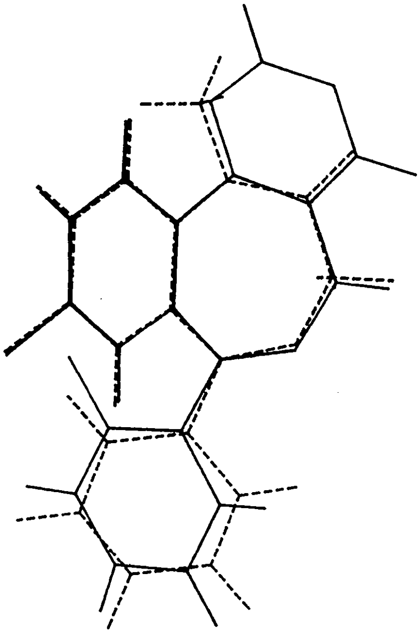

Fig. 2. Superposition of drawings of the title compound (full lines) and diazepam (dashed lines).

The C(7)—C(1′) bond length of 1·483 (2) Å corresponds to that of a single bond between trigonally hybridized C atoms and the C(7)—N(6) bond length of 1·285 (2) Å to that of a C=N double bond.

All intermolecular contacts are of the normal van der Waals type.

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Structure of an Unexpected Dibenz[*d*,*f*]azonine from the HBr Elimination of *N*-Formyl-*N*-norbromocodide

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Abstract. (+)-(*R*)-(*Z*)-7-Formyl-8,9-dihydro-2-methoxy-7*H*-dibenz[*d*,*f*]azonin-1-ol, $C_{18}H_{17}NO_3$, M_r = 295·34, orthorhombic, $P2_12_12_1$, a = 9·966 (2), b = 14·025 (3), c = 10·595 (2) Å, V = 1480·9 Å^3, Z = 4, D_x = 1·33 g cm^{-3}, λ(Cu *Kα*) = 1·54180 Å, μ = 7·44 cm^{-1}, F(000) = 608, T = 293 K, R = 0·036 for 1773 observed reflections. The title compound is formed *via* an acid-catalyzed rearrangement of 6-demethoxy-*N*-formyl-*N*-northebaine, the HBr elimination product from *N*-formyl-*N*-norbromocodide. The dibenzazonine consists of two phenyl rings, which are almost perpendicular to each other. The nine-membered ring is in a boat-like conformation with the *N*-formyl moiety practically planar.

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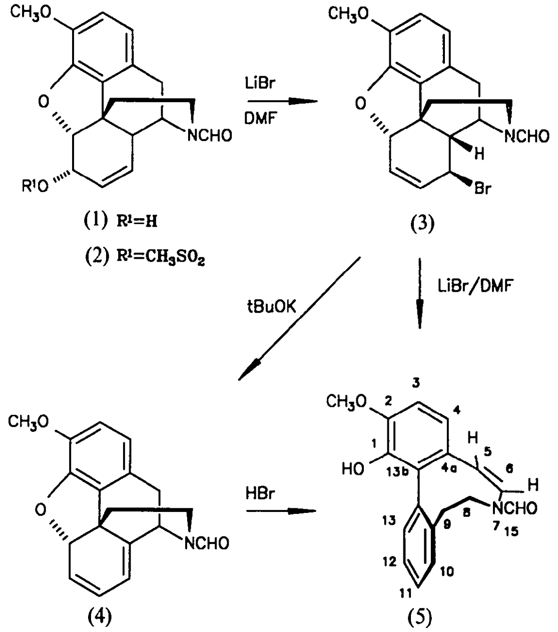
Introduction. Amino-substituted ethenomorphinans are valuable starting materials for the preparation of probes for narcotic receptor-mediated phenomena (Lessor, Rice, Streaty, Klee & Jacobson, 1984). The first synthesis of 7α-amino-6α,14α-ethenoisomorphinan started from the Diels–Alder adduct of thebaine and ethyl acrylate (Bentley, Hardy & Smith, 1969). Recently, a new route using the cycloaddition of thebaine derivatives with nitroethene was found. Because nitroethene polymerizes in the presence of base, it was necessary to convert thebaine into the neutral *N*-formyl-*N*-northebaine (Maat, Peters & Prazeres, 1985). In order to obtain novel ethenomorphinans with fewer oxygen-containing substituents, 6-demethoxy-*N*-formyl-*N*-northebaine (4) was synthesized starting from *N*-formyl-*N*-norcodeine (1) (Scheme 1), analogously to the preparation of 6-demethoxythebaine from codeine (Beyerman, Crabbendam, Lie & Maat, 1984). However, during the reaction of *N*-formyl-6-*O*-mesyl-*N*-norcodeine (2) with lithium bromide, the slow formation of an unknown product was observed. The same product was obtained when 6-demethoxy-*N*-formyl-*N*-northebaine (4) was boiled with a catalytic amount of HBr. Neither the mass spectrum nor the ^{1}H or ^{13}C NMR spectra could give unambiguous proof of the structure. Therefore, a single-crystal X-ray analysis was undertaken which proved the structure of the new compound to be (+)-(*R*)-(*Z*)-7-formyl-8,9-dihydro-2-methoxy-7*H*-dibenz[*d,f*]azonin-1-ol (5). To our knowledge, this is the first time a single-crystal X-ray study of such a dibenzazonine has been reported.



