(2)–O(22)	1·484 (3)
C(1)–C(11)	1·504 (5)	C(4)–C(41)	1·512 (5)
N(2)–C(2)	1·494 (5)	C(5)–C(52)	1·547 (5)
P(2)–O(21)	1·480 (3)	C(1)–O(10)	1·394 (5)
O(3)–C(4)	1·453 (4)	C(2)–C(3)	1·521 (6)
C(5)–C(51)	1·510 (5)	P(2)–O(1)	1·586 (2)
C(1)–C(2)	1·531 (5)	P(2)–O(3)	1·597 (2)
O(1)–C(6)	1·448 (4)	C(4)–C(5)	1·551 (4)
N(2)–C(20)	1·497 (6)	C(5)–C(6)	1·528 (5)
C(1)–H(1)	0·92 (5)	C(4)–H(4)	1·02 (4)
N(2)–H(22)	0·85 (4)	O(10)–H(10)	0·79 (4)
C(6)–H(62)	0·97 (4)	N(2)–H(21)	0·80 (5)
C(2)–H(2)	0·99 (4)	C(6)–H(61)	0·89 (4)

Cl(1)–C(42)–C(43)	117·5 (4)	Cl(1)–C(42)–C(41)	120·5 (3)
C(2)–C(1)–C(11)	109·5 (3)	O(10)–C(1)–C(2)	113·2 (4)
O(10)–C(1)–C(11)	108·6 (3)	P(2)–O(1)–C(6)	115·9 (2)
C(1)–C(2)–N(2)	109·7 (3)	C(1)–C(2)–C(3)	113·1 (4)
N(2)–C(2)–C(3)	110·1 (4)	C(2)–N(2)–C(20)	114·0 (3)
O(1)–P(2)–O(21)	108·7 (2)	O(1)–P(2)–O(22)	112·1 (1)
O(1)–P(2)–O(3)	101·6 (1)	O(21)–P(2)–O(22)	116·3 (2)
O(21)–P(2)–O(3)	108·1 (1)	O(22)–P(2)–O(3)	108·9 (1)
P(2)–O(3)–C(4)	115·8 (2)	O(3)–C(4)–C(41)	106·3 (3)
O(3)–C(4)–C(5)	108·2 (2)	C(5)–C(4)–C(41)	116·7 (3)
C(4)–C(5)–C(51)	113·0 (3)	C(4)–C(5)–C(52)	109·8 (3)
C(4)–C(5)–C(6)	107·6 (3)	C(51)–C(5)–C(52)	109·4 (3)
C(6)–C(5)–C(51)	110·7 (3)	C(6)–C(5)–C(52)	106·2 (3)
O(1)–C(6)–C(5)	112·5 (3)		

C(2)–N(2)–H(21)	113 (3)	C(2)–N(2)–H(22)	113 (3)
C(20)–N(2)–H(21)	103 (3)	C(20)–N(2)–H(22)	108 (3)
H(21)–N(2)–H(22)	106 (4)	C(1)–O(10)–H(10)	120 (3)

Possible hydrogen bonds.
Primed atoms: 1−x, 0·5+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)	172·6°	0·798 Å	1·937 Å	2·731 Å
N(2)–H(22)···O(21′)	147·8	0·852	2·183	2·942
O(10)–H(10)···O(22′)	166·2	0·789	1·926	2·700

* 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 43811 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The phosphorinane ring is in the usual chair conformation. The ephedrine is in the usual extended form.

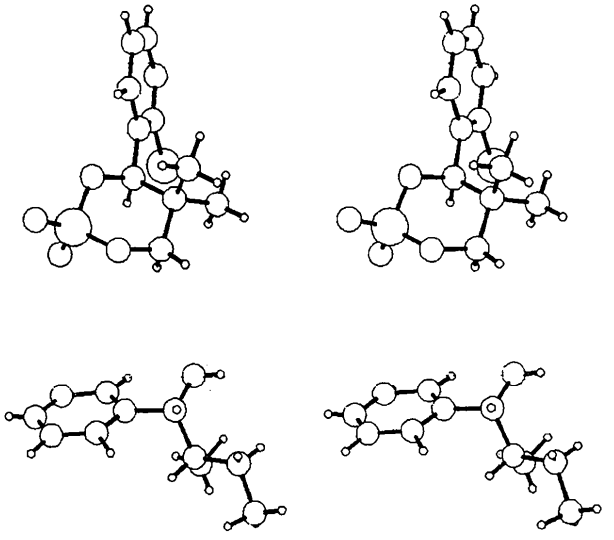


Fig. 1. Stereoview of the molecule, showing the molecular configuration. Top: (+)-dioxaphosphorinane moiety, bottom: (+)-ephedrine moiety. The ephedrine moiety is given as a projection along C(1)–H(1).

