

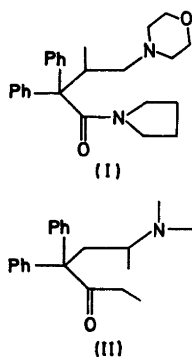
Crystal Structures of Synthetic Analgetics. III. Dextromoramide Bitartrate

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The molecular and crystal structure of dextromoramide (+)-bitartrate has been determined by X-ray methods. The crystals are orthorhombic, space group $P2_12_12_1$ with unit cell dimensions $a=7.976(3)$ Å; $b=17.024(5)$ Å; $c=20.046(5)$ Å. The structure was determined by direct methods and refined to a conventional R of 0.053 for 1909 observed reflections.

The morpholine moiety is in *anti* position relative to the quaternary carbon atom, the nitrogen atom being engaged in a comparatively strong N—H...O hydrogen bond of 2.76 Å to the ionized end of the bitartrate ion. Thus there is no interaction between the amino group and the carbonyl group. The pyrrolidine ring has the *C γ -exo* conformation, *C γ* being 0.61 Å out of the plane through the other atoms of the ring. The amide group is not strictly planar as the torsional angle about the C'—N bond is 6.4°. An extensive network of hydrogen bonds form molecular layers normal to the *z*-axis whereas the layers are connected through van der Waals forces only.



Moramide (I) is a tertiary amide related to methadone (II) and among the more potent analgetics.¹ The present structure determination was carried out as a part of the investigation

on morphine-like analgetics being in progress in this laboratory.²⁻³ Of the two isomers of moramide the *dextro* form is by far the most active. Thus analgesic activity resides in the same enantiomer as in the non-narcotic propoxyphene.¹

EXPERIMENTAL

Single crystals of dextromoramide (+)-bitartrate were obtained from the commercially available compound by recrystallization from ethanol. The crystals are prisms with orthorhombic symmetry. Systematically absent reflections $h00$, $0k0$, and $00l$ for odd indices are compatible with space group $P2_12_12_1$. Unit cell dimensions were determined on a Syntex PI diffractometer with graphite crystal monochromated MoK α -radiation ($\lambda=0.71069$ Å).

A crystal of dimensions 0.5 mm \times 0.2 mm \times 0.2 mm was employed for the collection of three-dimensional intensity data. The ω autocollection program was applied with a scan rate of 3° min⁻¹. The scan range was $2\theta(\alpha) \pm 0.5^\circ$ and the background were counted 0.7 times the scan time. The intensities of three standard reflections were measured periodically during the collection of data. They showed no systematic variation. E.s.d.'s in the intensities were taken as the square root of the total counts with a 2 % addition for instrumental instability.

A total of 2946 independent reflections were recorded within the limit of 0.59 for $\sin \theta/\lambda$; 1909 had a net count larger than $2\sigma_1$.

The data were corrected for Lorentz and polarization effects, and for secondary extinction.

All calculations were performed on a CDC 6600 computer using the programs described in Ref. 4, except for the phase determination which was done with MULTAN, written by P. Main *et al.*⁵ Atomic form factors were those of Hanson *et al.*⁶ for O, N, and C and of Stewart *et al.*⁷ for H.

CRYSTAL DATA

Dextromoramide (+)-bitartrate, $C_{25}H_{32}N_2O_8$.
 $C_8H_6O_6$, orthorhombic.

$a = 7.976(3)$ Å, $b = 17.024(5)$ Å, $c = 20.046(5)$ Å.
 $V = 2721.9$ Å³, $M = 524.27$, $Z = 4$.

$D_{\text{obs}} = 1.29$ g cm⁻³ (flotation), $D_{\text{calc}} = 1.28$ g cm⁻³.
 Systematic absences: $h00$, $0k0$, $00l$ for odd indices; space group $P2_12_12_1$.

STRUCTURE DETERMINATION

Normalized structure factors were calculated by means of the K -function.⁸ The phase determination was carried out with MULTAN, applying the 443 highest E -values (≥ 1.25). One of the resulting E -maps revealed the positions of all the 39 non-hydrogen atoms. Successive Fourier syntheses, isotropic and anisotropic full matrix least-squares refinement gave an R -factor of 0.09. Approximate positions of all the hydrogen atoms were calculated from stereochemical considerations, taking reasonable hydrogen bonds into account. All the hydrogen atoms were refined isotropically. But the three hydroxyl hydrogen atoms got large B -values and were excluded from further calculations. Hydrogen atoms bonded to the same carbon atom were given common B -values. The refinement finally converged at a conventional R of 0.053 ($R_w = 0.039$).

