Table 2. *Geometric parameters (Å, °)*

O(2)—C(2)	1.432 (3)	C(3)—C(4)	1.521 (4)
O(3)—C(3)	1.432 (4)	C(4)—C(5)	1.536 (4)
O(4)—C(4)	1.431 (3)	C(5)—C(6)	1.517 (4)
O(5)—C(5)	1.435 (3)	C(7)—C(8)	1.394 (4)
O(6)—C(6)	1.425 (4)	C(7)—C(12)	1.389 (4)
N(1)—N(2)	1.364 (3)	C(8)—C(9)	1.385 (4)
N(1)—C(1)	1.277 (4)	C(9)—C(10)	1.381 (4)
N(2)—C(7)	1.398 (4)	C(10)—C(11)	1.380 (4)
C(1)—C(2)	1.505 (4)	C(11)—C(12)	1.386 (4)
C(2)—C(3)	1.532 (4)		
N(2)—N(1)—C(1)	116.8 (2)	O(5)—C(5)—C(4)	110.7 (1)
N(1)—N(2)—C(7)	120.6 (2)	O(5)—C(5)—C(6)	110.9 (2)
N(1)—C(1)—C(2)	120.4 (2)	C(4)—C(5)—C(6)	113.3 (2)
O(2)—C(2)—C(1)	110.8 (2)	O(6)—C(6)—C(5)	109.6 (2)
O(2)—C(2)—C(3)	110.4 (2)	N(2)—C(7)—C(8)	117.4 (2)
C(1)—C(2)—C(3)	111.0 (2)	N(2)—C(7)—C(12)	123.3 (2)
O(3)—C(3)—C(2)	109.1 (2)	C(8)—C(7)—C(12)	119.2 (2)
O(3)—C(3)—C(4)	108.5 (2)	C(7)—C(8)—C(9)	120.2 (2)
C(2)—C(3)—C(4)	112.3 (2)	C(8)—C(9)—C(10)	120.6 (2)
O(4)—C(4)—C(3)	111.4 (2)	C(9)—C(10)—C(11)	119.1 (2)
O(4)—C(4)—C(5)	110.5 (2)	C(10)—C(11)—C(12)	121.2 (2)
C(3)—C(4)—C(5)	112.2 (1)	C(7)—C(12)—C(11)	119.7 (2)
C(1)—N(1)—N(2)—C(7)	158.4 (2)		
C(4)—C(5)—C(6)—O(6)	58.1 (3)		
N(1)—N(2)—C(7)—C(8)	−174.4 (2)		
N(1)—C(1)—C(2)—C(3)	−126.2 (3)		
N(2)—N(1)—C(1)—C(2)	179.9 (2)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	H···A	D···A	D—H···A
O(2)—H(2O)···N(1^{i})	2.10 (2)	2.923 (2)	173 (3)
O(3)—H(3O)···O(4^{ii})	1.99 (3)	2.752 (3)	169 (2)
O(4)—H(4O)···O(6^{iii})	1.95 (2)	2.718 (3)	164 (3)
O(5)—H(5O)···O(3^{i})	1.92 (2)	2.714 (3)	156 (3)
O(6)—H(6O)···O(5^{iv})	2.02 (3)	2.754 (3)	161 (3)
N(2)—H(2N)···O(2^{ii})	2.21 (3)	2.922 (2)	151 (3)

Symmetry codes: (i) $x, y, z-1$; (ii) $x-1, y, z$; (iii) $x, y, 1+z$; (iv) $1+x, y, z$.

Non-H atoms were refined anisotropically and H atoms were refined with isotropic displacement parameters fixed at approximately 1.2 times the isotropic equivalent of the attached atom [C—H distances 0.88 (3)–1.03 (2), N—H 0.79 (3), O—H 0.77 (3)–0.85 (3) Å].