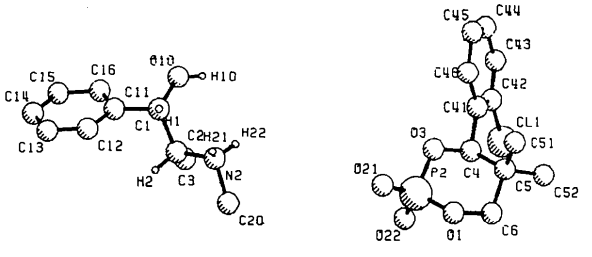


Fig. 2. Crystallographic atomic numbering scheme. The ephedrine moiety is given as a projection along C(1)–H(1).

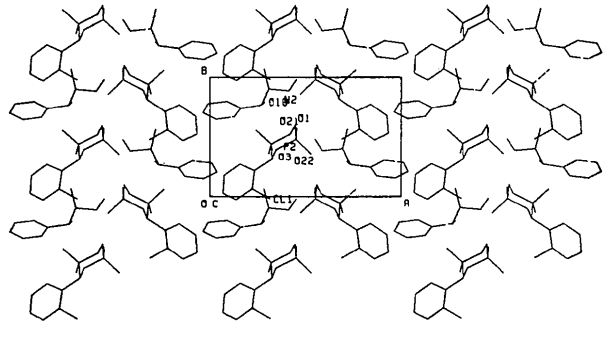


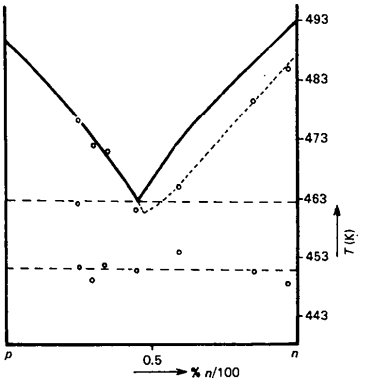
Fig. 3. Projection of the structure along the *c* axis.

All distances and angles are in the expected range. The shortest fourth-neighbour intramolecular contacts are C(46···C(51): 3·302 (8) and P(2)···C(51): 3·725 (6) Å. The shortest intermolecular contacts, excluding H atoms and apart from the contacts involved in hydrogen bonds, of which the longest is 2·942 (5) Å, are between O(21), O(22) and N(2), C(20) and range from 3·158 (5) to 3·199 (6) Å. Besides these, the bulky Cl atom takes part in many van der Waals contacts, of which the shortest is Cl(1)···O(10): 3·250 (6) Å. The shortest contact between the phenyl rings of the separate moieties is longer than 4·0 Å.

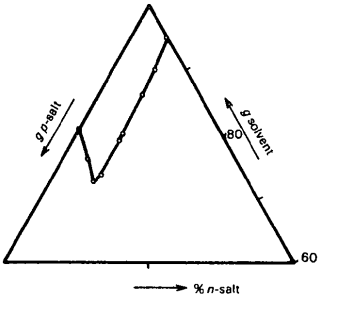
The binary melting point and ternary solubility diagrams, Fig. 4, result from the DSC and solubility data of the pure salts and of mixtures of salts. The binary diagram is complicated by polymorphism but the ternary diagram, eutectic at 0·22, gives information about the resolution.

Comparison of related structures

In this and the foregoing papers all the figures are presented in the same orientation.



(*a*)



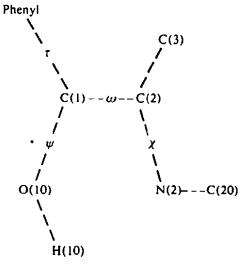
(*b*)

Fig. 4. (*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.

