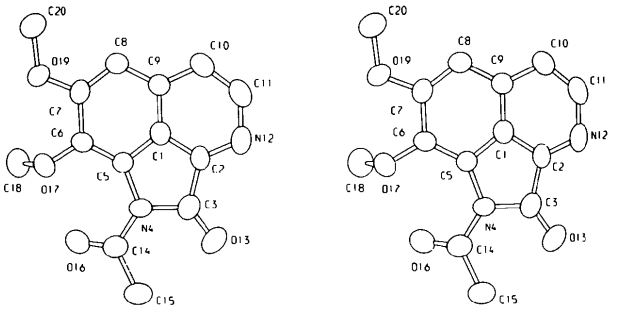
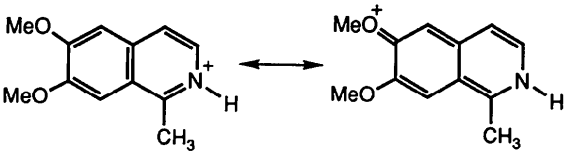


Fig. 1. Stereodrawing, after Johnson (1976), of (2) showing numbering scheme, and the 50% probability ellipsoids.

Discussion. The atomic parameters for 1-acetyl-7,8-dimethoxypyrrolo[2,3,4-*ij*]isoquinol-2-one, (2), are listed in Table 1.* Table 2 lists the total molecular geometry for (2), and Fig. 1 shows a stereoscopic drawing of the molecule with the numbering system used in the tables. The tricyclic heterocycle is essentially planar, each of the 12 ring atoms lying within 0·05 Å of their least-squares best plane. The five-membered ring is planar to within 0·012 Å and the benzene and pyridine rings to within 0·018 Å. The two imide carbonyl groups are arranged in an *anti* fashion. The extent of conjugation in the imide grouping is reflected in the dihedral angle of only 18° between the ring and its acetyl substituent. This near coplanarity in turn forces the adjacent methoxy group out of the plane of the benzene ring (80°); the remaining methoxy group achieves planarity (−3°) with the benzene ring by twisting its methyl away from its adjacent methoxy.

One may rationalize the preferred regioselectivity of electrophilic nitration of (1*a*) by assuming that substitution involves the 2-protonated species (1*a*)—H^+ and that this reduces [*cf.* resonance contributor (3)] the electron-releasing ability of the 6-methoxy group, allowing the influence of the 7-methoxy group to control the position of introduction of the electrophile.



(3)

We thank the SERC for a postdoctoral research assistantship (JDS).

* Lists of anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53831 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of 3-Methyl-1,2,3,4,5,6-hexahydro-1,6-methano-3-benzazocinium Hydrogen Oxalate

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Abstract. $C_{13}H_{18}N^+.C_2HO_4^-$, $M_r = 277·3$, orthorhombic, $P2_12_12_1$, $a = 5·752$ (1), $b = 15·502$ (2), $c = 15·910$ (2) Å, $V = 1418·6$ (6) Å^3, $Z = 4$, $D_x = 1·298$ g cm^{-3}, Mo $K\alpha$ ($\lambda = 0·71069$ Å), $\mu = 1·01$ cm^{-1}, $F(000) = 592$, $T = 295$ K. Final $R = 0·035$, $wR = 0·042$ for 1003 reflections with $I > 3\sigma(I)$. The compound is an ammonium hydrogen oxalate. Both O atoms of the ionized carboxyl group act as acceptors in the formation of two hydrogen bonds: (*a*) an N—H···O bond linking the cation and anion with N···O and H···O distances of 2·722 (4) and 1·78 (5) Å and (*b*) a strong O—H···O bond linking a chain of oxalate ions along **a** with O···O and H···O distances of 2·578 (4) and 1·59 (6) Å. The relative

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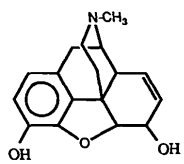
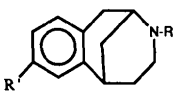
stereochemistry of the heterocyclic and aromatic rings in the cation is similar to that in morphine.

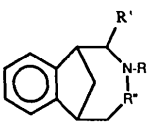
Introduction. Certain molecules, based on the condensed ring substructures of morphine (I), have the desirable analgesic activity and a lower degree of the undesirable opiate dependence liability, the most serious side effect of morphine-like drugs. The best known tricyclic ring system which has yielded compounds of this sort is the 6,7-benzomorphan system (II). The present paper reports the crystal structure of the hydrogen oxalate salt of one (III, $R = CH_3$, $R' = H$, $R'' = CH_2$) of the several members of a previously unknown ring system, the 1,2,3,4,5,6-hexahydro-1,6-methano-3-benzazocines. It has more than twice the analgesic potency of the corresponding 6,7-benzomorphan (II, $R = CH_3$, $R' = H$) and gave a lower physical dependence liability in primate studies (Mazzocchi & Harrison, 1978).