A complete list of observed and calculated structure factors may be obtained from the

author on request. The atomic parameters are given in Table 1 where the anisotropic temperature factor is given by

$$\exp - [B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl]$$

E.s.d's in bond lengths and angles are 0.005–0.007 Å and 0.3–0.5°, respectively.

DISCUSSION

The numbering of the atoms is shown in Fig. 1. Interatomic distances and angles are given in Tables 2 and 3, whereas some torsional angles are listed in Table 4.

According to earlier investigations of (+)-tartaric acid^{9–10} the absolute configuration of this isomer is found to be $2R,3R$. The drawings in the present paper depict this optical isomer, referred to as $27R, 28R$ with the present numbering. Usually the tartrate ion consists of two planar halves with a dihedral angle of 60°. In the present case, each of the two carboxyl groups, with the addition of C27 and C28, respectively, is planar. However, the two hydroxyl oxygen atoms O5 and O6 are situated 0.14 and 0.26 Å out of the planes, respectively. The dihedral angle between the planes is 65.2°. Ionization of one carboxyl group is obvious from the two equal C–O bond distances C26–O3 [1.248(5) Å] and C26–O4 [1.259(5) Å], whereas the other end of the tartrate ion is non-symmetrical.

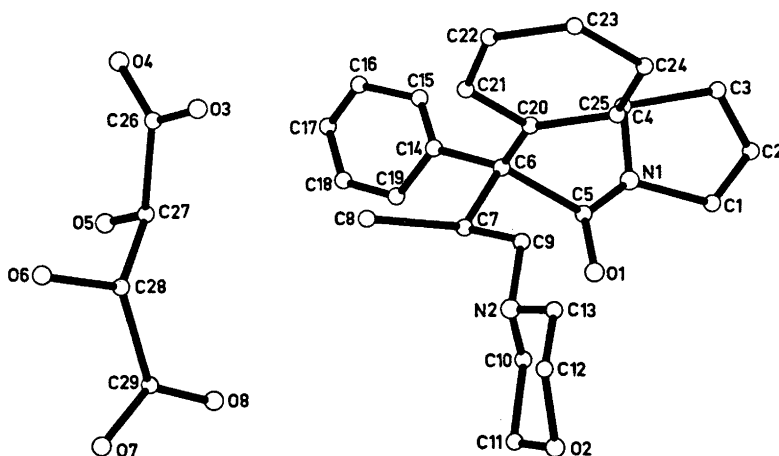


Fig. 1. The numbering of the atoms.

Table 1. Positional and thermal parameters for the heavy (10^4) and the hydrogen atoms (10^3), with e.s.d.'s in the parentheses.

