C4—C5	1.527 (4)	C18—C19	1.381 (4)
C5—C6	1.534 (5)	C19—C20	1.384 (4)
C9—O2	1.208 (4)	C20—C21	1.385 (4)
C9—O1	1.324 (3)	C20—N2	1.465 (4)
C9—C10	1.495 (4)	C21—C22	1.383 (4)
C10—C11	1.397 (4)	O3—N1	1.227 (3)
C10—C15	1.398 (4)	O4—N1	1.218 (3)
C11—C12	1.392 (4)	O7—N2	1.225 (4)
C12—C13	1.380 (4)	O8—N2	1.228 (4)
C7—Si—C2	110.8 (2)	O1—C3—C2	109.6 (2)
C7—Si—C6	113.3 (2)	C4—C3—C2	115.0 (2)
C2—Si—C6	103.83 (14)	O5—C4—C3	110.5 (2)
C7—Si—C8	110.2 (2)	O5—C4—C5	107.2 (2)
C2—Si—C8	108.81 (14)	C3—C4—C5	111.7 (2)
C6—Si—C8	109.7 (2)	C4—C5—C6	115.3 (3)
C3—C2—Si	109.1 (2)	C5—C6—Si	113.3 (2)
O1—C3—C4	107.6 (2)		

Molecule 1	
C6—Si—C2—C3	−44.1 (2)
Si—C2—C3—C4	61.3 (3)
O1—C3—C4—C5	168.5 (2)
C2—C3—C4—C5	−69.0 (3)
C3—C4—C5—C6	61.2 (3)
C4—C5—C6—Si	−49.8 (3)
O5—C16—C17—C18	−17.3 (4)
C14—C13—N1—O4	−161.9 (3)
C19—C20—N2—O7	0.6 (4)
C19—C20—N2—O8	−179.2 (3)
Molecule 2	
O5′—C16′—C17′—C18′	−6.4 (4)
C14′—C13′—N1′—O3′	7.4 (4)
C14′—C13′—N1′—O4′	−170.7 (3)
C19′—C20′—N2′—O7′	−8.2 (4)
C19′—C20′—N2′—O8′	170.1 (3)
Molecule 3	
O5*—C16*—C17*—C18*	−14.1 (4)
C14*—C13*—N1*—O4*	−175.0 (3)
C14*—C13*—N1*—O3*	4.9 (4)
C19*—C20*—N2*—O7*	−10.0 (4)
C19*—C20*—N2*—O8*	170.0 (3)
Molecule 4	
O5″—O16″—C17″—C18″	14.3 (4)
C14″—C13″—N1″—O3″	1.7 (5)
C14″—C13″—N1″—O4″	−163.5 (3)
C19″—C20″—N2″—O7″	9.5 (4)
C19″—C20″—N2″—O8″	−169.6 (3)

The title structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1990). Refinement was performed using *SHELXL*93 (Sheldrick, 1993), with anisotropic displacement parameters for all non-H atoms and isotropic displacement parameters for H atoms. The figures were drawn using *ORTEP*II (Johnson, 1976) and the tables prepared using *SHELXL*93. All calculations were carried out on a VAXstation 4000VLC computer system.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1071). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Methyl 9-Methyl-11-thioxo-8-oxa-10,12-diazatricyclo[7.3.1.$0^{2,7}$]trideca-2,4,6-triene-13-carboxylate

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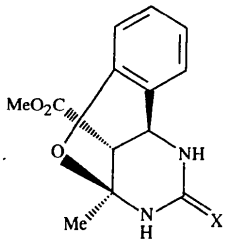
Abstract

The title compound, $C_{13}H_{14}N_2O_3S$, represents a conformationally restricted pyrimidine analogue of 1,4-dihydropyridine-type calcium antagonists and was designed to probe the chemical and spatial requirements of the dihydropyridine binding site on the calcium channel. The phenyl ring is fixed in a pseudo-axial and perpendicular orientation with respect to the pyrimidine ring by an O-atom bridge. Each of the two fused six-membered rings assumes an approximate sofa conformation distorted towards a half-chair. The molecules are linked by hydrogen bonds to form chains.