Table 3. *Selected torsion angles* (°)

	INAM	INAP	CLINAM	CLINAP	Angle *
Ephedrine					
O(10)–C(1)–C(2)–C(3)	57·2	−38·7	50·0	−43·0	
O(10)–C(1)–C(2)–N(2)	−65·3	85·0	−71·7	80·4	ω
O(10)–C(1) C(11) C(12)	171·7	−161·9	161·6	−161·2	
O(10)–C(1)–C(11)–C(16)	−7·9	21·1	−17·4	22·4	τ
C(2)–C(1)–C(11)–C(12)	−65·8	74·7	−74·8	74·7	
C(2)–C(1)–C(11)–C(16)	114·6	−102·4	106·1	−101·7	
C(1)–C(2)–N(2)–C(20)	−150·1	162·8	−72·3	162·6	χ
C(3)–C(2)–N(2)–C(20)	84·4	−72·1	163·5	−72·2	χ′
C(11)–C(1)–C(2)–N(2)	170·6	−153·3	167·0	−158·3	
C(11)–C(1)–C(2)–C(3)	−66·8	83·1	−71·2	78·3	
H(10)–O(10)–C(1)–C(2)	97·6	−57·5	62·6	−46·6	ψ
Phosphorinane					
O(1)–P(2)–O(3)–C(4)	52·1	55·0	52·3	56·4	*A*
P(2)–O(3)–C(4)–C(5)	−58·0	−61·2	−60·7	−64·2	*B*
O(3)–C(4)–C(5)–C(6)	57·1	58·4	59·2	59·7	*C*
C(4)–C(5)–C(6)–O(1)	−60·9	−59·7	−59·4	−57·9	*D*
C(5)–C(6)–O(1)–P(2)	62·5	60·3	58·7	58·1	*E*
C(6)–O(1)–P(2)–O(3)	−52·7	−52·5	−50·2	−51·8	*F*
P(2)–O(3)–C(4)–C(41)	175·8	172·5	172·7	169·7	
O(3)–C(4)–C(41)–C(42)	−148·2	−148·6	−137·6	−141·1	
O(3)–C(4)–C(41)–C(46)	31·4	30·0	40·1	36·0	
O(21)–P(2)–O(1)–C(6)	−166·1	−166·4	−162·9	−165·7	
O(21)–P(2)–O(3)–C(4)	166·2	169·4	164·4	170·8	
O(22)–P(2)–O(1)–C(6)	64·4	64·5	67·3	64·3	
O(22)–P(2)–O(3)–C(4)	−65·0	−63·5	−65·0	−62·0	

* Definitions, as given by Hearn, Freeman & Bugg (1973):



A comparison of the cell parameters of the four compounds shows that all but CLINAM have almost the same unit cell (see Table 6). The differences in packing density (INAM 1% less than INAP, CLINAM 2% more than CLINAP) are in agreement with the observed differences in the melting points.

In Tables 3, 4 and 5 torsion angles, showing the configuration of the ions, are presented and compared with data from other related structures. The changes in the signs in pairs (INAM/INAP, CLINAM/CLINAP) reflect the differences in D or L form. Otherwise most of the torsion angles are the same, showing that the ephedrines are in the same configuration. Only for CLINAM, χ and χ' are different, indicating a rotation around the central C(2)–N(2) bond. It has been commented by Mathew & Palenik (1977) that the χ angle is close to $\pm$ 180° in all cases, illustrating the extended nature of the side chain. As compared with other ephedrines (Table 4) we see that CLINAM is an exception indeed.

The phosphorinane configuration is the same in all compounds of our series (Table 5). The ring configurations are best described using torsion angles and Table 5 compares our results with literature data for 1,3,2-dioxaphosphorinane-2-oxo compounds in which the P=O is in either axial (POA) or equatorial (POE) position (Van Nuffel, Van Alsenoy, Lenstra & Geise, 1984).

Table 4. *Comparison of some torsion angles* (°) *in various ephedrines or ephedrine derivatives*

Ref.	Compound	Torsion angles* τ	ω	χ	ψ
(1)	Pseudoephedrine	44	52	−162	174
(2)	Pseudoephedrine hydrochloride	63	55	−171	162
(3)	Ephedrine hydrochloride	−21	−70	−170	175
(4)	Ephedrine dihydrogen phosphate	−21	−73	177	128
(5)	Ephedrine monohydrogen phosphate A	−36	−57	−168	85
(6)	Ephedrine monohydrogen phosphate B	−11	−69	−169	85
(7)	Ephedrine-*N*-benzyloxycarbonyl-L-leucine	−7·5	−66·2	−53·0	
(8)	Ephedrine-*N*-acetyl-L-valine	−18·5	−66·0	−159·9	
(9)	*p*-Hydroxyephedrine hydrochloride	−18·9	−59·7	−157·7	
(10)	INAM	−7·9	−65·3	−150·1	97·6
(11)	INAP	21·1	85·0	162·8	−57·5
(12)	CLINAM	−17·4	−71·7	−72·3	62·6
(13)	CLINAP	22·4	80·4	162·6	−46·6

References: (1)(2) Mathew & Palenik (1977); (3) Hearn & Bugg (1972); (4) Allen *et al.* (1979); (5)(6) Bergin (1971); (7)(8) Gorman *et al.* (1986); (9) Hearn, Freeman & Bugg (1973); (10)(11)(12)(13) present series.