ATOM	X	Y	Z	B11	B22	B33	B12	B13	B23
C1	-1669(7)	6587(3)	4897(2)	111(11)	21(2)	24(2)	32(8)	2(7)	4(3)
C2	-2774(8)	6636(3)	4647(3)	178(15)	26(2)	46(2)	49(11)	47(11)	6(4)
C3	-1893(8)	6546(3)	5284(3)	193(15)	33(2)	38(2)	-9(11)	79(10)	-29(4)
C4	-1374(7)	5715(3)	5187(2)	122(11)	35(2)	15(1)	11(9)	23(7)	-4(3)
C6	189(6)	6354(3)	4813(2)	78(9)	17(2)	16(1)	-14(8)	-1(6)	-3(3)
C6	1668(6)	4637(2)	4338(2)	85(9)	17(2)	11(1)	3(8)	7(6)	-8(3)
C7	2139(6)	4265(3)	3758(2)	91(9)	21(2)	12(1)	-7(8)	8(6)	0(3)
C8	2716(7)	3431(3)	3880(2)	128(11)	23(2)	16(1)	26(8)	18(7)	-8(3)
C9	3638(6)	4799(3)	3666(2)	111(10)	26(2)	12(1)	-8(8)	21(6)	-4(3)
C10	3488(6)	4771(3)	2356(2)	100(10)	31(2)	14(1)	-4(8)	-5(7)	0(3)
C11	4833(7)	4641(3)	1743(2)	110(11)	44(3)	13(1)	-8(10)	7(7)	3(3)
C12	7889(6)	5981(3)	2279(3)	72(9)	41(2)	21(2)	-3(9)	28(7)	9(4)
C13	6888(6)	5134(3)	2923(2)	92(10)	29(2)	18(1)	-28(9)	0(7)	12(3)
C14	-331(6)	4683(2)	4581(2)	63(9)	18(2)	16(1)	8(7)	3(6)	0(3)
C16	-719(7)	3984(3)	5217(2)	133(12)	28(2)	13(1)	0(8)	8(7)	0(3)
C16	-2681(6)	3423(3)	8388(2)	153(12)	25(2)	16(1)	-13(9)	12(8)	18(3)
C17	-3889(7)	3877(3)	4899(3)	181(11)	26(2)	24(2)	-28(9)	18(8)	4(3)
C18	-2666(6)	3224(3)	4232(3)	85(10)	27(2)	22(2)	-8(8)	18(7)	1(3)
C19	-1355(7)	3717(3)	4872(2)	93(10)	29(2)	12(1)	0(8)	-4(7)	-4(3)
C20	2251(6)	4894(3)	4904(2)	61(9)	20(2)	12(1)	17(8)	21(6)	-1(3)
C21	2085(7)	4328(3)	6319(2)	132(11)	30(2)	10(1)	13(9)	0(7)	1(3)
C22	4878(8)	4542(3)	6622(3)	127(12)	42(3)	22(2)	23(11)	-13(8)	-1(4)
C23	4495(7)	5318(4)	5918(3)	188(11)	56(3)	17(1)	-32(10)	0(7)	-7(4)
C24	3787(7)	5889(3)	5587(3)	119(12)	38(3)	19(2)	-39(10)	-3(8)	-14(3)
C25	2788(7)	6676(3)	5981(2)	189(11)	84(2)	17(1)	1(8)	14(7)	-4(3)
C26	-3985(7)	2645(3)	1185(2)	118(10)	36(2)	18(2)	43(9)	0(7)	0(3)
C27	-2285(6)	2582(3)	2866(2)	77(10)	22(2)	19(2)	11(7)	11(6)	0(3)
C28	-962(7)	2281(3)	2537(2)	121(10)	22(2)	14(1)	4(8)	6(7)	-8(3)
C29	847(7)	2543(3)	2377(3)	115(11)	32(2)	20(2)	-21(9)	-11(8)	-18(3)
N1	-886(5)	6796(2)	4399(2)	97(8)	25(2)	13(1)	14(7)	4(5)	4(2)
N2	4551(5)	4682(2)	2962(2)	96(8)	19(2)	14(1)	4(6)	8(5)	-8(2)
O1	219(4)	6478(2)	3415(1)	162(8)	25(1)	11(1)	6(6)	9(4)	7(2)
O2	5903(5)	6138(2)	1713(2)	161(8)	49(2)	10(1)	-28(8)	24(5)	18(2)
O3	-4189(6)	3133(2)	2756(2)	158(8)	32(1)	22(1)	54(6)	13(5)	-7(2)
O4	-5886(6)	2214(2)	2829(2)	115(8)	53(2)	37(1)	-27(7)	-13(6)	-26(3)
O5	-2292(5)	2686(2)	1443(2)	188(8)	48(2)	14(1)	54(6)	11(5)	-11(2)
O6	-1131(5)	1468(2)	2545(2)	111(7)	28(1)	19(1)	-3(5)	1(5)	6(2)
O7	1984(4)	2818(2)	2487(2)	88(7)	33(2)	32(1)	18(6)	0(5)	-8(2)
O8	1112(5)	3207(2)	2181(2)	135(8)	39(2)	61(2)	-36(7)	-18(7)	25(3)

