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The Crystal and Molecular Structure of Dipipanone Hydrochloride Hydrate

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The crystal and molecular structure of the opiate agonist 3-oxo-4,4-diphenyl-6-piperidylheptane has been determined by X-ray crystallographic methods using 4057 reflections observed by counter methods. The crystals are triclinic, space group $P\bar{1}$ with unit cell dimensions $a=8.922(2)$ Å, $b=9.029(1)$ Å, $c=15.444(2)$ Å, $\alpha=97.70(1)°$, $\beta=100.74(1)°$, $\gamma=109.63(1)°$. The structure was refined to a conventional R-factor of 0.057. Estimated standard deviations are 0.004 Å and 0.2° in interatomic distances and angles when hydrogen atoms are not involved. Spatial features common to "opiate" type analgesics is discussed in relationship to the "receptor".

In recent years a number of methadone-related substances have been studied by X-ray crystallographic methods[1-10] in order to define the structural characteristics that are associated with their biological activity. However, as the reported structures reflect a number of conformational states, further structural studies of such molecules by X-ray methods appear to be of interest. In this paper the crystal and molecular structure of 3-oxo-4,4-diphenyl-6-piperidylheptane (Dipipanone), which has been shown to have agonistic activity on opiate receptors,[11,12,13] and which is closely related to methadone, is presented.

EXPERIMENTAL

Colourless plate-formed crystals of dipipanone hydrochloride separated from an acetonic solution by slow addition of diethyl ether. Oscillation and Weissenberg photographs indicated triclinic symmetry.

For the general experimental procedure, see table below.

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Cell parameters were determined by a least squares fit to the diffractometer settings for 15 general reflections. The standard deviations in the measured intensities were calculated as $\sigma(I)=|C_T+(0.02\ C_N)^2|^{\frac{1}{2}}$ where C_T is the total number of counts and C_N is the scan count minus the background count.

The intensity data were corrected for Lorentz and polarization effects. The variation in the intensities of the test reflections was less than 1 % and no corrections were made on this basis.

Experimental conditions

Instrument	SYNTEX $P\bar{1}$
Radiation	Graphite crystal monochromated Mo$K\alpha$ $\lambda=0.71069$ Å
Crystal dimensions/mm	$0.4\times0.3\times0.1$
Scanning mode	$\theta/2\theta$
Scan speed/° min^{-1}	2–3 depending on intensity
Scan range/°	$2\theta\alpha_1-0.9$ to $2\theta\alpha_2+1.0$
Background counts	For 0.35 of scan time at scan limits
Temperature/K	291
2θ range/°	$2<2\theta<65$
Number of reflections meas.	4997
Number of reflections $I>2.5\sigma(I)$	4057
Number of standard reflections	3
Number of reflections between standard reflections	57

Scattering factors used were those of Doyle and Turner[14] for C, N, O and Cl^- and of Stewart, Davidson and Simpson[15] for H.

Table 1. Fractional atomic coordinates and thermal parameters for the nonhydrogen atoms in dipipanone hydrate HCl. The anisotropic temperature factor is given by $\exp-(B_{11}h^2+B_{22}k^2+\cdots B_{23}kl)$.