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1257). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(±)-1,11-Dimethyl-3,9-dinitro-5,7-dihydrodibenz[*c*,*e*]oxepine

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Abstract

Racemic crystals of the atropisomeric title compound, $C_{16}H_{14}N_2O_5$, are composed of independent molecules separated by normal van der Waals distances. The molecule, as well as its central seven-membered ring, has an approximate C_2 symmetry. The nitro groups are twisted from coplanarity with the phenyl rings by 11.5 (3) and 15.6 (3)°.

Comment

Optically active inherently chiral biphenyls such as 1,11-dimethyl-3,9-dinitro-5,7-dihydrodibenz[*c*,*e*]oxepine, (I), are known to induce a twisted cholesteric phase when doped into a nematic liquid crystal (Gottarelli *et al.*, 1983). The propensity of this dopant to induce a

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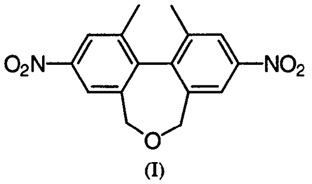
cholesteric structure in a cyanobiphenyl nematic host was found to be dependent on the nature of the substituents at the 3- and 9-positions (Williams & Lemieux, 1996). Current investigation of this structural dependence is aimed at providing new insight on the nature of arene–arene π-stacking interactions.



(I)

Typically 2,2′,6,6′-substituted biphenyls exhibit an interplanar angle between the least-squares planes of the two phenyl rings of *ca* 90° [for instance, 89.9° in 2,2′,4,4′,6,6′-hexamethylbiphenyl (Fröhlich & Musso, 1985)]. On the other hand, the 6,6′-(C—O—C)-bridging of the biphenyl introduces a constraint in the axial twist of the molecule with the strain-free conformation more likely in the structures of 6,6′-(C—O—C)-bridged biphenyls which are lacking substituents at the 2,2′ positions. In three independent 5,7-dihydrodibenz[*c*,*e*]-oxepine ligands of *trans*-dibromotetrakis(5,7-dihydrodibenz[*c*,*e*]oxepine)magnesium(II)–toluene (1:2) solvate (Engelhardt, Leung, Raston & White, 1985), the Ph–Ph interplanar angle was found to be 38.0, 37.8 and 39.3°. Similarly, this angle is 37.4° in the structure of (±)-4,9,10-triacetoxy-2-methoxydibenzo[*c*,*e*]oxepin-5-one (Ladd & Povey, 1976). It was therefore expected that the simultaneous 2,2′-methyl substitution and the 6,6′-(C—O—C)-bridging of the title biphenyl, (I), would produce a Ph–Ph dihedral angle between 40 and 90° at the expense of some strain in the molecule.

Fig. 1 shows a perspective view of (I) projected perpendicular to the phenyl ring C1–C4,C14,C15. The dihedral angle between two phenyl rings in this molecule is 56.6 (1)°. The compromise between the opposite effects of the steric repulsions of the C12- and C13-methyl groups and of the limited-size C5—O6—C7 bridging led to strain and several distortions in the molecule. The first and most evident is the difference between the endocyclic and exocyclic torsion angles about the C15—C16 bond which are −53.5 (2) and −60.0 (3)°, respectively. Using all four torsion angles about this bond, the so-called 'out-of-plane deformations' can be calculated using formulae proposed by Winkler & Dunitz (1971); the 'twist' about the C15—C16 bond is 56.8 (3)° while the out-of-plane bending at atoms C15 and C16 is 2.3 (3) and 4.1 (3)°, respectively. The two phenyl rings show slight distortions from planarity with r.m.s. deviations of 0.010 and 0.013 Å for the C1–C4,C14,C15 and C8–C11,C16,C17 rings, respectively, and with the C15 and C16 atoms deviating the furthest from their respective least-squares planes [C15 by 0.016 (1) and C16 by 0.021 (1) Å]. The exocyclic bond angles at C15 and C16 are 5–6° larger than the seven-membered-ring endocyclic angles at these atoms; similar differences are observed for the two exocyclic bond angles at C1 and C11 leading to even larger separation between methyl groups. Finally, the methyl-C atoms C12 and C13 are very much out of their respective phenyl-ring planes, C12 by 0.136 (4) and C13 by 0.076 (4) Å, in directions such as to maximize the distance between them. As a result of the twist at the C15—C16 bond and of the distortions mentioned above, the intramolecular separation between the two methyl groups is as much as 3.198 (4) Å, and the shortest H···H contact in this region is 2.07 (5) Å.