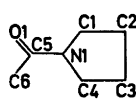
ATOM	X	Y	Z	B	ATOM	X	Y	Z	B
H1C1	-87(8)	694(3)	389(2)	3,7(1,3)	H2C11	495(6)	483(3)	167(2)	4,4(8)
H2C1	-215(8)	642(3)	366(2)	3,7(9)	H1C12	798(6)	539(2)	223(2)	3,0(4,2)
H1C2	-385(8)	655(4)	468(3)	6,3(1,1)	H2C12	752(6)	443(2)	225(2)	3,0(7)
H2C2	-272(8)	745(4)	461(3)	6,3(1,3)	H1C13	556(6)	572(3)	297(2)	3,1(3)
H1C3	-254(7)	654(3)	573(3)	5,1(1,4)	H2C13	677(6)	497(3)	328(2)	3,1(9)
H2C3	-87(7)	692(3)	538(2)	6,1(1,8)	H1C18	-13(7)	413(3)	561(2)	5,7(1,2)
H1C4	-242(8)	539(3)	515(3)	4,5(2,1)	H1C16	-217(7)	337(3)	594(2)	5,5(1,5)
H2C4	-44(8)	556(3)	539(2)	4,5(1,1)	H1C17	-392(7)	275(3)	566(3)	6,0(1,5)
H1C7	140(8)	425(3)	332(2)	3,3(1,3)	H1C18	-335(6)	284(3)	383(2)	4,0(1,3)
H1C8	329(6)	316(3)	349(2)	3,2(1,5)	H1C19	-118(5)	382(2)	368(2)	1,5(9)
H2C8	178(6)	313(3)	397(2)	3,2(2,3)	H1C21	276(9)	376(3)	529(3)	6,0(1,8)
H3C8	342(6)	338(3)	423(2)	3,2(7)	H1C22	451(8)	497(3)	615(2)	6,9(1,6)
H1C9	442(6)	475(2)	395(2)	1,9(1,9)	H1C23	527(6)	547(3)	632(2)	5,1(1,3)
H2C9	328(6)	539(2)	356(2)	1,9(7)	H1C24	418(8)	648(2)	564(2)	2,2(9)
H1C10	313(5)	535(3)	241(2)	2,8(1,7)	H1C25	332(6)	615(3)	466(2)	5,0(1,1)
H2C10	251(5)	438(2)	233(2)	2,8(7)	H1C27	-193(7)	397(3)	183(3)	3,4(1,6)
H1C11	483(7)	498(3)	294(2)	3,9(1,3)	H1C28	-129(6)	255(2)	392(2)	2,1(1,8)
H1C11	387(6)	473(2)	132(2)	4,4(1,9)					

Table 2. Bond lengths (Å).

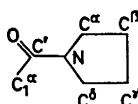
DISTANCE	(Å)	DISTANCE	(Å)	DISTANCE	(Å)
C1 = N1	1,480(6)	C1 = C2	1,519(7)	C2 = C3	1,540(8)
C3 = C4	1,517(7)	C4 = N1	1,482(6)	C5 = N1	1,346(5)
C5 = O1	1,221(5)	C5 = C6	1,570(6)	C6 = C7	1,578(6)
C7 = C8	1,517(6)	C7 = C9	1,526(6)	C9 = N2	1,514(5)
N2 = C10	1,503(6)	C10 = C11	1,582(6)	C11 = O2	1,422(6)
C12 = O2	1,421(6)	C12 = C13	1,588(6)	C13 = N2	1,583(6)
C6 = C14	1,544(6)	C14 = C15	1,397(6)	C15 = C16	1,384(7)
C16 = C17	1,527(7)	C17 = C18	1,388(6)	C18 = C19	1,378(6)
C19 = C14	1,393(6)	C6 = C20	1,355(5)	C20 = C21	1,481(6)
C21 = C22	1,383(7)	C22 = C23	1,376(7)	C23 = C24	1,394(7)
C24 = C25	1,384(7)	C25 = C26	1,391(7)	C26 = O3	1,259(6)
C26 = O4	1,246(6)	C26 = C27	1,536(7)	C27 = O5	1,489(6)
C27 = C28	1,539(7)	C28 = O6	1,489(5)	C28 = C29	1,542(7)
C29 = O7	1,298(6)	C29 = O8	1,211(8)		

To make the comparison with other pyrrolidine residues easier, the conventional nomenclature¹²⁻¹³ of proline peptides is put into parentheses in the further text.

The puckering of the pyrrolidine ring is revealed by the atom C3 (C γ) being situated 0.61 Å out of a plane through N1, C1, C2, and C4 (N, C α , C β , C δ), given in Table 5.