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl	0.8585(1)	0.6800(1)	0.5709(0)	0.0181(1)	0.0143(1)	0.0039(0)	0.0115(2)	0.0003(1)	0.0007(1)
O1	0.2991(2)	0.3785(2)	0.0732(1)	0.0195(4)	0.0194(4)	0.0040(1)	0.0256(6)	0.0004(3)	0.0022(3)
O2	1.0545(4)	0.6431(3)	0.4136(2)	0.0384(7)	0.0299(6)	0.0094(2)	0.0397(10)	0.0129(6)	0.0175(5)
N	0.6528(2)	0.6324(2)	0.3698(1)	0.0125(3)	0.0081(3)	0.0026(1)	0.0073(5)	0.0017(3)	0.0015(2)
C1	0.2113(6)	0.1634(5)	0.0873(2)	0.0670(14)	0.0241(8)	0.0040(1)	0.0437(17)	−0.0121(7)	−0.0018(5)
C2	0.2764(4)	0.1242(4)	0.0013(2)	0.0235(6)	0.0164(5)	0.0038(1)	0.0150(9)	−0.0024(5)	0.0003(4)
C3	0.3380(3)	0.2638(3)	0.0784(2)	0.0103(4)	0.0130(4)	0.0030(1)	0.0085(7)	0.0030(3)	0.0027(3)
C4	0.4547(3)	0.2595(3)	0.1664(1)	0.0098(3)	0.0093(3)	0.0025(1)	0.0081(6)	0.0027(3)	0.0013(3)
C5	0.4778(3)	0.4110(3)	0.2369(2)	0.0109(4)	0.0098(3)	0.0028(1)	0.0089(6)	0.0029(3)	0.0017(3)
C6	0.6128(3)	0.4583(3)	0.3228(2)	0.0130(4)	0.0086(3)	0.0030(1)	0.0099(6)	0.0016(3)	0.0008(3)
C7	0.5789(3)	0.3523(3)	0.3907(2)	0.0196(5)	0.0100(4)	0.0039(1)	0.0098(7)	0.0010(4)	0.0039(4)
C8	0.6230(3)	0.2812(3)	0.1465(1)	0.0100(4)	0.0093(3)	0.0028(1)	0.0080(6)	0.0030(3)	0.0008(3)
C9	0.6759(3)	0.3690(3)	0.0842(2)	0.0126(4)	0.0159(4)	0.0041(1)	0.0111(7)	0.0052(4)	0.0063(4)
C10	0.8337(4)	0.4055(4)	0.0727(2)	0.0154(5)	0.0221(6)	0.0058(2)	0.0123(9)	0.0100(5)	0.0097(5)
C11	0.9410(3)	0.3541(4)	0.1234(2)	0.0116(5)	0.0206(6)	0.0071(2)	0.0119(8)	0.0088(5)	0.0034(5)
C12	0.8926(3)	0.2684(4)	0.1870(2)	0.0137(5)	0.0186(5)	0.0064(2)	0.0190(8)	0.0040(5)	0.0046(5)
C13	0.7344(3)	0.2309(3)	0.1983(2)	0.0135(5)	0.0148(4)	0.0042(1)	0.0143(7)	0.0049(4)	0.0052(4)
C14	0.3718(3)	0.0979(3)	0.1919(1)	0.0096(4)	0.0101(4)	0.0027(1)	0.0055(6)	0.0017(3)	0.0012(3)
C15	0.3909(3)	−0.0420(3)	0.1542(2)	0.0169(5)	0.0108(4)	0.0035(1)	0.0096(7)	0.0041(4)	0.0018(3)
C16	0.3082(4)	−0.1894(3)	0.1731(2)	0.0205(6)	0.0107(4)	0.0050(2)	0.0093(8)	0.0008(5)	0.0012(4)
C17	0.2075(4)	−0.2001(3)	0.2311(2)	0.0166(5)	0.0135(5)	0.0061(2)	−0.0012(8)	0.0019(5)	0.0064(5)
C18	0.1873(3)	−0.0649(4)	0.2688(2)	0.0133(5)	0.0183(5)	0.0057(2)	0.0014(8)	0.0071(4)	0.0051(5)
C19	0.2656(3)	0.0821(3)	0.2481(2)	0.0113(4)	0.0129(4)	0.0045(1)	0.0044(7)	0.0049(4)	0.0013(4)
C20	0.5072(3)	0.6705(3)	0.3849(2)	0.0152(4)	0.0098(4)	0.0038(1)	0.0112(6)	0.0063(4)	0.0027(3)
C21	0.5612(4)	0.8384(3)	0.4413(2)	0.0229(6)	0.0109(4)	0.0042(1)	0.0154(8)	0.0069(4)	0.0018(4)
C22	0.6664(4)	0.9634(3)	0.3993(2)	0.0245(6)	0.0085(4)	0.0053(2)	0.0119(8)	0.0023(5)	0.0022(4)
C23	0.8084(4)	0.9202(3)	0.3799(2)	0.0175(5)	0.0109(4)	0.0056(2)	0.0023(8)	0.0025(5)	0.0045(4)
C24	0.7523(3)	0.7525(3)	0.3243(2)	0.0135(4)	0.0120(4)	0.0046(1)	0.0067(7)	0.0059(4)	0.0042(4)

The density of the crystalline compound was measured by means of flotation.