Comment

As a continuation of our study on the structure–activity relationships within 1,4-dihydropyridines (and related compounds) as the most potent class of calcium channel antagonists (Goldmann & Stoltefuss, 1991), we have recently described a diastereoselective synthesis of oxygen-bridged pyrimidines, (1) (Světlik, Hanuš & Bella, 1991). By analogy with sulfur-bridged 1,4-dihydropyridines (Baldwin *et al.*, 1987), the calcium antagonist activity of the molecules (1) was confirmed in both *in vitro* and radioligand-binding experiments (Kettmann, Dřimal & Světlik, 1995). The relative stereochemistry of the molecules (1), especially the α-configuration of the methoxycarbonyl group, has been determined by NMR measurements. To check our conclusions and at the same time to determine the detailed

molecular conformation of the molecules (1), and hence to gain a better knowledge of the dihydropyridine receptor, an X-ray analysis of (1*a*) was undertaken.



(1*a*) X = S
(1*b*) X = O

The molecular structure is shown in Fig. 1. The bond lengths and angles are close to those generally expected. As observed in a number of similar structures (Kojić-Prodić, Liminga, Šljukić & Ružić-Toroš, 1974; Kojić-Prodić, Kvick & Ružić-Toroš, 1976; Hanick & Kishi, 1983; Read, Randall, Hursthouse & Short, 1988; Sulmon, De Kimpe, Schamp & Declercq, 1989), C(11)—N(12) [1.295 (3) Å] shows greater double-bond character than C(11)—N(10) [1.346 (3) Å].

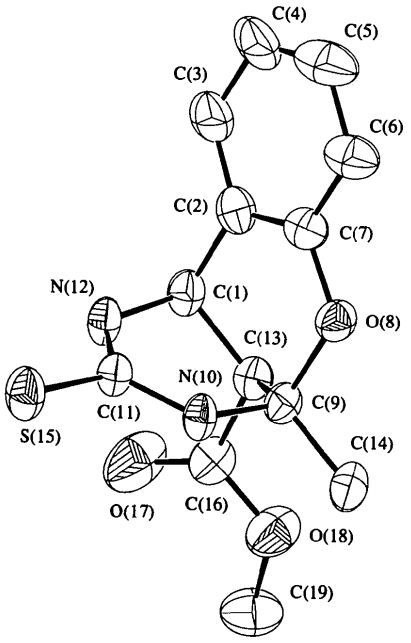


Fig. 1. *ORTEP* (Johnson, 1971) drawing of the title compound (1*a*), showing the labelling of the non-H atoms; H atoms are omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.

From the pharmacological point of view the most important aspect of the molecule concerns the spatial disposition of the key functional groups (*i.e.* the phenyl and ester substituents), which in turn depends on the conformation of the central pyrimidine ring. Calculation of the least-squares planes has shown that the ring is puckered in such a manner that the four atoms C(9), N(10), C(11) and N(12) are coplanar to within 0.016 (2) Å, but the atoms C(1) and C(13) are unequally displaced from this plane on opposite sides, with out-of-plane displacements of 0.158 (3) and −0.595 (2) Å, respectively. This is also reflected in the values of the dihedral angles N(10)—C(11)—N(12)—C(1) and C(11)—N(10)—C(9)—C(13), the latter being substantially larger than the former (Table 2). Thus, the pyrimidine ring exhibits an unsymmetrical half-chair conformation [considering the small deviation of C(1) from the four-atom plane, the ring may be regarded as being close to the C(13)-sofa conformation] and exists in the thione form: the C(11)—S(15) distance of 1.670 (2) Å has double-bond character (Abrahams, 1956). As shown from the dihedral angles in Table 2, a very similar conformation is also exhibited by the unsaturated ring containing the O-atom bridge; the coplanar atoms are C(1), C(2), C(7) and O(8) (r.m.s. deviation 0.016 Å) and C(9) and C(13) are displaced by 0.132 (2) and −0.662 (2) Å, respectively, from the least-squares plane. While the observed conformation of the latter ring is obviously caused by electronic factors [unsaturation and conjugation of the lone pair of electrons on O(8) with the phenyl ring], the conformation of the pyrimidine ring most likely results from the rigidity of the polycyclic system. As to the pyrimidine ring substituents, the phenyl ring is exactly planar (χ^2 = 17.6) and fixed in an approximately perpendicular orientation with respect to the mean plane of the pyrimidine ring [dihedral angle 86.6 (3)°], and the methoxycarbonyl