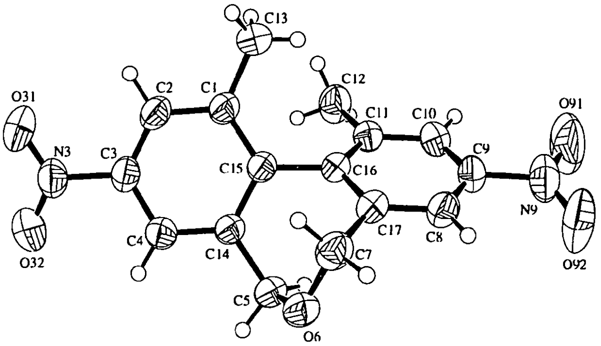


Fig. 1. Molecular structure of the title compound with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as unlabelled spheres of arbitrary size.

The seven-membered ring has a virtually C_2 symmetrical skew (*v*) conformation (Kashiwabara, Hanaki & Fujita, 1980) with the twofold axis passing through the atom O6 and the mid-point between atoms C15 and C16. A very low value of the asymmetry parameter (Duax, Weeks & Rohrer, 1976), C_2[O6] = 2.5 (2), confirms the C_2 symmetry of the ring.

The molecule as a whole is also close to being C_2 symmetrical with the exception of the nitro groups. Neither of the nitro groups is coplanar with the phenyl ring to which it is bonded: the N3 group forms a dihedral angle of 15.6 (3)° with the C1 phenyl ring while the N9 group forms an angle of 11.5 (3)° with the C11 phenyl ring. Additionally, the direction of rotation about the N—C bond (looking from N to C) from coplanarity with their respective phenyl rings is opposite for the two groups (see the opposite signs for the appropriate torsion angles) and this violates the twofold symmetry.

The similar approximate C_2 symmetry of the molecule, the skew (*v*) conformation of the seven-membered ring and an interplanar angle between the phenyl rings of 60.5° were also found in the structure of (−)-(*R*)-1,11-bis(diphenylphosphino)-5,7-dihydrodibenz[*c*,*e*]oxepine (Schmid, Cereghetti, Heiser, Schönholzer & Hansen, 1988).

Experimental

Compound (I) was synthesized in racemic form starting from 2-iodo-3-methyl-5-nitrobenzoic acid (Cassebaum, 1964) *via* modification of a route developed by Mislow *et al.* (1962). Suitable crystals were obtained by slow evaporation from methanol solution.

Crystal data

$C_{16}H_{14}N_2O_5$
$M_r = 314.29$
Monoclinic
$P2_1/c$
$a = 8.1693\,(5)$ Å
$b = 21.7076\,(12)$ Å
$c = 8.3750\,(8)$ Å
$\beta = 96.515\,(9)°$
$V = 1475.6\,(2)$ Å^3
$Z = 4$
$D_x = 1.415$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 40$–$50°$
$\mu = 0.898$ mm^{-1}
$T = 293\,(2)$ K
Plate
$0.20 \times 0.20 \times 0.06$ mm
Pale yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
3240 measured reflections
3033 independent reflections
2021 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0279$
$\theta_{\rm max} = 74.92°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 27$
$l = 0 \rightarrow 10$
3 standard reflections frequency: 60 min intensity variation: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0498$
$wR(F^2) = 0.1691$
$S = 1.116$
3033 reflections
265 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0898P)^2 + 0.2454P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.002$