Crystal data. Dipipanone hydrochloride hydrate, $C_{24}H_{31}NO\cdot HCl\cdot H_2O$, triclinic $a=8.922(2)$ Å, $b=9.029(1)$ Å, $c=15.444(2)$ Å, $\alpha=97.70(1)°$, $\beta=100.74(1)°$, $\gamma=109.63(1)°$, $V=1125.0$ Å^3, $M=403.97$, $Z=2$ F(000)=416.0, $D_x=1.186$ g cm^{-3}, $D_o=1.192$ g cm^{-3}. Space group $P\bar{1}$ (No. 2).

STRUCTURE DETERMINATION

The structure was solved by direct methods using the program assembly MULTAN.[16] Of the 34 hydrogen atoms, 25 were introduced from stereochemical considerations whereas the 9 H-atoms belonging to the N-atom, the methyl groups and the water molecule were located from a difference map. In the final least squares calculations all positional parameters, anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms were refined. The refinement terminated at an R factor of 0.057 and a goodnes of fit $S=[\Sigma w\Delta^2/(m-n)]^{\frac{1}{2}}=2.8$.

The final parameters are given in Tables 1 and 2 and describe the molecule in the $S(C_a)$ configuration.

Tables of observed and calculated structure factors are available from the authors.

DESCRIPTION

The labelling of the atoms is shown in Fig. 1. The bond lengths and angles are presented in Table 3 and the torsion angles in Table 4. The overall conformation of the dipipanone molecule as it appears in the crystalline hydrated hydrochloride is depicted in the stereoscopic drawing in Fig. 2. The molecule exists in the crystal with an extended hexylamine chain. A least squares plane through the atoms C1–C6 and N show that

Table 2. Fractional atomic coordinates and isotropic temperature factor for the hydrogen atoms in dipipanone hydrate HCl. Standard deviations in the coordinates is 4×10^{-3}.

	X	*Y*	*Z*	*B*
HO1	1.081	0.657	0.455	5.6
HO2	1.051	0.561	0.406	5.7
HN	0.715	0.646	0.424	3.7
H11	0.173	0.062	−0.137	3.0
H12	0.300	0.253	−0.101	3.0
H13	0.117	0.198	−0.082	3.0
H21	0.359	0.086	0.001	5.8
H22	0.187	0.054	0.012	5.9
H51	0.375	0.402	0.252	3.3
H52	0.504	0.501	0.205	2.4
H61	0.716	0.458	0.305	3.4
H71	0.571	0.241	0.364	5.2
H72	0.684	0.384	0.423	7.7
H73	0.465	0.342	0.407	4.8
H91	0.606	0.408	0.048	4.0
H101	0.857	0.459	0.027	4.8
H111	1.044	0.381	0.113	5.1
H121	0.964	0.230	0.221	5.2
H131	0.697	0.167	0.242	3.7
H151	0.466	−0.031	0.116	3.8
H161	0.329	−0.274	0.146	5.1
H171	0.158	−0.295	0.247	4.6
H181	0.116	−0.070	0.308	5.7
H191	0.248	0.165	0.274	2.9
H291	0.452	0.591	0.412	3.4
H202	0.439	0.660	0.327	3.0
H211	0.624	0.842	0.496	3.5
H212	0.470	0.858	0.450	5.1
H222	0.597	0.966	0.349	4.8
H221	0.705	1.065	0.438	5.9
H231	0.876	0.924	0.437	4.3
H232	0.866	0.986	0.344	5.8
H241	0.684	0.743	0.267	3.2
H242	0.834	0.719	0.313	4.1

none of these seven atoms deviates by more than 0.28 Å from the plane. The present conformation is most similar to that of acetylmethadole HCl,[4] the main conformational difference between the two crystal structures being the difference in the torsion angle about the C6–N bond and about the two C4–ϕ bonds.

The arrangement of the molecules in the crystal is illustrated in Fig. 3. Double molecular layers parallel to the (001) plane are held together through van der Waals forces only, whereas these layers are connected by hydrogen bonds to chloride ions. The chloride ions and the water molecules form hydrogen-bonded binary units between the molecular layers. The geometry concerning the hydrogen bonding is described in Table 5.

Table 3. Bond lengths and angles in dipipanone·H_2O·HCl. Estimated standard deviations in bond lengths and angles not involving hydrogen atoms are $4 \cdot 10^{-3}$ Å and 0.2°, respectively. Bond lengths involving hydrogen atoms are given as mean values. The numbers in parentheses are standard deviation of the mean value.