(I)



(II)



(III)

Experimental. Colorless crystals from a methyl alcohol–acetone solution of the racemic compound; 0·2 × 0·4 × 0·5 mm crystal; Picker FACS-I diffractometer, graphite monochromator, cell parameters from 12 manually centered reflections at $\pm 2\theta$, 2θ–θ scan at 2° min^{-1}, 10 s background, scan width (1·35 + 0·7tanθ)°; 3 standards measured every 100 reflections with average and maximum deviations 1·23% and 1·34%; $\theta_{max} = 25°$. No absorption correction. 1540 reflections measured, 1472 unique reflections, 1003 with $I > 3\sigma(I)$; index range for $h, k, l = 0$ to 6, 0 to 18, 0 to 18; equivalent intensity data not measured. Calculations performed with the *XRAY*76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) on a UNISYS 1100/92 computer and with the *TEXSAN* system (Molecular Structure Corporation, 1985) on a DEC MicroVAX II computer; structure solved with direct-methods programs *GENSIN* and *TANGEN* of *XRAY*76 system. Full-matrix least-squares refinement with anisotropic temperature factors for C, N and O atoms and individual isotropic terms for H atoms; $\sum w(F_o - F_c)^2$ minimized, $w = 1/\sigma^2(F_o)$, reflections with $I_o < 3\sigma(I_o)$ excluded from refinement; maximum Δ/σ of 0·11 in the final least-squares cycle; min. and max. $\Delta\rho$ of −0·15 and 0·13 e $Å^{-3}$; final R, wR and $S = 0·035$, 0·042 and 1·18, respectively. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Atomic coordinates are listed in Table 1.* The *PLOTMD* program (Luo, Ammon & Gilliland, 1989) was used to display Figs. 1–3 on a VaxStation II monitor, label the diagrams and prepare print files for a Hewlett-Packard Laser-Jet II printer.

Discussion. Bond lengths and bond angles are given in Table 2; an *ORTEP* (Johnson, 1965) drawing is shown in Fig. 1. The structure is an ammonium hydrogen oxalate. Bond lengths and angles in the cation are normal. The ionized carboxyl portion of the hydrogen oxalate anion has, as expected, two nearly equal C—O bonds of 1·242 (4) and 1·235 (4) Å. The two carboxyl groups of the anion are twisted by 7·8 (6)°.

Table 3 summarizes the intermolecular hydrogen bond parameters. In most hydrogen oxalate species (Newkome, Theriot & Fronczek, 1986; Vijayalakshmi & Srinivasan, 1983; Adams, 1978; Thomas & Liminga, 1978; Thomas, 1975; Thomas & Pramatus, 1975; Thomas & Renne, 1975) the anions form linear hydrogen-bonded chains. The present structure contains the same feature: that is, the hydrogen oxalate anions (Fig. 2) parallel to the a axis are joined by strong O—H···O hydrogen bonds [O4···O1($1 + x,y,z$) = 2·578 (4) Å]. The anion and cation are linked by strong and weak N—H···O bonds of N···O2 = 2·722 (4) and N···O4 = 3·055 (4) Å, respectively.

The structures of morphine (I) and the free base form of the benzazocine (III) are shown in Fig. 3 in orientations that illustrate the similarities in the aromatic ring and tertiary nitrogen geometries. (III) has the requisite tertiary nitrogen atom two–three carbons distant from an aromatic ring believed to be necessary for a compound to show morphine-like analgesic properties. The heterocyclic and aromatic rings are approximately perpendicular to each other in (I) and (III) and the distance from the center of the aromatic ring to the N atom is 4·5 and 4·3 Å, respectively.

A search of the Cambridge Structural Database (1990) identified the crystal structure of only one other (III)-type compound, *exo*-2-methoxy-3-aza-4-keto-7,8-benzobicyclo[4.2.1]nonene (III, $R = H$, $R' = OCH_3$, $R'' = C{=}O$; Ammon, Mazzocchi, Kopecky, Tamburin & Watts, 1973). The conformations of the aza regions of the eight-membered rings in the two type-(III) structures are substantially different because of geometry differences between the amide *vs* amino moieties.

