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Structure of 1,3-Dimethyl-1,2,3,4,5,6-hexahydro-1,5-methano-3-benzazocin-9-ol Hydrobromide, $C_{14}H_{20}NO^+.Br^-$

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Abstract. $M_r = 298{\cdot}23$, orthorhombic, $P2_12_12_1$, $a = 12{\cdot}371\,(5)$, $b = 14{\cdot}394\,(6)$, $c = 7{\cdot}571\,(3)$ Å, $V = 1348\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}467$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}5402$ Å, $\mu = 4{\cdot}04$ mm^{-1}, $F(000) = 616$, $T = 293$ K, $R = 0{\cdot}032$ for 1512 observed reflections. The title compound is a synthetic analgesic whose activity is as strong as codeine. The N-containing ring makes a right angle with the plane of the remaining part of the molecule. The H atom at the cationic N atom, which is shifted to the next position in the *C* ring in benzomorphan, is oriented towards the benezene ring. The distance between the N atom and the center of the benzene ring is 4·11 Å.

Introduction. In the course of our search for better analgesics, a number of attempts have been made to modify the morphine structure. Among them, the 6,7-benzomorphan structure has been one of the most promising starting points for the design of strong analgesics with insignificant abuse potentials, because selective ligands to these receptors were most likely to be found in the 6,7-benzomorphan series (Gilbert & Martin, 1976). Belleau, Conway, Ahmed & Hardy (1974) proposed that some geometrical requirements should be satisfied for the spatial orientation of the N lone-electron pair and the benzene ring. Opheim & Cox (1976) and Schiller, Yam & Lis (1977) suggested that the cationic form of the opiate drug is active and interacts with the receptors *via* ionic association; they therefore suggested that the distance from the cationic N atom to the benzene ring is critical for opiate–receptor interaction. In order to elucidate the structure–activity relationships and to verify the proposals described above, several modified benzomorphans, such as those with the *C* ring enlarged or with the N atom shifted to the next position in the *C* ring, were synthesized and their activities tested (Shiotani, Kometani, Mitsuhashi, Nozawa, Kurobe & Futsukaichi, 1976; Shiotani, Kometani & Mitsuhashi, 1975). All these compounds were shown to possess fairly strong analgesic activities (Shiotani, Kometani, Iitaka & Itai, 1978). The chemical structure of the title compound (1) (and the atomic numbering) is shown in Fig. 1, together with those of 2,9β-dimethyl-6,7-benzomorphan (2) and morphine (3).

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Experimental. Single crystals obtained from aqueous methanol solutions as colorless prisms. Crystal approx. 0·3 × 0·2 × 0·1 mm. Philips PW 1100 diffractometer, Cu $K\alpha$ radiation monochromated by a graphite plate. Cell dimensions by least-squares refinement of the setting angles of 18 independent reflections within the θ range 20–40°. 1849 reflections measured using θ–2θ scanning method ($2\theta_{\max} = 156°$, $0 \le h \le 15$, $0 \le k \le 18$, $0 \le l \le 9$). Three reference reflections monitored every 120 min throughout data collection process showed no significant changes in intensity. 1512 reflections with $I \ge 2\sigma(I)$ used for structure determination, no absorption correction. Heavy-atom method using the Br-atom position obtained from Patterson map. Block-diagonal least-squares refinement (on F) of coordinates and anisotropic temperature factors of non-hydrogen atoms (Okaya & Ashida, 1967). H atoms located on a difference map and refined with isotropic thermal parameters. Final $R = 0{\cdot}032$, $R_w = 0{\cdot}035$, $(\Delta/\sigma)_{\max} < 0{\cdot}58$. Weighting scheme $\sqrt{w} = 1{\cdot}4$, when $F_o < 30{\cdot}0$ and $\sqrt{w} = 30{\cdot}0/F_o$ when $F_o \ge 30{\cdot}0$. Final difference map had no features of chemical significance, largest peak 0·3 e Å^{-3}. Atomic scattering factors for non-H atoms taken from *International Tables for X-ray Crystallography* (1974) and those for H from Stewart, Davidson & Simpson (1965).