Bond lengths (Å)		Bond angles (°)	
C1–C2	1.484	C1–C2–C3	113.5
C2–C3	1.508	C2–C3–C4	119.5
C3–C4	1.564	C2–C3–O1	119.8
C4–C5	1.558	O1–C3–C4	120.7
C5–C6	1.516	C3–C4–C5	106.7
C6–C7	1.516	C3–C4–C8	107.7
C6–N	1.532	C3–C4–C14	106.9
N–C20	1.500	C4–C8–C9	120.6
C20–C21	1.513	C8–C9–C10	121.6
C21–C22	1.512	C9–C10–C11	120.2
C22–C23	1.513	C10–C11–C12	119.6
C23–C24	1.505	C11–C12–C13	120.3
C24–N	1.499	C12–C13–C8	120.7
C4–C8	1.542	C13–C8–C9	117.6
C8–C9	1.378	C13–C8–C4	121.3
C9–C10	1.385	C8–C4–C5	107.6
C10–C11	1.364	C4–C14–C15	121.3
C11–C12	1.375	C14–C15–C16	121.2
C12–C13	1.387	C15–C16–C17	120.4
C13–C8	1.392	C16–C17–C8	119.3
C4–C14	1.539	C17–C18–C19	120.6
C14–C15	1.396	C18–C19–C14	121.5
C15–C16	1.388	C19–C14–C15	116.9
C16–C17	1.373	C19–C14–C4	121.6
C17–C18	1.363	C14–C4–C5	114.7
C18–C19	1.388	C8–C4–C14	113.7
C19–C14	1.385	C4–C5–C6	117.6
C3–O1	1.205	C5–C6–C7	115.7
		C5–C6–N	110.2
		N–C6–C7	108.4
		C6–N–C20	114.9
The mean value of		N–C20–C21	110.8
the X–H distances		C20–C21–C22	111.6
		C21–C22–C23	110.5
		C22–C23–C24	112.3
C–H	0.95(4)	C23–C24–N	110.4
N–H	0.88	C24–N–C20	110.4
O–H	0.67(6)	C24–N–C6	112.6

Table 4. Torsion angles in dipipanone·H_2O·HCl.

Angle	(°)	Angle	(°)
C1–C2–C3–O1	16.5	C4–C5–C6–C7	−73.7
C1–C2–C3–C4	−162.3	C4–C5–C6–N	162.8
C2–C3–C4–C5	−174.0	C5–C6–N–C20	51.8
C2–C3–C4–C14	51.3	C5–C6–N–C24	−75.8
C2–C3–C4–C8	71.3	C7–C6–N–C20	−75.8
O1–C3–C4–C5	7.3	C7–C6–N–C24	156.6
O1–C3–C4–C14	129.9	C6–N–C20–C21	173.1
O1–C3–C4–C8	−107.5	C6–N–C24–C23	−172.0
C3–C4–C8–C13	−158.4	N–C20–C21–C22	56.1
C3–C4–C8–C9	29.9	N–C24–C23–C22	−56.3
C3–C4–C14–C15	85.1	C20–C21–C22–C23	−53.2
C3–C4–C14–C19	−90.2	C24–C23–C22–C21	53.7
C3–C4–C5–C6	−167.5	C23–C24–N–C20	58.1
C9–C8–C4–C5	−83.7	C24–N–C20–C21	−58.2
C13–C8–C4–C5	88.1	C4–C8–C9–C10	172.5
C15–C14–C4–C5	−158.1	C4–C8–C13–C12	−172.1
C19–C14–C4–C5	26.6	C4–C14–C15–C16	−176.1
C8–C4–C5–C6	−52.7	C4–C14–C19–C18	178.1
C14–C4–C5–C6	75.0		