Scheme 1. Synthesis of (4) and (5) from *N*-formyl-*N*-norcodeine (1).

Experimental. Title compound (5) was prepared in the Department of Organic Chemistry (Linders, Booth, Lie, Kieboom & Maat, 1989). Crystals grown from ethanol, m.p. 499–500·5 K, $[\alpha]_D^{27\cdot0\,^\circ\mathrm{C}} = +369^\circ$[chloroform/ethanol 9:1, 1·0 g dm^{-3}]. Crystal of dimensions 0·35 × 0·18 × 0·18 mm selected for data collection. Cell parameters from least-squares refinement of the setting angles of 25 reflections with $28 < \theta < 71^\circ$; Enraf–Nonius CAD-4 diffractometer. Intensity data collected for 1788 reflections in range $0 \le h \le 12$, $0 \le k \le 17$, $0 \le l \le 13$ using graphite-monochromated Cu $K\alpha$ radiation and $\omega/2\theta$ scan mode, width = $(0\cdot85 + 0\cdot15\tan\theta)^\circ$, $\theta_{\max} = 76\cdot0^\circ$. Max. recording time 90 s, $\sigma_{\rm count}(I)/I < 0\cdot02$ requested in a scan. Three reference reflections showed no decay. No correction was made for absorption effects. Structure solved by direct methods (*MULTAN*; Germain, Main & Woolfson, 1971). Full-matrix least-squares refinement on F of anisotropic non-H atoms (H atoms from ΔF map with fixed isotropic thermal parameters) carried out using *XRAY72* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Model converged with 1773 observations [1719 with $I > 1\cdot0\sigma(I)$ plus those for which $F_c > F_o$], 251 variables to $R = 0\cdot036$, $wR = 0\cdot036$, $w = 1$, $S = 1\cdot77$, max. shift/e.s.d. = 0·6 and average shift/e.s.d. = 0·04. Final ΔF synthesis has $|\rho| < 0\cdot15$ e Å^{-3}. All calculations performed on the Delft University Amdahl 470/V7B computer. Atomic scattering factors from *XRAY72*.

Discussion. The final atomic parameters are listed in Table 1.* Fig. 1 shows the conformation and atom numbering. Bond distances and angles are given in Table 2. The molecules are linked in the x direction by an intermolecular hydrogen bond of 2·982 (4) Å [O(2)···O(3)]. As can be seen from Fig. 1, dibenzazonine (5) consists of two phenyl rings, which are almost perpendicular to each other [the angle between the two phenyl rings is 83·6 (4)°]. The nine-membered ring is in a boat-like conformation. The *N*-formyl amide moiety is practically planar: the maximum deviation of the plane through C(6), C(8), N(7), C(15) and O(3) is 0·15 Å [N(7)]. The H atoms in the saturated part of the ring are in a *gauche* position. The olefinic bond has the *cis* configuration and is rotated out of the plane of the aromatic ring over an angle of approximately 55°. The rotation of the C—C bond of the biphenyl moiety is restricted because of the ring system.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52234 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and U_{eq} (Å²) values*