* Lists of structure factors, anisotropic temperature factors and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53803 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates, equivalent isotropic temperature factors* (Å^2) *and e.s.d.'s in parentheses*

$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
O1	−0·4052 (4)	0·0440 (2)	−0·0993 (1)	3·5 (1)
O2	−0·2433 (5)	0·0512 (2)	0·0267 (1)	4·7 (1)
O3	0·0299 (5)	0·0299 (3)	−0·1670 (2)	5·4 (2)
O4	0·1773 (5)	0·0564 (2)	−0·0415 (2)	4·0 (1)
N	0·0910 (5)	0·0498 (2)	0·1479 (2)	2·7 (1)
C1	−0·1400 (7)	0·1369 (3)	0·2575 (2)	3·5 (2)
C2	−0·0583 (8)	0·0499 (3)	0·2258 (2)	3·4 (2)
C3	0·2819 (7)	0·1166 (2)	0·1458 (2)	2·9 (2)
C4	0·2021 (8)	0·2054 (3)	0·1173 (2)	3·4 (2)
C5	0·0379 (7)	0·2532 (3)	0·1777 (3)	3·5 (2)
C6	0·1340 (7)	0·2525 (2)	0·2661 (2)	3·4 (2)
C7	0·0406 (7)	0·1842 (3)	0·3109 (2)	3·4 (2)
C8	0·114 (1)	0·1664 (3)	0·3912 (2)	4·3 (2)
C9	0·283 (1)	0·2186 (3)	0·4264 (3)	5·4 (3)
C10	0·377 (1)	0·2863 (4)	0·3823 (3)	5·5 (3)
C11	0·304 (1)	0·3042 (3)	0·3020 (3)	4·3 (2)
C12	−0·1910 (8)	0·2035 (3)	0·1889 (3)	4·2 (2)
C13	0·191 (1)	−0·0381 (3)	0·1370 (3)	4·0 (2)
C14	−0·2364 (7)	0·0465 (3)	−0·0507 (2)	2·7 (1)
C15	0·0063 (6)	0·0432 (3)	−0·0940 (2)	3·0 (2)

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

O1—C14	1·242 (4)	C4—C5	1·538 (6)
O2—C14	1·235 (4)	C5—C6	1·512 (6)
O3—C15	1·188 (4)	C5—C12	1·535 (6)
O4—C15	1·307 (5)	C6—C7	1·384 (5)
N—C13	1·488 (5)	C6—C11	1·388 (6)
N—C2	1·508 (5)	C7—C8	1·373 (6)
N—C3	1·510 (5)	C8—C9	1·382 (7)
C1—C2	1·515 (6)	C9—C10	1·373 (7)
C1—C7	1·529 (6)	C10—C11	1·373 (7)
C1—C12	1·531 (6)	C14—C15	1·558 (5)
C3—C4	1·520 (5)		

C13—N—C2	108·4 (3)	C8—C7—C6	120·9 (4)
C13—N—C3	110·2 (3)	C8—C7—C1	129·0 (4)
C2—N—C3	115·5 (3)	C6—C7—C1	110·1 (3)
C2—C1—C7	113·7 (4)	C7—C8—C9	118·3 (5)
C2—C1—C12	115·0 (3)	C10—C9—C8	121·1 (5)
C7—C1—C12	101·7 (3)	C9—C10—C11	120·7 (5)
N—C2—C1	116·8 (3)	C10—C11—C6	118·7 (5)
N—C3—C4	114·1 (3)	C1—C12—C5	104·9 (4)
C3—C4—C5	115·8 (3)	O2—C14—O1	126·7 (4)
C6—C5—C12	101·6 (4)	O2—C14—C15	118·2 (3)
C6—C5—C4	110·7 (3)	O1—C14—C15	115·1 (3)
C12—C5—C4	111·0 (4)	O3—C15—O4	124·5 (4)
C7—C6—C11	120·3 (4)	O3—C15—C14	122·7 (3)
C7—C6—C5	110·1 (3)	O4—C15—C14	112·8 (3)
C11—C6—C5	129·5 (4)		

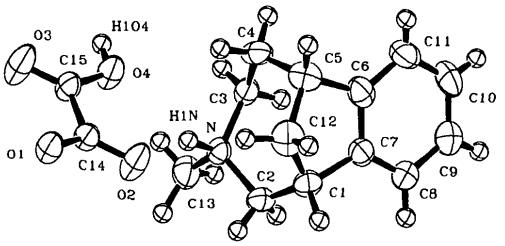


Fig. 1. An *ORTEP* diagram for 3-methyl-1,2,3,4,5,6-hexahydro-1,6-methano-3-benzazocinium hydrogen oxalate. The C, N and O atoms are shown as 50% ellipsoids; H atoms are drawn as spheres with B's of 1·5 Å^2.