Discussion. The positional and thermal parameters are given in Table 1, and bond lengths and bond angles for non-hydrogen atoms are listed in Table 2.* Fig. 2 shows *ORTEP* drawings (Johnson, 1971) of the molecule, viewed from two directions. As is easily seen from Fig. 2, the molecule is L-shaped with the N-containing *C* ring protruding from the rest of the molecule. In the present compound, the N atom which in benzomorphans is usually in the 4 position has been shifted to the 3 position. The *C* ring adopts a chair conformation and the H atom at the protonated N takes a β, axial position, oriented towards the benzene ring. This orientation is opposite to those of morphine (Gylbert, 1973), and 2,9β-dimethyl-6,7-benzomorphan (Cochran & Abola, 1975). The distance between the N atom and

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

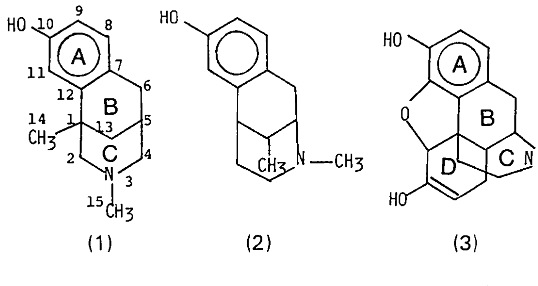
For non-hydrogen atoms: $B_{eq} = \frac{4}{3}\sum_i\sum_j \mathbf{a}_i.\mathbf{a}_j\beta_{ij}$.

	x	y	z	B_{eq} or B_{iso}
Br	122832 (3)	25400 (3)	22558 (5)	4·25 (0·01)
O	12799 (2)	6622 (2)	3305 (4)	3·62 (0·03)
N	10086 (2)	3142 (2)	4577 (4)	2·77 (0·04)
C(1)	9496 (3)	4817 (2)	4766 (4)	2·57 (0·04)
C(2)	9870 (3)	3948 (2)	5779 (5)	2·67 (0·04)
C(4)	9134 (3)	2943 (2)	3394 (5)	3·46 (0·05)
C(5)	8718 (3)	3799 (3)	2414 (5)	3·58 (0·05)
C(6)	9494 (3)	4166 (3)	1016 (5)	3·81 (0·05)
C(7)	10361 (3)	4813 (2)	1711 (5)	2·79 (0·04)
C(8)	11160 (3)	5122 (2)	564 (5)	3·12 (0·05)
C(9)	11964 (3)	5724 (2)	1090 (5)	3·10 (0·05)
C(10)	11994 (2)	6016 (2)	2851 (5)	2·77 (0·04)
C(11)	11210 (3)	5718 (2)	4024 (5)	2·58 (0·04)
C(12)	10373 (3)	5125 (2)	3463 (4)	2·39 (0·04)
C(13)	8457 (3)	4569 (3)	3747 (6)	3·40 (0·05)
C(14)	9243 (3)	5562 (3)	6149 (5)	3·55 (0·05)
C(15)	10345 (3)	2292 (2)	5656 (6)	3·93 (0·05)
H(O)	1275 (4)	680 (3)	436 (7)	7· (1·)
H(N)	1072 (3)	325 (3)	394 (6)	4· (1·)
H(C2)	1055 (3)	399 (2)	648 (5)	3· (1·)
H′(C2)	927 (3)	372 (3)	659 (6)	5· (1·)
H(C4)	940 (3)	246 (3)	246 (5)	4· (1·)
H′(C4)	852 (3)	271 (3)	415 (5)	4· (1·)
H(C5)	794 (4)	353 (3)	181 (6)	6· (1·)
H(C6)	982 (3)	360 (3)	42 (6)	5· (1·)
H′(C6)	908 (4)	441 (4)	22 (7)	7· (1·)
H(C8)	1122 (3)	491 (3)	−75 (6)	4· (1·)
H(C9)	1250 (3)	600 (3)	33 (5)	4· (1·)
H(C11)	1131 (3)	595 (3)	531 (5)	4· (1·)
H(C13)	815 (3)	512 (3)	312 (5)	4· (1·)
H′(C13)	777 (4)	434 (3)	477 (5)	5· (1·)
H(C14)	905 (3)	614 (3)	550 (6)	5· (1·)
H′(C14)	858 (4)	534 (3)	698 (6)	6· (1·)
H″(C14)	981 (4)	572 (3)	700 (6)	6· (1·)
H(C15)	1102 (3)	243 (3)	631 (5)	4· (1·)
H′(C15)	1058 (4)	179 (3)	479 (6)	6· (1·)
H″(C15)	970 (4)	211 (3)	630 (7)	5· (1·)

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

O–C(10)	1·368 (4)	C(5)–C(6)	1·524 (5)
N–C(2)	1·499 (4)	C(5)–C(13)	1·534 (5)
N–C(4)	1·507 (5)	C(6)–C(7)	1·514 (5)
N–C(15)	1·505 (5)	C(7)–C(8)	1·389 (5)
C(1)–C(2)	1·538 (5)	C(7)–C(12)	1·401 (5)
C(1)–C(12)	1·532 (5)	C(8)–C(9)	1·378 (5)
C(1)–C(13)	1·541 (5)	C(9)–C(10)	1·398 (5)
C(1)–C(14)	1·531 (5)	C(10)–C(11)	1·383 (5)
C(4)–C(5)	1·527 (5)	C(11)–C(12)	1·408 (4)