DISCUSSION

Through investigations of relationships between molecular structure and the analgesic activity of compounds with affinity for opiate receptors, a number of features have been shown to be of importance. Among them are the presence of an aromatic group and a cationic nitrogen,[17] the position of the nitrogen atom relative to the aromatic moiety,[18,19] the direction of the lone pair on the nitrogen atom relative to the aromatic ring,[20] or the position of the hydrogen atom on the cationic nitrogen.[21] However, the crucial property of molecules exhibiting analgesic activity is their ability to interact in a specific manner with "acceptor" groups on the opiate receptors. A single "acceptor" group for the aromatic part of an agonistic compound may be difficult to define, but it seems reasonable to suggest that the "acceptor" group interacting with the nitrogen atom should be positioned somewhere in the general direction of the axis of the nitrogen lone pair (or the N–H bond) and at a certain distance from the N-atom, say 2.8 Å. The distance from a position defined in this manner (*A*) to the centers of the phenyl rings (ϕ) is found in dipipanone to be 6.5 and 7.2 Å, respectively. A compilation of such ϕ–A distances calculated in the same way for a variety of analgesic compounds is presented in Table 6 together with ϕ–N distances and the angle α between the ϕ–A vector and the plane of the benzene ring. The data in the table indicates that the position of the N atom relative to the phenyl ring may be of lesser importance than its ability to interact with an acceptor group about 6.5 Å away from the ring center. The data for the

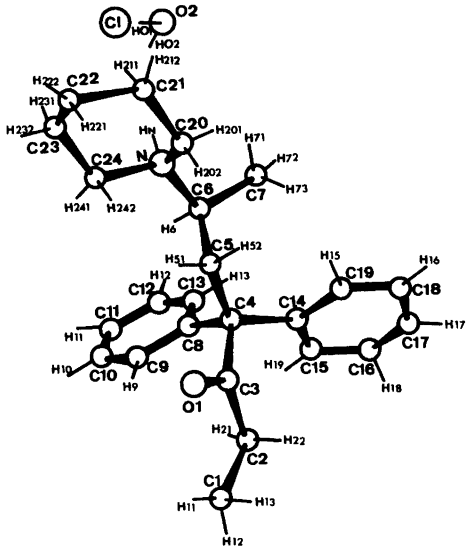


Fig. 1. The numbering of the atoms in the crystal structure of dipipanone·H_2O·HCl.

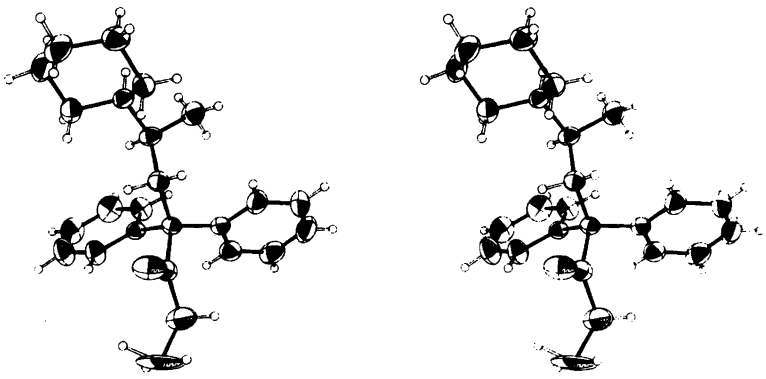


Fig. 2. Stereoscopic drawing of the dipipanone molecule.

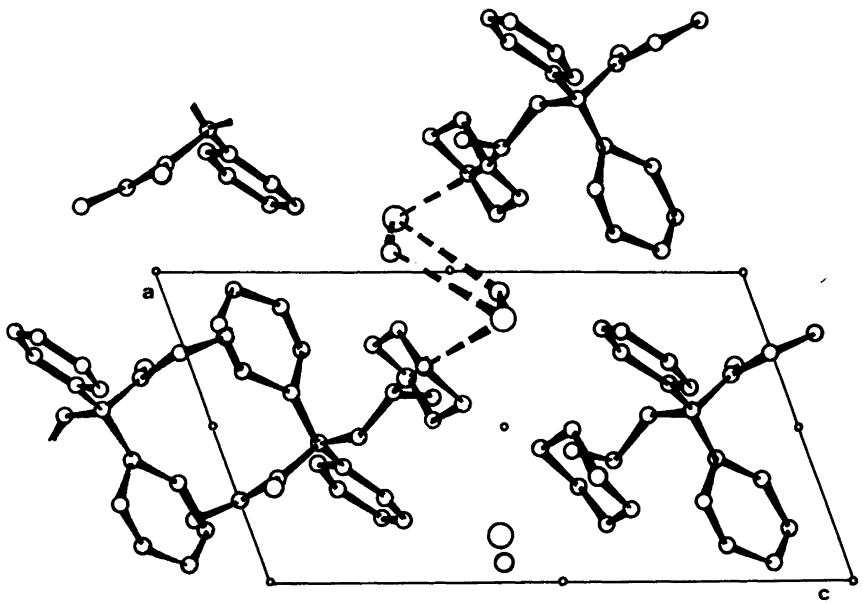
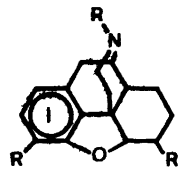


Fig. 3. Packing of dipipanone H_2O·HCl in the crystal as seen down the *b*-axis.