$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$

	x	y	z	U_{eq}
C(1)	0·3772 (2)	0·5107 (2)	0·3348 (2)	0·034 (1)
C(2)	0·4387 (2)	0·6003 (2)	0·3231 (2)	0·039 (1)
C(3)	0·3712 (3)	0·6811 (2)	0·3584 (3)	0·047 (1)
C(4)	0·2417 (3)	0·6737 (2)	0·4041 (3)	0·042 (1)
C(4a)	0·1777 (2)	0·5861 (2)	0·4161 (2)	0·036 (1)
C(5)	0·0429 (3)	0·5831 (2)	0·4754 (3)	0·043 (1)
C(6)	−0·0727 (3)	0·5448 (2)	0·4404 (3)	0·044 (1)
N(7)	−0·1069 (2)	0·4992 (1)	0·3261 (2)	0·038 (1)
C(8)	−0·0203 (2)	0·5030 (2)	0·2142 (2)	0·039 (1)
C(9)	0·0616 (3)	0·4114 (2)	0·1950 (2)	0·039 (1)
C(9a)	0·1007 (2)	0·3633 (2)	0·3174 (2)	0·031 (1)
C(10)	0·0433 (2)	0·2754 (2)	0·3477 (3)	0·039 (1)
C(11)	0·0743 (3)	0·2298 (2)	0·4600 (3)	0·043 (1)
C(12)	0·1646 (3)	0·2702 (2)	0·5429 (3)	0·043 (1)
C(13)	0·2206 (3)	0·3585 (2)	0·5147 (2)	0·039 (1)
C(13a)	0·1887 (2)	0·4059 (2)	0·4030 (2)	0·031 (1)
C(13b)	0·2474 (3)	0·5026 (2)	0·3812 (2)	0·032 (1)
C(14)	0·6360 (4)	0·6837 (2)	0·2542 (4)	0·070 (2)
C(15)	−0·2262 (3)	0·4534 (2)	0·3191 (3)	0·048 (1)
O(1)	0·5674 (2)	0·5963 (1)	0·2764 (2)	0·055 (1)
O(2)	0·4449 (2)	0·4292 (1)	0·3029 (2)	0·044 (1)
O(3)	−0·2687 (2)	0·4136 (1)	0·2242 (2)	0·057 (1)

Table 2. *Bond lengths* (Å) *and bond angles* (°)

C(1)—C(2)	1·404 (3)	C(8)—C(9)	1·535 (4)
C(1)—O(2)	1·369 (3)	C(9)—C(9a)	1·513 (3)
C(1)—C(13b)	1·389 (3)	C(9a)—C(10)	1·397 (3)
C(2)—O(1)	1·376 (3)	C(9a)—C(13a)	1·396 (3)
C(2)—C(3)	1·370 (4)	C(10)—C(11)	1·385 (4)
C(3)—C(4)	1·383 (4)	C(11)—C(12)	1·379 (4)
C(4)—C(4a)	1·390 (4)	C(12)—C(13)	1·391 (4)
C(4a)—C(5)	1·483 (4)	C(13)—C(13a)	1·394 (3)
C(4a)—C(13b)	1·411 (4)	C(13a)—C(13b)	1·495 (3)
C(5)—C(6)	1·324 (4)	C(14)—O(1)	1·423 (4)
C(6)—N(7)	1·411 (3)	C(15)—O(3)	1·226 (4)
C(8)—N(7)	1·468 (3)	C(15)—N(7)	1·353 (3)

