possibly caused by the presence of Cl substituents at the Si atoms.

The Si–Cl bond length of 2·091 (1) Å is somewhat longer than the values obtained earlier [2·074 (1) and 2·080 (1) Å in $SiPh_3Cl$ (Lobkovsky, Fokin & Semenenko, 1981); it is still shorter in other (however, less accurate) studies]. The remaining bond lengths and angles are unexceptional.

In the crystal of (I) there are no intermolecular distances shorter than the sums of the van der Waals radii. The shortest intermolecular contact involving a Cl atom is Cl···H(33)($-x$, $2-y$, $2-z$) 3·06 (3) Å.

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Structure of 9-Hydroxy-3,7-dimethyl-2,3,4,5,6,7-hexahydro-2,7-methano-1*H*-3-benzazonine Hydrobromide, $C_{15}H_{22}NO^+.Br^-$

BY AKIKO ITAI AND YOICHI IITAKA

Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Tokyo, Japan

AND TADASHI KOMETANI AND SHUNSAKU SHIOTANI*

Department of Chemistry, Toyama Technical College, Hongo 13, *Toyama-shi, Japan*

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Abstract. $M_r = 312·25$, orthorhombic, $P2_12_12_1$, $a = 10·766$ (5), $b = 16·137$ (7), $c = 8·291$ (3) Å, $V = 1440$ (1) Å^3, $Z = 4$, $D_x = 1·440$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5402 Å, μ(Cu $K\alpha$) = 3·8 mm^{-1}, $F(000) = 648$, $T = 293$ K. $R = 0·052$ for 1589 observed reflections. The title compound is a synthetic analgesic which has a *C*-ring-enlarged benzomorphan structure. The N-containing ring protrudes from the molecular plane, and the H atom at the cationic N atom orientates toward the benzene ring. The distance of the N atom from the center of the benzene ring is 4·45 (1) Å.

Introduction. During extensive efforts to search for better analgesics, many kinds of chemical modifications have been applied to the morphine structure. Synthetic compounds containing only a portion of the morphine structure proved to be as effective as, or more effective than, the parent compound. Among them, the 6,7-benzomorphan compounds proved to be a particularly interesting and important class of analgesics and to give the most promising starting point in designing strong analgesics with low undesirable side effects, because the selective ligands for multiple opiate receptors were most likely to be found in this series (Gilbert & Martin, 1976). Some of them show useful narcotic antagonist activity.

By comparing the X-ray structures of several opiates (Gylbert, 1973; Hardy & Ahmed, 1975; Cochran & Abola, 1975), some structural requirements for possession of analgesic activity are proposed and discussed. Hardy & Ahmed (1975) ascribed the biological inactivity of 3-hydroxy-*N*-methyl-(+)-morphinan to the orientation of the lone electron pair of the N atom based on its X-ray structure. Opheim & Cox (1976) and Shiller, Yam & Lis (1977) suggested that the cationic form of the opiate drug is the active species, to interact with the receptor *via* ionic association. They also deduced that the distance of the cationic N atom from the benzene ring is important for analgesic activity. Moreover, Belleau, Conway, Ahmed & Hardy (1974) pointed out the importance of the relative geometry between the spacial orientation of the N lone electron pair and the benzene ring.

To elucidate the structure–activity relationships and to verify the proposals described above, several modified benzomorphans, with, for example, the *C* ring enlarged to a seven-membered ring or the N atom shifted to the next position in the carbon ring, were synthesized and analyzed crystallographically (Shiotani, Kometani & Mitsuhashi, 1975; Shiotani, Kometani, Mitsuhashi, Nozawa, Kurobe & Futsukaichi, 1976; Itai, Iitaka, Kometani & Shiotani, 1985). All these compounds were shown to possess fairly strong analgesic activities and the relationships between the X-ray structures and activities have been

* Present address: College of General Education, Toyama University, Gofuku, Toyama-shi, Japan.