$\Delta\rho_{\rm max} = 0.306$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.210$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0025 (7)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C1	0.7635 (2)	0.70857 (9)	0.7407 (3)	0.0438 (5)
C2	0.6683 (3)	0.76044 (9)	0.6998 (3)	0.0476 (5)
C3	0.5268 (2)	0.75562 (9)	0.5961 (3)	0.0462 (5)
N3	0.4296 (2)	0.81140 (9)	0.5515 (3)	0.0590 (5)
O31	0.4591 (3)	0.85762 (8)	0.6311 (3)	0.0817 (6)
O32	0.3271 (3)	0.80893 (9)	0.4349 (3)	0.0947 (7)
C4	0.4705 (3)	0.69976 (9)	0.5310 (3)	0.0473 (5)
C5	0.5024 (3)	0.58556 (9)	0.5113 (3)	0.0509 (5)
O6	0.4386 (2)	0.55000 (7)	0.6356 (2)	0.0588 (4)
C7	0.5405 (3)	0.54971 (11)	0.7887 (3)	0.0563 (6)
C8	0.8008 (3)	0.48758 (10)	0.8030 (3)	0.0510 (5)
C9	0.9632 (3)	0.48207 (10)	0.7751 (3)	0.0540 (5)
N9	1.0469 (3)	0.42275 (10)	0.8064 (3)	0.0764 (7)
O91	1.1930 (3)	0.41951 (11)	0.7969 (5)	0.1300 (12)
O92	0.9644 (4)	0.37834 (10)	0.8330 (4)	0.1109 (9)
C10	1.0477 (3)	0.52928 (10)	0.7114 (3)	0.0547 (5)
C11	0.9690 (2)	0.58540 (9)	0.6757 (3)	0.0467 (5)
C12	1.0630 (3)	0.63358 (12)	0.5949 (4)	0.0610 (6)
C13	0.9144 (3)	0.71632 (12)	0.8596 (4)	0.0619 (6)
C14	0.5633 (2)	0.64753 (9)	0.5714 (2)	0.0429 (4)
C15	0.7122 (2)	0.65162 (8)	0.6734 (2)	0.0403 (4)
C16	0.8059 (2)	0.59294 (8)	0.7094 (2)	0.0419 (4)
C17	0.7209 (3)	0.54321 (9)	0.7696 (3)	0.0459 (5)

Table 2. *Selected geometric parameters (Å, °)*

C1—C13	1.504 (3)	C9—N9	1.467 (3)
C3—N3	1.473 (3)	N9—O91	1.208 (3)
N3—O31	1.213 (3)	N9—O92	1.211 (3)
N3—O32	1.213 (3)	C11—C12	1.503 (3)
C5—C14	1.501 (3)	C14—C15	1.408 (3)
C5—O6	1.440 (3)	C15—C16	1.499 (3)
O6—C7	1.447 (3)	C16—C17	1.408 (3)
C7—C17	1.507 (3)		
C2—C1—C13	117.8 (2)	C10—C11—C12	117.2 (2)
C15—C1—C13	123.4 (2)	C16—C11—C12	123.7 (2)
C3—N3—O31	118.2 (2)	C5—C14—C15	119.4 (2)
C3—N3—O32	118.1 (2)	C1—C15—C14	119.8 (2)
O31—N3—O32	123.7 (2)	C1—C15—C16	123.1 (2)
O6—C5—C14	111.8 (2)	C14—C15—C16	117.1 (2)
C5—O6—C7	115.1 (2)	C11—C16—C17	120.1 (2)
O6—C7—C17	112.1 (2)	C11—C16—C15	122.3 (2)
C9—N9—O91	118.9 (2)	C15—C16—C17	117.5 (2)
C9—N9—O92	118.3 (2)	C7—C17—C16	119.6 (2)
O91—N9—O92	122.7 (2)		
C1—C15—C16—C11	−60.0 (3)	O6—C7—C17—C16	72.0 (2)
C1—C15—C16—C17	124.1 (2)	C14—C5—O6—C7	−45.8 (2)
C14—C15—C16—C17	−53.5 (2)	C5—O6—C7—C17	−41.9 (2)
C14—C15—C16—C11	122.3 (2)	C2—C3—N3—O31	−14.3 (3)
C5—C14—C15—C16	2.9 (3)	C4—C3—N3—O32	−16.1 (3)
C15—C16—C17—C7	2.5 (3)	C8—C9—N9—O92	10.6 (4)
O6—C5—C14—C15	73.6 (2)	C10—C9—N9—O91	10.2 (4)