C(2)—C(1)—C(13b)	120·7 (2)	C(8)—C(9)—C(9a)	113·3 (2)
O(2)—C(1)—C(13b)	118·6 (2)	C(9)—C(9a)—C(10)	119·1 (2)
O(2)—C(1)—C(2)	120·7 (2)	C(13a)—C(9a)—C(10)	119·0 (2)
C(1)—C(2)—C(3)	120·2 (2)	C(9)—C(9a)—C(13a)	121·9 (2)
O(1)—C(2)—C(3)	126·1 (2)	C(9a)—C(10)—C(11)	120·9 (2)
O(1)—C(2)—C(1)	113·7 (2)	C(10)—C(11)—C(12)	120·2 (2)
C(2)—C(3)—C(4)	119·5 (2)	C(11)—C(12)—C(13)	119·4 (2)
C(3)—C(4)—C(4a)	121·8 (2)	C(12)—C(13)—C(13a)	121·1 (2)
C(4)—C(4a)—C(5)	118·6 (2)	C(13)—C(13a)—C(13b)	118·3 (2)
C(13b)—C(4a)—C(5)	122·2 (2)	C(9a)—C(13a)—C(13b)	122·2 (2)
C(4)—C(4a)—C(13b)	118·9 (2)	C(13)—C(13a)—C(9a)	119·4 (2)
C(4a)—C(5)—C(6)	132·9 (3)	C(13a)—C(13b)—C(1)	119·5 (2)
C(5)—C(6)—N(7)	129·4 (3)	C(4a)—C(13b)—C(1)	118·9 (2)
C(6)—N(7)—C(15)	118·3 (2)	C(13a)—C(13b)—C(4a)	121·4 (2)
C(8)—N(7)—C(15)	119·3 (2)	C(2)—O(1)—C(14)	118·2 (2)
C(6)—N(7)—C(8)	122·3 (2)	N(7)—C(15)—O(3)	124·4 (3)
N(7)—C(8)—C(9)	112·9 (2)		

Similar compounds have been obtained under completely different conditions. When thebaine was treated with alkyl Grignards (Freund, 1905; Small & Fry, 1939; Small, Sargent & Bralley, 1947), the 6-alkyl substituted dibenz[*d,f*]azonines were obtained in good yields. This reaction has been used recently (Herrmann & Satzinger, 1985) for the preparation of asocainol (6, $R = CH_2—CH_2—Ph$), a new antiarrhythmic drug (Späh, 1986). Reduction of thebaine with metal hydrides in the presence of Lewis acids (Bentley, 1967; Bentley, Lewis & Taylor, 1969) gave the unsubstituted parent compound, neodihydrothebaine (6, R = H).

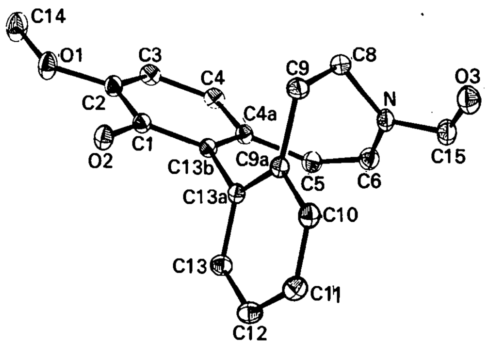
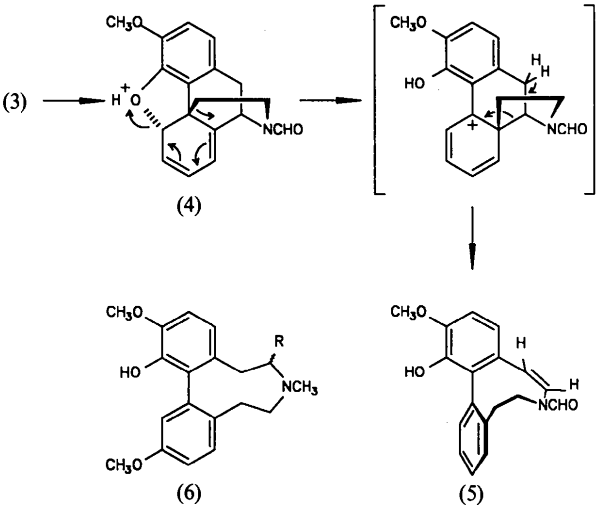


Fig. 1. *ORTEP* plot (Johnson, 1965) of the title compound. Boundary surfaces are drawn to enclose 50% probability.