Table 3. *Hydrogen-bond parameters* (Å,°)

	A—H	H···O	*A*—H···O	*A*···O
O4—H1O4···O1^a	0·98 (5)	1·59 (6)	179 (4)	2·578 (4)
N—H1N···O2	1·03 (5)	1·78 (5)	150 (4)	2·722 (4)
N—H1N···O4	1·03 (5)	2·37 (4)	123 (3)	3·055 (4)

Symmetry operator: (*a*) 1 + *x*, *y*, *z*.

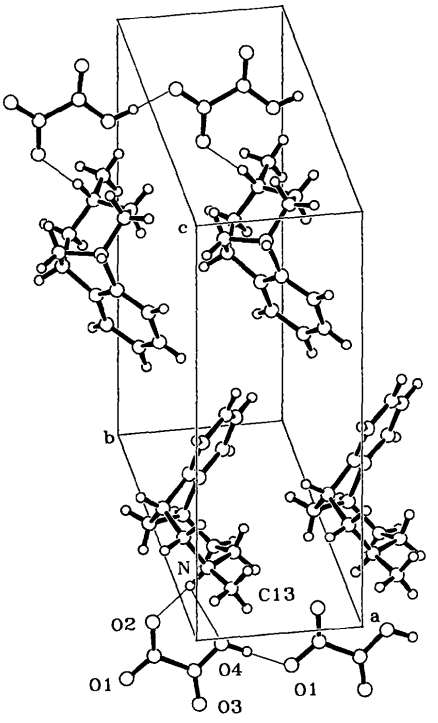


Fig. 2. An *ORTEP* diagram illustrating the intermolecular hydrogen bonding.

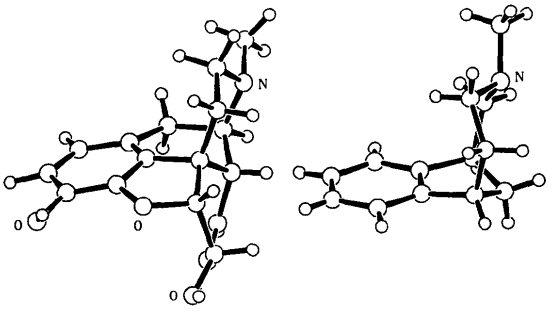


Fig. 3. Drawings of morphine [(I), left] and benzazocine [(III), right] which illustrate the similar aromatic ring and tertiary nitrogen geometries.

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Structures de Trois Pyrroles Substitués Dérivés de Munchnones

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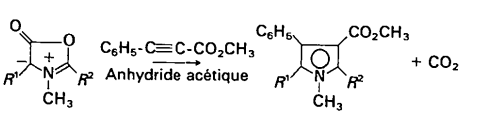
(*Reçu le* 2 *mars* 1990, *accepté le* 10 *décembre* 1990)

Abstract. Methyl 2-methoxyphenyl-1-methyl-4,5-diphenylpyrrole-3-carboxylate (I), $C_{26}H_{23}NO_3$, M_r = 281·3, orthorhombic, *Pbcn*, a = 13·086 (9), b = 11·805 (9), c = 19·580 (7) Å, V = 3025 (2) Å^3, Z = 8, D_x = 1·23 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 0·76 cm^{-1}, $F(000)$ = 1296, T = 293 K, R = 0·037 for 1058 observations. Methyl 5-methoxyphenyl-1-methyl-2,4-diphenylpyrrole-3-carboxylate (II), $C_{26}H_{23}NO_3$, M_r = 281·3, orthorhombic, *Pbcn*, a = 13·086 (9), b = 11·805 (9), c = 19·580 (7) Å, V = 3025 (2) Å^3, Z = 8, D_x = 1·23 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 0·76 cm^{-1}, $F(000)$ = 1296, T = 293 K, R = 0·043 for 1058 observations. Methyl 1-methyl-2-nitrophenyl-4,5-diphenylpyrrole-3-carboxylate (III), $C_{25}H_{20}N_2O_4$, M_r = 281·3, orthorhombic, *Pbcn*, a = 13·086 (9), b = 11·805 (9), c = 19·580 (7) Å, V = 3025 (2) Å^3, Z = 8, D_x = 1·23 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 0·76 cm^{-1}, $F(000)$ = 1296, T = 293 K, R = 0·042 for 1058 observations. These studies confirm the orientation of the reaction predicted by theoretical calculations. The lactone substituent controls the reaction.

Introduction. Les pyrroles (I), (II) et (III) sont obtenus par cycloaddition des munchnones correspondantes au phénylpropiolate de méthyle (Mazari, 1989; Texier, Mazari, Yebdri, Tonnard & Carrié, 1990).



(I): R^1 = C_6H_5; R^2 = $C_6H_4pOCH_3$
(II): R^1 = pCH_3O-C_6H_4; R^2 = C_6H_5
(III): R^1 = C_6H_5; R^2 = $C_6H_4pNO_2$

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