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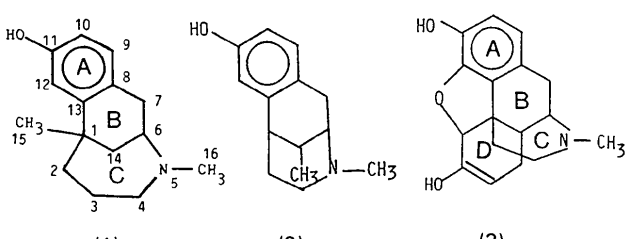
discussed in the previous paper (Shiotani, Kometani, Iitaka & Itai, 1978). Fig. 1 shows the chemical structure of the title compound (1) along with the atomic numbering and ring designation, together with the structures of 2,9β-dimethyl-6,7-benzomorphan (2) and morphine (3).

Experimental. Single crystals obtained from aqueous methanol solution as colorless prisms, approximate dimensions of a crystal 0·4 × 0·2 × 0·15 mm. Philips PW 1100 diffractometer, Cu $K\alpha$ radiation monochromated by a graphite plate. Lattice parameters from least squares of setting angles of 15 reflections. θ–2θ scan, within the θ range 20–40°, with a scan speed of 4° (θ) min^{-1}, $2\theta_{max} = 156°$, $0 \le h \le 12$, $0 \le k \le 20$, $0 \le l \le 9$. Three reference reflections monitored every 120 min throughout data collection showed no significant changes in intensity. Corrections for Lorentz–polarization, but not for absorption. 1593 reflections measured, 1589 with $I > \sigma(I)$ used for structure determination. Heavy-atom method using the position of the Br atom obtained from a Patterson map. H atoms located on a difference map, and refined with isotropic thermal motion. Final $R = 0{\cdot}052$, $wR = 0{\cdot}056$, $(\Delta/\sigma)_{max} = 0{\cdot}65$. Unit weights applied for all reflections. $\sum(\Delta F)^2$ minimized. Final difference map had no feature of chemical significance, largest peak 0·35 e Å^{-3}. Atomic scattering factors for non-H atoms taken from *International Tables for X-ray Crystallography* (1974) and those for H atoms from Stewart, Davidson & Simpson (1965).

Discussion. The atomic positional and thermal parameters are given in Table 1, and bond lengths, bond angles and selected torsion angles for non-H atoms are listed in Table 2.* Fig. 2 illustrates the molecular structure drawn by *ORTEP* (Johnson, 1971).

* Lists of atomic coordinates, bond lengths involving H atoms, and selected torsion angles, together with structure factors and anisotropic thermal parameters, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42029 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.



(1) (2) (3)

Fig. 1. Chemical structures of the title compound (1), 2,9β-dimethyl-6,7-benzomorphan (2), and morphine (3) along with the atomic numbering and ring designation.

Table 1. *Final fractional atomic coordinates* ($\times 10^4$, *for* Br $\times 10^5$, *for* H $\times 10^3$) *and isotropic thermal parameters* (Å^2) *with estimated standard deviations in parentheses*

For non-hydrogen atoms: $B_{eq} = \frac{4}{3}\sum_i\sum_j \mathbf{a}_i.\mathbf{a}_j\beta_{ij}$.