C(2)–N–C(4)	111·6 (3)	C(8)–C(7)–C(6)	118·9 (3)
C(2)–N–C(15)	109·7 (3)	C(8)–C(7)–C(12)	118·8 (3)
C(4)–N–C(15)	109·6 (3)	C(6)–C(7)–C(12)	122·3 (3)
C(2)–C(1)–C(12)	110·1 (3)	C(9)–C(8)–C(7)	122·3 (3)
C(2)–C(1)–C(13)	108·2 (3)	C(10)–C(9)–C(8)	118·9 (3)
C(2)–C(1)–C(14)	106·9 (3)	C(11)–C(10)–O	123·1 (3)
C(12)–C(1)–C(13)	109·6 (3)	C(11)–C(10)–C(9)	120·1 (3)
C(12)–C(1)–C(14)	112·5 (3)	O–C(10)–C(9)	116·7 (3)
C(13)–C(1)–C(14)	109·5 (3)	C(12)–C(11)–C(10)	120·6 (3)
C(5)–C(4)–N	113·5 (3)	N–C(2)–C(1)	112·4 (3)
C(6)–C(5)–C(4)	113·9 (3)	C(1)–C(12)–C(7)	120·6 (3)
C(6)–C(5)–C(13)	109·8 (3)	C(1)–C(12)–C(11)	120·2 (3)
C(4)–C(5)–C(13)	109·5 (3)	C(7)–C(12)–C(11)	119·2 (3)
C(7)–C(6)–C(5)	114·7 (3)	C(1)–C(13)–C(5)	108·7 (3)



(1) (2) (3)

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

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* Lists of structure factors, anisotropic thermal parameters, distances and angles involving H atoms, and selected torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39795 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

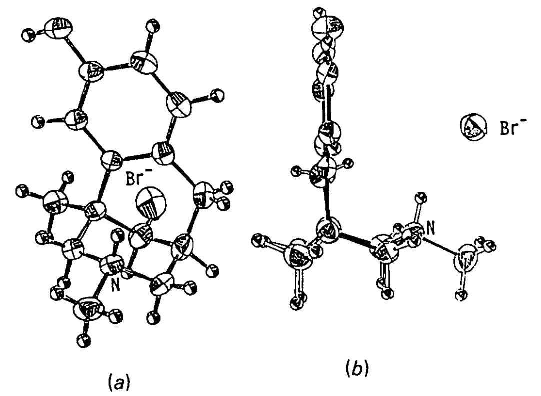

Fig. 2. Perspective views of the molecule (*a*) normal to the molecular plane and (*b*) from the side.

the center of the benzene ring, 4·11 Å, is rather short compared to the corresponding value in (2), 4·69 Å. It is noteworthy that, in spite of these considerable structural differences, the present compound still retains analgesic activity. A Br atom connects two adjacent molecules by two hydrogen bonds, O···Br 3·23 Å [H(O)···Br 2·39 Å] and N···Br 3·35 Å [H(N)···Br 2·53 Å], resulting in an infinite chain in the crystal packing.

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Structure of 2,4-Hexadiynylene Bis(benzenesulphonate), $C_{18}H_{14}O_6S_2$

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Abstract. $M_r = 390·43$, monoclinic, $P2_1/c$, $a = 13·079\,(3)$, $b = 5·280\,(1)$, $c = 13·977\,(6)$ Å, $\beta = 111·19\,(3)°$, $U = 899·95$ Å^3, $Z = 2$, $D_m = 1·42\,(1)$, $D_x = 1·441$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1·54184$ Å, $\mu = 2·832$ mm^{-1}, $F(000) = 404$, $T = 300$ K, $R = 0·0438$ for 1271 counter reflections. The diacetylene molecules pack so that the potentially reacting carbon atoms, for *trans*-1,4-addition polymerization of adjacent molecules, are separated by a distance of 3·746 (6) Å. This accounts for the occurrence of solid-state polymerization for this compound. The bond lengths and angles agree with those of similar compounds.

Introduction. The fact that many disubstituted diacetylenes (general formula *R*-C⁝C·C⁝C-*R′*) can be polymerized in the solid state to give extended-chain polymers was first recognized by Wegner (1969, 1971, 1972). Since this discovery there have been extensive investigations of the solid-state chemistry of diacetylenes (see Bloor, 1982, 1983*a*, and references therein) and of the properties of the resulting polymers (see Bloor, 1981, 1983*b*, and references therein). The solid-state reactivity of the diacetylene monomers is determined by the packing of the molecules in the crystal, which is in turn dependent on the properties of the monomer end groups *R* and *R′* (Baughman, 1974; Wegner, 1977; Bloor, 1982). Crystal structure data have been used to test the criteria proposed for solid-state reactivity (Baughman, 1974; Schmidt, 1967). Available data show that Schmidt's criterion

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