* See Table 3 for a definition of the torsion angles.

Table 5. *Comparison of some torsion angles* (°) *of phosphorinane in various compounds*

Compound	OPOC	⟨OPOC⟩	POCC	⟨POCC⟩	OCCC	⟨OCCC⟩	Torsion angles
INAM	52·4		60·3		59·0		*p*
INAP	53·8		60·9		59·1		*p*
CLINAM	51·3		59·7		59·3		*p*
CLINAP	54·1		61·1		58·8		*p*
p: average		52·9		60·5		59·1	
MEOXPI	44·6		54·2		57·1		*e*
MEOXPH20 Mol. I	41·9		54·6		61·9		*e*
Mol. II	43·3		54·5		59·0		*e*
BCMOPH	42·8		52·4		57·0		*e*
PCMOXP	41·3		54·0		58·0		*e*
ZZZANMIO Mol. I	38·3		51·8		59·5		*e*
Mol. II	45·1		54·5		57·1		*e*
e: average		43·5		54·2		58·8	
POA1	55·4		59·9		55·8		*a*
POA2 Mol. I	52·2		58·8		58·8		*a*
Mol. II	51·2		56·4		57·3		*a*
a: average		52·9		58·3		57·3	

Angle OPOC is the mean of the angles *A* and *E* as defined in Table 3, angle POCC of the angles *B* and *E*, and OCCC of the angles *C* and *D*.
a: conformation with axial P=O; average as given by Van Nuffel, Van Alsenoy, Lenstra & Geise (1984).
e: conformation with equatorial P=O; average as for axial conformation.
p: present compound.
References:

MEOXPI	Van Nuffel, Lenstra & Geise (1980).
MEOXPH20	Bukowska-Strzyzewska & Dobrowolska (1978).
BCMOPH	Wagner, Jensen, Wadsworth & Johnson (1973*a*).
PCMOXP	Wagner, Jensen, Wadsworth & Johnson (1973*b*).
ZZZANM10	Bukowska-Strzyzewska & Dobrowolska (1980).
POA1	Wagner, Jensen, Wadsworth & Johnson (1973*c*).
POA2	Van Nuffel, Lenstra & Geise (1982).

Most of the references were found by searching the Cambridge Crystallographic Database (Allen *et al.*, 1979).

The bond distances P(2)–O(21) and P(2)–O(22), with mean values of 1·486 and 1·482 Å respectively, are equal within the accuracy of our determinations, and only slightly longer than the mean values of doubly bonded axial P=O (1·472 Å) and equatorial P=O (1·453 Å), as reported by Van Nuffel *et al.* (1984), while a single P–O is mostly found in the range 1·56–1·59 Å. We may therefore describe the present 1,3,2-dioxaphosphorinanes as having a chair conformation with P=O in both axial and equatorial position.

Table 5 shows that our torsion angles agree very well with the literature data for axial P=O, and deviate significantly from the data for equatorial P=O. As the axial substituent is most important for the ring conformation [see Fig. 3 in Van Nuffel *et al.* (1984)], the present axial P=O causes the conformation to be the same as for other 1,3,2-dioxaphosphorinanes with P=O in axial position.

It is interesting to observe that in our compounds the equatorial P=O is involved in two O(21)···H–N(2)$^+$ hydrogen bonds and the axial P=O is involved in one O(22)···H–O(10) hydrogen bond, with the exception of CLINAM, in which the two hydrogen bonds from O(21) are linked to N(2)$^+$ and O(10), and the one from O(22) is linked to N(2). The neutral acid molecules will have P–OH in equatorial position and the ring will have the same conformation as 1,3,2-dioxaphosphorinanes with axial P=O. Thus, during the process of crystallization, the neutral molecule may enter the crystal lattice without any change of conformation except for the transfer of one proton to the ephedrine moiety.

It is worthwhile to compare the set (+)-phenylphosphonic acid with (+)- and (–)-ephedrine (INAM and INAP) on the one hand, and the set (+)-*o*-chlorophenylphosphonic acid with (+)- and (–)-ephedrine (CLINAM and CLINAP) on the other hand.