Table 5. Distances and angles concerning donor atoms (*D*) in the unit described in Table 1, and surrounding acceptor atoms (*A*).

D	A		D–A	H–A	∠D–H–A
N	Cl	(x, y, z)	3.192	2.30	175
O2	Cl	(x, y, z)	3.291	2.94	119.4
Cl	O2	$(2-x, 1-y, 1-z)$	3.287	2.61	157.6
Angle	Cl–O2–Cl	$(2-x, 1-y, 1-z)$:	105.5°		

Table 6. Comparison of distances from the center of an aromatic moiety (ϕ) to the active nitrogen atom (N) and to the group (A) interacting with that nitrogen atom, in a number of compounds with reported affinity to opiate receptors. The angle between the $\phi - A$ vector and the plane of the ϕ-ring is given as α. The aromatic rings are numbered I and II for distinction.



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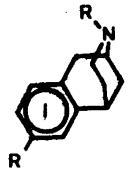

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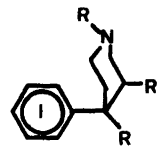

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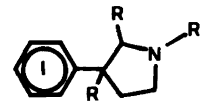

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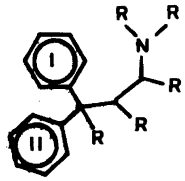

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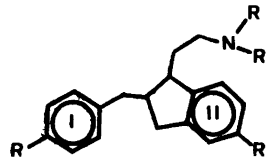

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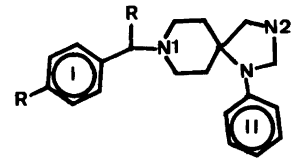

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Name		$\phi-N$		$\phi-A$		α		Ref.
		I	II	I	II	I	II	
Morphine (*1*)		4.6	–	6.8	–	1	–	22
Cyclozozine·HBr		4.5	–	6.8	–	7	–	23
NCBME	(*2*)	4.5	–	6.8	–	12	–	24
NME		4.4	–	6.7	–	16	–	24
Pethidine·HCl		5.6	–	6.1	–	38	–	25
Betaprodine·HCl	(*3*)	5.7	–	6.3	–	28	–	26
DL-Phenoperidine		5.7	–	6.1	–	40	–	27
Prodilidine (*4*)		5.0	–	6.6	–	14	–	28
Isomethadone·HCl		5.3	6.3	6.6	6.3	46	13	4
α-Methadole·HCl		5.3	6.1	6.0	5.5	17	15	4
α-Acetylmethadole HCl		5.3	5.1	6.7	4.1	22	4	4
Methadone·HBr		5.2	6.2	6.1	8.7	64	8	1
Methadone		4.7	5.8	4.6	4.4	4	29	2,3
Normethadone·HCl	(*5*)	5.0	6.3	6.0	8.7	70	11	9
Dextromoramide Bitart.		5.1	6.4	6.2	6.7	48	40	6
Dextromoramide		5.2	6.1	6.4	5.5	40	51	7
Dextropropoxyphene·HCl		5.3	7.7	5.7	9.0	74	5	5
Dextropropoxypheme		5.2	6.1	6.0	6.5	53	26	8
Dipipanone		4.9	5.9	6.5	7.2	58	44	
Etonitazene (*6*)		4.4	5.7	6.9	5.7	68	16	29
R 6372 (*7*)	N1	3.9	5.6	6.4	4.3	5	0	
	N2	7.3	5.0	8.4 8.4	6.7 6.8	62 67	21 18	30
TGGP	N_{TYR}	4.0	–	6.4	–	51	–	31
(Tyr – Gly – Gly – Phe)	N_{GLY}	5.7	–	6.5	–	18	–	

conformationally flexible molecules of the methadone type show that such molecules can easily accomodate conditions demanding a $\phi-A$ distance of about 6.5 Å.

It follows that if such a distance is of any importance for the interaction between opiate drugs and the analgesic receptor, the conformation found for methadone in the crystal structure of the free base is probably not the active conformation, the $\phi-A$ distances being only 4.4 and 4.6 Å.

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