This work


 Conventional
nomenclature

The present envelope conformation is thus similar to that found in most of the earlier reported proline determinations.¹³⁻¹⁴ C5(C') is situated 0.05 Å out of the plane described above and on the opposite side relative to C3 (C γ). Applying the proposed notation in Ref. 13, the present conformation may be referred to as C3-*exo* (C γ -*exo*.) Although the atoms N1, C1, C4, C5 (N, C α , C β , C γ , C') are coplanar the amide group is not strictly planar and subsequently the non-planarity may be described by a rotation about the C5-N1 (C'-N) amide bond. The torsional angle is 6.4° and is probably due to intramolecular strain, as reported for other

Table 3. Bond angles (°).

ANGLE	(°)	ANGLE	(°)
C1 = N1 = C4	111,2(4)	N1 = C1 = C2	104,4(4)
C1 = C2 = C3	102,6(5)	C2 = C3 = C4	103,4(4)
C3 = C4 = N1	101,9(4)	C1 = N1 = C5	110,4(4)
C4 = N1 = C5	130,3(4)	N1 = C6 = O1	120,3(4)
N1 = C5 = C6	119,7(4)	O1 = C5 = C6	119,0(4)
C5 = C6 = C7	106,0(3)	C5 = C6 = C14	105,1(4)
C6 = C6 = C20	112,1(4)	C7 = C6 = C14	110,4(3)
C7 = C6 = C28	109,0(4)	C14 = C6 = C20	113,8(3)
C6 = C7 = C8	114,5(4)	C6 = C7 = C9	109,0(4)
C8 = C7 = C9	110,5(4)	C7 = C9 = N2	115,1(4)
C9 = N2 = C10	112,5(4)	C9 = N2 = C13	109,1(3)
C13 = N2 = C10	100,8(3)	N2 = C10 = C11	109,9(4)
C10 = C11 = O2	113,0(4)	C11 = O2 = C12	109,9(4)
O2 = C12 = C13	111,8(4)	C12 = C13 = N2	110,8(4)
C6 = C14 = C15	123,9(4)	C6 = C14 = C19	119,4(4)
C14 = C15 = C16	121,4(5)	C15 = C16 = C17	120,2(5)
C16 = C17 = C10	120,0(5)	C17 = C18 = C19	110,9(5)
C18 = C19 = C14	122,0(4)	C19 = C14 = C15	116,5(4)
C6 = C20 = C21	120,1(4)	C6 = C20 = C25	121,9(4)
C20 = C21 = C22	121,0(5)	C21 = C22 = C23	120,0(5)
C22 = C23 = C24	119,3(5)	C23 = C24 = C25	120,3(5)
C24 = C25 = C20	121,0(5)	C25 = C20 = C21	117,9(5)
O3 = C26 = O4	127,0(5)	O3 = C26 = C27	115,0(5)
O4 = C26 = C27	116,4(5)	C26 = C27 = O5	109,0(4)
C26 = C27 = C28	111,1(4)	O5 = C27 = C28	110,9(4)
C27 = C28 = O6	112,0(4)	C27 = C28 = C29	111,1(4)
O6 = C28 = C29	113,4(4)	C28 = C29 = O7	114,7(5)
C28 = C29 = O8	120,1(5)	O7 = C29 = O8	120,1(6)

Table 4. Torsional angles (°).

DIMEDRAL ANGLE	()	DIMEDRAL ANGLE	()
C1 = C2 = C3 = C4	-40,3(6)	C1 = N1 = C5 = O1	-9,5(7)
C4 = N1 = C5 = O1	173,4(5)	C1 = N1 = C5 = C6	174,0(4)
C4 = N1 = C5 = C6	-2,2(7)	N1 = C5 = C6 = C14	63,7(5)
N1 = C5 = C6 = C29	-60,5(5)	C5 = C6 = C14 = C15	-110,0(5)
C5 = C6 = C20 = C25	-14,5(6)	C15 = C14 = C6 = C7	135,2(5)
C21 = C20 = C6 = C7	-73,7(5)	C14 = C6 = C7 = C8	-48,3(5)
C20 = C6 = C7 = C8	77,5(5)	C14 = C6 = C7 = C9	-172,7(4)
C20 = C6 = C7 = C9	-46,9(5)	C6 = C7 = C9 = N2	-166,5(4)
C7 = C9 = N2 = C10	65,2(5)	C7 = C9 = N2 = C13	-174,0(4)
C9 = N2 = C10 = C11	176,0(4)	C9 = N2 = C13 = C12	-177,0(4)
N2 = C10 = C11 = O2	-59,1(5)	N2 = C13 = C12 = O2	56,0(5)
C10 = C11 = O2 = C12	63,1(5)	C11 = O2 = C12 = C13	-57,9(5)
O4 = C26 = C27 = O5	5,7(7)	C26 = C27 = C28 = C29	-155,0(4)
O5 = C27 = C28 = O6	-46,2(6)	O7 = C29 = C28 = O6	-12,5(6)
O3 = C26 = C29 = O7	119,7(6)		