	x	y	z	B_{eq}(Å^2)
Br	8873 (10)	20092 (7)	20582 (13)	3.43 (1)
O	3309 (7)	−526 (4)	−377 (9)	3·22 (10)
N	6723 (7)	2834 (4)	1739 (9)	2·50 (10)
C(1)	5413 (8)	1267 (5)	3540 (10)	2·05 (11)
C(2)	4368 (9)	1898 (6)	3652 (11)	2·68 (13)
C(3)	4439 (8)	2612 (5)	2436 (12)	2·70 (13)
C(4)	5550 (9)	3174 (6)	2567 (12)	3·29 (15)
C(6)	7338 (8)	2070 (6)	2474 (11)	2·63 (12)
C(7)	7544 (9)	1417 (6)	1142 (12)	2·79 (14)
C(8)	6393 (8)	921 (5)	800 (11)	2·18 (12)
C(9)	6336 (9)	486 (6)	−701 (11)	2·68 (13)
C(10)	5333 (10)	−7 (6)	−1106 (12)	2·72 (13)
C(11)	4349 (8)	−70 (5)	−22 (11)	2·32 (12)
C(12)	4381 (8)	352 (5)	1460 (11)	2·16 (12)
C(13)	5402 (8)	836 (5)	1874 (10)	1·94 (11)
C(14)	6670 (9)	1671 (6)	3899 (11)	2·56 (13)
C(15)	5178 (11)	621 (7)	4866 (12)	3·83 (17)
C(16)	7646 (11)	3517 (7)	1587 (15)	4·30 (18)
H(O)	354 (10)	−92 (6)	−108 (13)	6 (3)
H(N5)	660 (14)	263 (9)	82 (18)	12 (5)
H(C2)	436 (9)	216 (5)	486 (11)	3 (2)
H'(C2)	362 (8)	157 (5)	366 (11)	2 (2)
H(C3)	374 (10)	300 (7)	288 (13)	5 (3)
H'(C3)	443 (14)	234 (9)	147 (17)	8 (5)
H(C4)	549 (10)	386 (6)	212 (14)	3 (3)
H'(C4)	577 (14)	333 (9)	375 (18)	5 (5)
H(C6)	819 (16)	222 (11)	292 (24)	6 (6)
H(C7)	842 (10)	95 (6)	170 (14)	6 (3)
H'(C7)	779 (11)	166 (7)	21 (15)	4 (3)
H(C9)	708 (14)	55 (8)	−156 (19)	6 (4)
H(C10)	540 (8)	−37 (5)	−217 (12)	3 (2)
H(C12)	363 (9)	23 (6)	223 (13)	4 (3)
H(C14)	636 (8)	198 (6)	481 (11)	3 (2)
H'(C14)	721 (9)	120 (6)	437 (13)	2 (2)
HC(15)	414 (12)	36 (7)	481 (14)	8 (3)
HC'(15)	569 (9)	18 (6)	468 (11)	5 (2)
HC''(15)	520 (14)	90 (9)	581 (18)	5 (4)
HC(16)	823 (8)	338 (5)	122 (12)	4 (2)
HC'(16)	782 (10)	377 (7)	287 (16)	6 (3)
HC''(16)	735 (13)	405 (9)	83 (18)	8 (4)

Table 2. *Bond lengths* (Å) *and bond angles* (°) *for non-hydrogen atoms with estimated standard deviations in parentheses*

O–C(11)	1·371 (11)	C(6)–C(7)	1·542 (14)
N–C(4)	1·538 (12)	C(6)–C(14)	1·527 (13)
N–C(6)	1·526 (12)	C(7)–C(8)	1·503 (13)
N C(16)	1·490 (14)	C(8)–C(9)	1·431 (13)
C(1)–C(2)	1·521 (13)	C(8)–C(13)	1·397 (12)
C(1)–C(13)	1·546 (12)	C(9)–C(10)	1·382 (14)
C(1)–C(14)	1·531 (13)	C(10)–C(11)	1·393 (14)
C(1)–C(15)	1·536 (13)	C(11)–C(12)	1·406 (13)
C(2)–C(3)	1·534 (13)	C(12)–C(13)	1·391 (12)
C(3)–C(4)	1·505 (13)		

C(4)–N–C(6)	117·8 (7)	C(9)–C(8)–C(7)	117·4 (8)
C(4)–N–C(16)	108·7 (7)	C(9)–C(8)–C(13)	118·3 (8)
C(6)–N–C(16)	110·0 (7)	C(7)–C(8)–C(13)	124·3 (8)
C(2)–C(1)–C(13)	110·5 (7)	C(10)–C(9)–C(8)	121·8 (9)
C(2)–C(1)–C(14)	110·9 (7)	C(11)–C(10)–C(9)	118·7 (9)
C(2)–C(1)–C(15)	106·8 (7)	C(12)–C(11)–O	117·9 (8)
C(13)–C(1)–C(14)	111·8 (7)	C(12)–C(11)–C(10)	120·6 (8)
C(13)–C(1)–C(15)	109·4 (7)	O–C(11)–C(10)	121·5 (8)
C(14)–C(1)–C(15)	107·2 (7)	C(13)–C(12)–C(11)	120·5 (8)
C(3)–C(2)–C(1)	115·2 (7)	N–C(4)–C(3)	113·9 (8)
C(4)–C(3)–C(2)	116·4 (8)	C(1)–C(13)–C(8)	121·3 (7)
C(7)–C(6)–N	109·2 (7)	C(1)–C(13)–C(12)	118·6 (7)
C(7)–C(6)–C(14)	109·5 (8)	C(8)–C(13)–C(12)	120·1 (8)
N–C(6)–C(14)	116·5 (7)	C(1)–C(14)–C(6)	116·5 (8)
C(8)–C(7)–C(6)	112·3 (8)		