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *Xtal*3.0 (Hall & Stewart, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1226). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(–)-Thebaine

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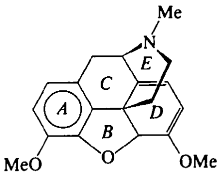
Abstract

The structure of the opioid thebaine, 6,7,8,14-tetradehydro-4,5-epoxy-3,6-dimethoxy-17-methylmorphinan, $C_{19}H_{21}NO_3$, has been determined by single-crystal X-ray diffraction techniques at low temperature. The thebaine molecule adopts the same T-shaped conformation of the five fused rings as found in closely related rigid opioids. The geometry of the double bond at the bridgehead C atom is significantly distorted from planarity.

Comment

Thebaine (1) is a metabolite of morphine and is found in small quantities in opium extracts (Lentz, Evans, Walters & Hopfinger, 1986; Bentley, 1971). Thebaine has often been used as the starting point for the synthesis of opioid derivatives. We have determined the structure of thebaine as part of a study of its reactivity with metals to form useful organometallic intermediates.



(1)

Compared with other members of the opioid family, the distinctive structural feature of thebaine is the presence of two double bonds in ring *D*. The general conformation of the molecule is similar to morphine (Bye, 1976; Gylbert, 1973) and codeine (Kartha, Ahmed & Barnes, 1962), which have one double bond, and to naloxone (Karle, 1974; Klein, Majeste & Stevens, 1987), which has no double bonds. Significant differences are observed in the bond distances and angles in ring *D*, as expected from the placement of the double bonds. The C6—C7 and C8—C14 bond lengths [1.339 (3) and 1.338 (2) Å, respectively] confirm the location of the double bonds, and the C7—C8 single-bond length [1.456 (3) Å], which is intermediate between the C7═C8 double-bond distance of 1.313 (6) Å in morphine (Bye, 1976) and the C7—C8 single-bond distance of 1.501 (1) Å in naloxone (Klein, Majeste & Stevens, 1987), suggests conjugation of the double bonds. The C6—C7—C8—C14 torsion angle is −1.4 (3)°. Compared with the other opioids, the other bonds to C6 and C9 are shorter in thebaine as a result of the change in hybridization at those C atoms. The

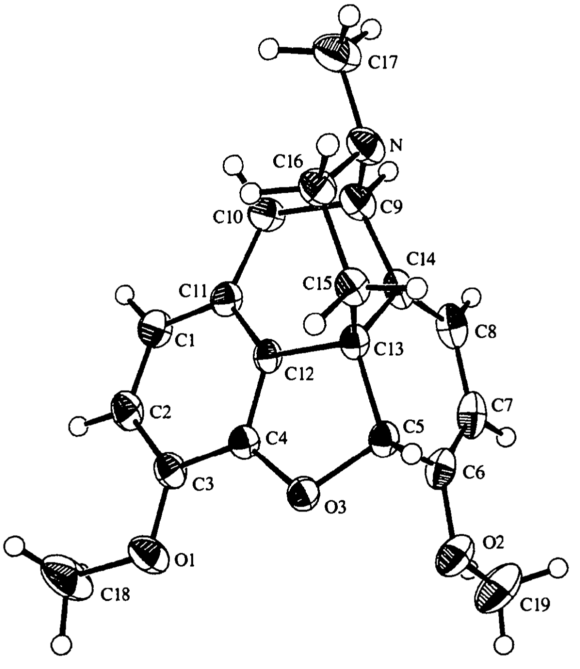


Fig. 1. *ORTEPII* (Johnson, 1976) plot of the thebaine molecule. Displacement ellipsoids are drawn at the 50% probability level.

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