amides containing the pyrrolidine ring.¹³ This may be caused by the close approaches C4...C6 (C δ ...C1 α , 3.09 Å) and C1...O1 (C α -O, 2.68 Å).

An amide group containing an unsubstituted pyrrolidine ring may be looked upon as both a *cis* and a *trans* peptide. As such a unit, the dimensions of the correspondent standard peptide units¹⁴⁻¹⁶ may indicate the non-symmetrical *sp*³-configuration of the nitrogen atom. The rather large difference between the two angles C1-N1-C5 (C α -N-C') and C4-N1-C5 (C β -N-C') of 118.4 and 130.3°, respectively, is in agreement with values found in related compounds.^{13,17,18} Also the standard values¹⁴⁻¹⁶ imply an opening of the latter bond angle compared to the former. The C5-N1 bond of 1.346(5) Å is somewhat longer than normal for C-N single bonds in peptides (1.325 Å).¹⁴ A corresponding lengthening is also reported by Kartha *et al.*,¹⁸ although that amide group is essentially planar.¹⁸

As the moramide molecule is highly crowded, with four large groups bonded to C6, the C-C single bonds involving this quaternary carbon atom is long as compared to the normal values.¹⁹ The bond lengths C5-C6 (1.570 Å), C6-C7 (1.578 Å), C6-C14 (1.544 Å), and C6-C20 (1.555 Å) clearly exhibit the increased interatomic distances in this part of the molecule. Inspection of Table 3 shows the deformations of the bond angles around C6, the values varying from 105.1° (C5-C6-C14) to 113.9° (C14-C6-C20). C6 is coplanar with one of the two strictly planar aromatic rings (C20,...,C25), whereas it is 0.07 Å out of the other. This non-planarity and the above mentioned angular deformations are attributed to steric repulsions, as reported for propoxyphene HCl² and methadone.^{3,20}

The conformation of the propylamine chain

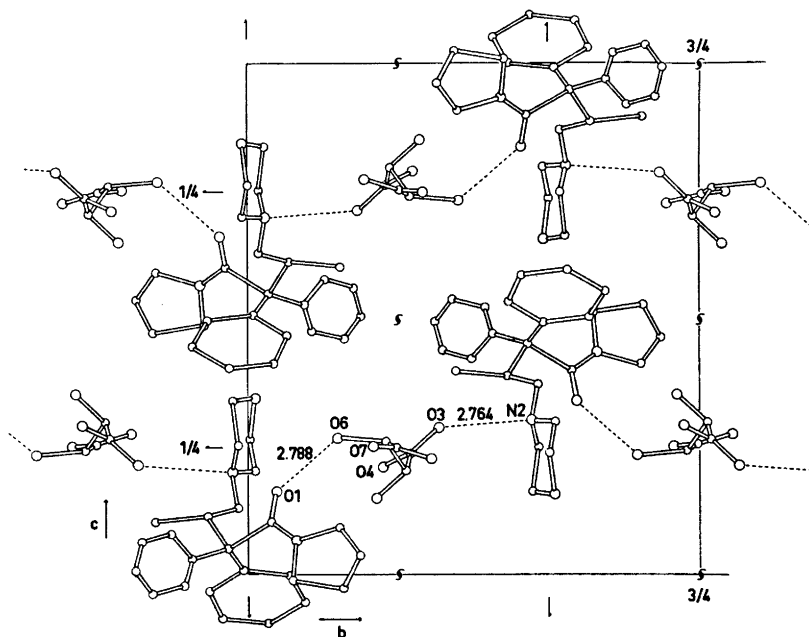


Fig. 2. The crystal structure as seen along the a -axis [the intermolecular distance $O7 \cdots O4$ (i) is 2.544 Å].

Table 5. Least square planes and deviations (Å) of the individual atoms.