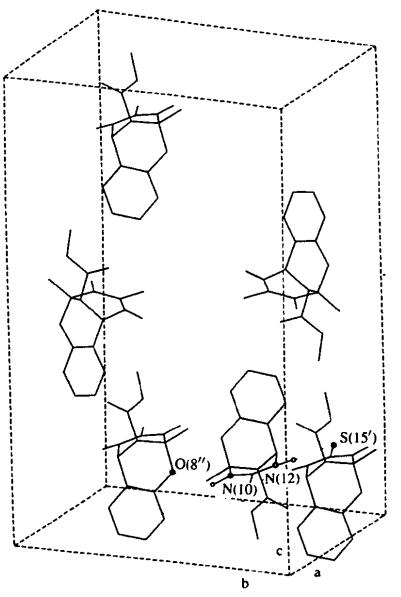


Fig. 2. A view of the unit-cell contents. Two additional molecules are also shown to illustrate hydrogen bonding (dashed lines). Only H atoms involved in hydrogen bonds are shown (open unlabelled circles) for clarity.

group is in an axial position and makes an angle of 86.9 (3)° with the pyrimidine ring. As shown above, the conformation of the pyrimidine ring in (1*a*) is different from the flattened boat conformation generally found in classical 1,4-dihydropyridines (Goldmann & Stoltefuss, 1991). The geometrical aspects and their relation to the biological activity will be discussed in detail elsewhere (Kettmann, Dřimal & Světlik, 1995).

The crystal packing (Fig. 2) is dominated by two short intermolecular contacts, N(12)—H···S(15^i) and N(10)—H···O(8^{ii}) [N(12)—H 0.98 (2), H···S(15^i) 2.31 (2), N(12)···S(15^i) 3.276 (2) Å, N(12)—H···S(15^i) 166 (2)°; N(10)—H 0.96 (2), H···O(8^{ii}) 2.27 (3), N(10)···O(8^{ii}) 3.083 (2) Å, N(10)—H···O(8^{ii}) 142 (2)°; symmetry codes: (i) $-x+1, -y, -z$; (ii) $-x+1, -y+1, -z$]. Based on their geometry, these contacts may be regarded as weak hydrogen bonds, which link the molecules into chains running parallel to the *ab* plane (at z = 0 and 1/2). The chains are held together by van der Waals forces.

Experimental

Crystals of (1*a*) were prepared by a Biginelli-type reaction (Světlik, Hanuš & Bella, 1991) followed by recrystallization from chloroform.

Crystal data

$C_{13}H_{14}N_2O_3S$
M_r = 278.33
Monoclinic
$P2_1/n$
a = 7.442 (3) Å
b = 10.255 (5) Å
c = 16.128 (8) Å
β = 90.92 (5)°
V = 1230.7 (8) Å^3
Z = 4
D_x = 1.502 Mg m^{-3}
D_m = 1.50 (1) Mg m^{-3}
D_m measured by flotation in *c*-hexane–bromoform
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 15 reflections
θ = 6–17°
μ = 0.26 mm^{-1}
T = 293 K
Prism
0.45 × 0.30 × 0.10 mm
Colourless

Data collection

Syntex $P2_1$ diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2466 measured reflections
2183 independent reflections
1465 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.026
θ_{max} = 25°
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 12$
$l = -19 \rightarrow 19$
2 standard reflections monitored every 98 reflections
intensity decay: 4%

Refinement

Refinement on F
R = 0.057
wR = 0.065
S = 1.23
1465 reflections
214 parameters
H-atom coordinates refined, each with B_{iso} fixed at B_{eq} of the bonded atom
$w = 1/[\sigma^2(F) + 0.0016F^2]$
$(\Delta/\sigma)_{max}$ = 0.02
$\Delta\rho_{max}$ = 0.52 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
C(1)	0.8405 (3)	0.1974 (2)	0.0187 (1)	2.77 (6)
C(2)	0.8555 (3)	0.2472 (2)	−0.0677 (1)	3.03 (6)
C(3)	0.9146 (3)	0.1698 (3)	−0.1306 (2)	3.97 (7)
C(4)	0.9186 (4)	0.2195 (3)	−0.2100 (2)	4.99 (8)
C(5)	0.8626 (4)	0.3449 (3)	−0.2266 (2)	5.11 (9)
C(6)	0.8060 (3)	0.4229 (3)	−0.1631 (2)	3.97 (7)
C(7)	0.8028 (3)	0.3726 (2)	−0.0850 (1)	2.81 (6)
O(8)	0.7489 (2)	0.4565 (1)	−0.0235 (1)	2.83 (4)
C(9)	0.7190 (3)	0.4065 (2)	0.0595 (1)	2.37 (6)
N(10)	0.5490 (2)	0.3416 (2)	0.0601 (1)	2.56 (5)
C(11)	0.5221 (3)	0.2145 (2)	0.0433 (1)	2.49 (5)
N(12)	0.6612 (2)	0.1421 (2)	0.0300 (1)	2.76 (5)
C(13)	0.8669 (3)	0.3085 (2)	0.0794 (1)	2.48 (6)
C(14)	0.7109 (3)	0.5265 (2)	0.1104 (1)	3.23 (6)
S(15)	0.31245 (8)	0.15641 (6)	0.04113 (4)	3.34 (2)
C(16)	0.8751 (3)	0.2637 (2)	0.1668 (1)	3.07 (6)
O(17)	0.8605 (3)	0.1544 (2)	0.1886 (1)	6.14 (7)
O(18)	0.9098 (2)	0.3591 (2)	0.2181 (1)	4.39 (5)
C(19)	0.9509 (4)	0.3328 (3)	0.3055 (2)	4.87 (9)