An important observation is that the first set does not lead to resolution, while the second set does. To rationalize this difference on the basis of X-ray data in combination with other physical data is a considerable challenge.

From Table 6 it is evident that in the first set (INAM, INAP) no appreciable difference is noted in the physical parameters (melting point, enthalpy of fusion and solubility) of the diastereomeric salts. By contrast, in the second set, the successful resolution of racemic ephedrine using *o*-chlorophosphonic acid, the differences in the enthalpy of fusion and solubility of the diastereomeric salts are considerable. The polymorphic behaviour of the salts in the second set is presumably responsible for the relatively small difference in melting points.

The lack of difference in these parameters in the first set is also reflected by the similarity in the X-ray structures and packing patterns of the two diastereomeric salts (INAM, Fig. 3 of paper I, and INAP, Fig. 2 of paper II). By contrast, the X-ray structures and crystal packings of the second set reveal distinct differences (CLINAM, Fig. 2 of paper III, and CLINAP, Fig. 3 of the present paper). For example, the fit of the moieties in the molecular layers of the second set of diastereomeric salts (CLINAM and CLINAP) seems to be better in the less soluble salt, showing a shorter contact between the phenyl rings of the separate phosphonic acid moieties of 3·498 Å instead of a distance longer than 4·0 Å in the case of the more soluble salt.

Table 6. *Physical data for the diastereomeric salts*

	Unit-cell volume (Å^3)	Melting point (K)	Enthalpy of fusion (kJ mol^{-1})	Solubility (g/100 g) 100% EtOH	50% EtOH
INAM	1096·9	505·3	51·58	8·6	32·2
INAP	1087·3	508·5	51·21	8·3	31·6
CLINAM	1102·7	492·6	48·95	5·6	8·6
CLINAP	1122·1	489·4	41·42	19·3	12·8

The observation that the least soluble salt (CLINAM) contains ephedrine molecules in a rather 'unique' configuration, also found for ephedrine in a diastereomeric salt with *N*-benzyloxycarbonl-L-leucine (Gorman *et al.*, 1986), is surprising. The observation that this 'unique' configuration in the case of Gorman *et al.* (1986). leads to the *more* soluble salt of the pair, while in our case the salt with the ephedrine in the 'unique' configuration leads to the *less* soluble salt of the pair, is important. More information, in combination with force field calculations, from similar cases is needed before predictions on the basis of X-ray structure determinations alone are warranted.

However, important clues can be obtained from melting points, heats of fusion and solubilities. For example, recent work in our laboratory on the resolution of camphorsulfonic acid derivaties of α-phenylethanesulfonic acid (Tanabe Seiy, 1984), shows large differences (factors of 10 to 80) in the solubilities of the diastereomeric salts.

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The Crystallography of Nitramine–Solvent Complexes. VI.* Structure of the 1:1 Molecular Complex Formed between 1,7-Diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane (BSX) and 4-Hydroxybutanoic Acid Lactone

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Abstract. $C_8H_{14}N_6O_{10}.C_4H_6O_2$, $M_r = 440{\cdot}3$, monoclinic, $P2_1/c$, $a = 14{\cdot}966\ (3)$, $b = 6{\cdot}594\ (1)$, $c = 20{\cdot}792\ (5)$ Å, $\beta = 106{\cdot}77\ (2)°$, $Z = 4$, $D_x = 1{\cdot}488$, $D_m = 1{\cdot}49$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu = 1{\cdot}063$ mm^{-1}, $F(000) = 920$, $T = 293$ K, $R = 0{\cdot}075$ for 3349 observed reflexions. Molecules of BSX form centrosymmetric dimers, weakly bound by N···O interactions [2·951 (4) and 3·096 (4) Å]; the solvent molecules are bound by similar interactions to the dimers. This structural entity (two BSX and two solvent molecules) resembles that found in the other two types of BSX complex reported previously. The three types differ in the modes of packing of the weakly bound units. The 4-hydroxybutanoic acid lactone molecule is positionally disordered (0·65/0·35) between two orientations.

Introduction. 1,7-Diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane (BSX) forms complexes with a wide variety of organic solvents and the complexes can be divided into four distinct types (*A*, *B*, *C* or *D*) within each of which the cell dimensions are similar and the internal symmetry the same (Cobbledick & Small, 1973*a*). The structures of the type *A* complex formed with *N*,*N*-dimethylformamide, BSX–DMF (Cobbledick & Small, 1973*b*), the type *C* complex formed with 1,4-dioxane, BSX–DOX (Cobbledick & Small, 1973*c*) and the

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