The mechanism we propose for this rearrangement is depicted in Scheme 2. In accordance with this mechanism and the known chirality of morphinan-like structures, the chirality around the central phenyl—phenyl bond is concluded to have the *R* configuration.



Scheme 2. Mechanism for the formation of (5) from (3).

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Structure of Dibromo(2-methoxycyclohexyl)phenyltellurium

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Abstract. $[TeBr_2(C_6H_5)(C_7H_{13}O)]$, $M_r = 477{\cdot}4$, orthorhombic, *Pbca*, $a = 32{\cdot}683\,(9)$, $b = 10{\cdot}962\,(3)$, $c = 8{\cdot}830\,(3)$ Å, $V = 3164\,(2)$ Å^3, $Z = 8$, $D_x = 2{\cdot}00$, $D_m = 2{\cdot}02$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 66{\cdot}85$ cm^{-1}, $F(000) = 1808$, $T = 294\,(1)$ K, $R = 0{\cdot}0298$ for 1470 reflections $[I > 3\sigma(I)]$. The phenyl and cyclohexyl rings are present at the equatorial and the Br atoms at the axial positions in a pseudo trigonal bipyramidal geometry around the Te atom. The mean Te—Br and Te—C distances are 2·673 (3) and 2·16 (2) Å respectively. Tellurium is involved in one intermolecular (Te···Br) and one intramolecular (Te···O) secondary-bond interaction. $PhTeBr_2$ and OCH_3 groups occupy equatorial positions on adjacent C atoms of the cyclohexyl ring, so that the compound has *trans* geometry.

Introduction. $ArTeX_3$ (X = Cl, Br) reacts with terminal and cyclic olefins in CH_3OH to give (β-methoxyalkyl)aryltellurium dihalides (Uemura & Fukuzawa, 1983). The reaction is regiospecific in the case of terminal olefins, and the addition of $ArTeX_2$ and OCH_3 groups to the olefins occurs in a *trans* fashion (Uemura, Fukuzawa & Toshimitsu, 1983). To understand the conformation of the product obtained from the addition of an $ArTeX_3$ to a cyclic olefin, a crystallographic analysis of dibromo(2-methoxycyclohexyl)phenyltellurium, (1), was undertaken, the results of which are reported here.

Experimental. Preparation as described by Uemura, Fukuzawa & Toshimitsu (1983), followed by slow evaporation of CH_2Cl_2, density measured by flotation in CCl_4/CH_3I. A single crystal was mounted along the largest dimension, subsequently shown to be the c axis. Data were collected on a Syntex $P2_1$ diffractometer. Lattice parameters from 15 strong reflections, $15 < 2\theta < 30°$. The space group *Pbca* was determined from Laue symmetry and systematic absences, $0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$. Three monitor reflections measured after every 100 reflections indicated no decay over 66 h of X-ray exposure. Lorentz and polarization corrections applied; analytical absorption correction with *ABSORB* (Templeton & Templeton, 1973). Min. and max. corrections and other relevant details are given in Table 1. Position of the Te atom was obtained from a sharpened Patterson synthesis. Remaining non-H atoms revealed from ΔF calculations. Structure refined anisotropically by full-matrix least-squares methods. H atoms included in idealized positions (C—H 0·95 Å and CCH 120 or 109·5°). Refinement minimizing the function $\sum w(|F_o| - |F_c|)^2$ converged to $R = 0{\cdot}0298$ and $wR = 0{\cdot}0320$. Weights were assigned as $w = 1/[\sigma^2(F) + pF^2]$, with a final p value of 0·00001. Computation was carried out on the University of Manitoba Computer Services Department's Amdahl 580/5850 mainframe computer. Scattering factors for all non-H atoms, including anomalous-dispersion correction for Te and Br, obtained from Ibers & Hamilton (1974), for H atoms from Stewart, Davidson & Simpson (1965). Programs used include *SHELX76* (Sheldrick, 1976), *XANADU* (Roberts & Sheldrick, 1975) and *ORTEP* (Johnson, 1965). The atomic coordinates and equivalent parameters for non-H atoms are given in Table 2 and distances and angles in Table 3.†

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† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52198 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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