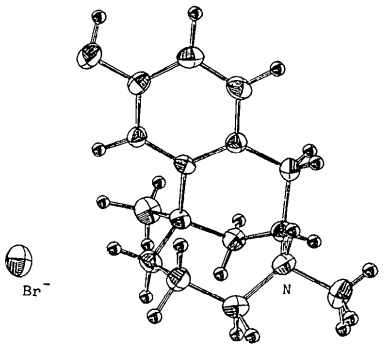


Fig. 2. *ORTEP* drawing of the molecule. Non-hydrogen atoms are depicted by 30% probability ellipsoids and H atoms are on an arbitrary scale for clarity.

Like the usual benzomorphans, the molecule is L-shaped with the N-containing *C* ring protruding from the molecular plane. In the title compound, the *C* ring of the benzomorphan is enlarged from a six-membered to a seven-membered ring. The *C* ring adopts a chair conformation with an approximate mirror plane passing through C(2) and the midpoint of N—C(6). The H atom at the cationic N atom occupies a β, axial-like position. This orientation is opposite to those of morphine (3) and 2,9β-dimethyl-6,7-benzomorphan (2). From inspection of the molecular model, an alternative chair conformation with a mirror plane through the N atom and the midpoint of C(1)—C(2) also seems to be stable, and would allow the α, axial orientation for the H atom on the cationic N atom, if the *N*-methyl group were preferably to take the equatorial configuration. The distance between the N atom and the center of the benzene ring is 4·45 Å, whereas the values in morphine (3) and (2) are 4·71 and 4·69 Å, respectively. It is noteworthy that in spite of these structural differences, compound (1) still retains an analgesic activity as strong as that of morphine. More precise and extensive stereochemical studies may be necessary for the elucidation of the structure–activity relationships in opiates. The crystalline cohesion is ensured by two hydrogen bonds N···Br 3·32 (1) Å [(N)H···Br 2·4 (1) Å] and N···Br 3·28 (1) Å [(N)H···Br 2·6 (1) Å], and by van der Waals contacts.

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1,4,5,6,7,8-Hexahydro-7-methyl-3-phenylcinnoline-1-carboxamide, $C_{16}H_{19}N_3O$

BY GIAIME MARONGIU* AND GABRIELE NAVARRA

Dipartimento di Scienze Chimiche dell'Università di Cagliari, Via Ospedale 72, 09100 *Cagliari, Italy*

AND ANTONIO MACCIONI AND ANTONIO PLUMITALLO

Istituto di Chimica Farmaceutica dell'Università di Cagliari, Via Ospedale 72, 09100 *Cagliari, Italy*

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Abstract. $M_r = 269·3$, triclinic, $P\bar{1}$, $a = 13·37$ (1), $b = 15·41$ (1), $c = 11·75$ (1) Å, $\alpha = 75·1$ (3), $\beta = 69·4$ (3), $\gamma = 94·0$ (3)°, $V = 2155$ (7) Å^3, $Z = 6$, $D_m = 1·24$, $D_x = 1·25$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 5·99$ cm^{-1}, $F(000) = 864$, $T \simeq 293$ K, final $R = 0·093$ for 2943 observed reflections. Bond distances and angles in the three independent molecules show good overall agreement. Molecules are hydrogen-

* To whom correspondence should be addressed.

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