Equations:

Plane A (pyrrolidine ring)
 $(0.0966a + 0.0335b + 0.0142c) R - 7.605 = 0$

Plane B (amide group)
 $(0.0992a + 0.0322b + 0.0136c) R - 7.261 = 0$

Plane A	Deviations	Plane B	Deviations
N1 (N)	-0.024	N1 (N)	-0.014
C1 (C α)	0.027	C1 (C α)	0.005
C2 (C β)	-0.016	C4 (C δ)	0.005
C3* (C γ)	0.606	C5 (C ϵ)	0.006
C4 (C δ)	0.017	C6* (C α_1)	0.111
C5* (C γ')	-0.047	O1* (O)	-0.136

Atoms with an * do not define the plane.

is nearly staggered, the dihedral angle $C6 - C7 - C9 - N2$ being -166.5° . The extension of this chain is to some extent attributed to the hydrogen bonds in the crystal - more precisely the comparatively strong hydrogen bond of 2.764 Å which links the morpholino nitrogen atom N2 to the ionized end of the bitartrate

ion. The morpholine ring has the chair conformation, and the acidic proton on N2 is in axial position. The average $C - N2^+$ distance of 1.507 Å is normal for $C - N$ single bonds with a protonated nitrogen atom.

The three-dimensional molecular arrangement is shown in Figs. 2 and 3. Although the hydroxyl hydrogen atoms are not located, the distances and angles given in Table 6 support the assumption that the contacts $O7 \cdots O4$ (2.544 Å) and $O6 \cdots O1$ (2.788 Å) are hydrogen bonds. Fig. 2 depicts the layers normal to the z -axis whereas the extension of each single layer is shown in Fig. 3. This figure also visualizes the infinite chains of bitartrate ions along the a -axis. Each organic anion is additionally connected to two different moramide moieties.

A cyclic conformation similar to that found in methadone^{3,20} is not preferred in the present structure. The presence of a hydrogen bonded nitrogen atom in the propylamin chain results in an overall shape of the present analgetic similar to that reported for methadone HBr²¹ and dextropropoxyphene HCl.²

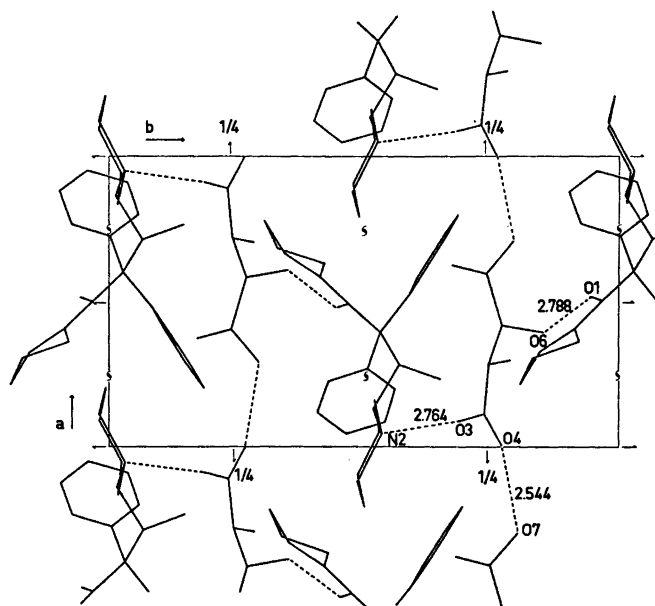


Fig. 3. One single layer of the crystal structure as seen along the z -axis.

Table 6. Distances (Å) and angles ($^{\circ}$) of the hydrogen bonds. The letters (i) and (ii) give the symmetry code of the acceptor atom.

Distances		Angles	
O7...O4(i)	2.544	C29-O7-O4(i)	119.5
O6...O1(iii)	2.788	C26(i)-O4(i)-O7	124.5
N2...O3(i)	2.764	C28-O6-O1(ii)	117.5
		C5(ii)-O1(ii)-O6	150.1
		C9-N2-O3(i)	118.9
		C10-N2-O3(i)	103.7
		C13-N2-O3(i)	103.0
		C26(i)-O3(i)-N2	140.0
(i) $x+1$ y z		N2-HN2-O3(i)	163.8
(ii) $-x$ $y-\frac{1}{2}$ $\frac{1}{2}-z$			

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