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

C(1)—C(13)	1.512 (3)	C(13)—C(16)	1.482 (4)
C(13)—C(9)	1.521 (3)	C(16)—O(17)	1.181 (3)
C(9)—N(10)	1.430 (3)	C(16)—O(18)	1.305 (3)
N(10)—C(11)	1.346 (3)	C(2)—C(3)	1.366 (4)
C(11)—N(12)	1.295 (3)	C(3)—C(4)	1.379 (4)
C(11)—S(15)	1.670 (2)	C(4)—C(5)	1.377 (5)
C(1)—N(12)	1.464 (3)	C(5)—C(6)	1.371 (4)
C(1)—C(2)	1.491 (4)	C(6)—C(7)	1.361 (4)
C(2)—C(7)	1.372 (3)	C(9)—C(14)	1.480 (4)
C(7)—O(8)	1.378 (3)	O(18)—C(19)	1.436 (3)
O(8)—C(9)	1.454 (3)		
N(12)—C(1)—C(13)	108.7 (2)	C(1)—C(2)—C(3)	121.6 (3)
C(2)—C(1)—C(13)	109.6 (2)	C(2)—C(7)—O(8)	121.9 (2)
C(2)—C(1)—N(12)	109.3 (2)	C(6)—C(7)—O(8)	116.0 (2)
C(1)—C(13)—C(9)	106.0 (2)	C(7)—O(8)—C(9)	119.5 (2)
C(13)—C(9)—N(10)	109.2 (2)	O(8)—C(9)—C(13)	107.8 (2)
C(9)—N(10)—C(11)	125.3 (2)	O(8)—C(9)—C(14)	103.0 (2)
N(10)—C(11)—N(12)	118.2 (2)	C(1)—C(13)—C(16)	112.6 (2)
N(10)—C(11)—S(15)	119.0 (2)	C(9)—C(13)—C(16)	115.1 (2)
N(12)—C(11)—S(15)	122.7 (2)	C(13)—C(16)—O(17)	125.1 (3)
C(11)—N(12)—C(1)	122.0 (2)	C(13)—C(16)—O(18)	112.1 (2)
C(1)—C(2)—C(7)	119.1 (2)	O(17)—C(16)—O(18)	122.7 (3)

C(9)—N(10)—C(11)—N(12)	4.1 (4)
N(10)—C(11)—N(12)—C(1)	−10.6 (4)
C(11)—N(12)—C(1)—C(13)	40.1 (3)
N(12)—C(1)—C(13)—C(9)	−59.5 (3)
C(1)—C(13)—C(9)—N(10)	53.3 (3)
C(13)—C(9)—N(10)—C(11)	−27.6 (3)
C(1)—C(2)—C(7)—O(8)	4.8 (4)
C(2)—C(7)—O(8)—C(9)	−9.7 (3)
C(7)—O(8)—C(9)—C(13)	40.1 (3)
O(8)—C(9)—C(13)—C(1)	−64.5 (2)
C(9)—C(13)—C(1)—C(2)	60.1 (2)
C(13)—C(1)—C(2)—C(7)	−31.2 (3)

Data collection and cell refinement: Syntex $P2_1$ diffractometer software. Data reduction: $XP2_1$ (Pavelčík, 1987). Structure solution and refinement: *NRC* (Ahmed & Singh, 1973). Molecular graphics: *ORTEP*II (Johnson, 1971).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1026). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two Mesogenic Nitrobenzoxazoles

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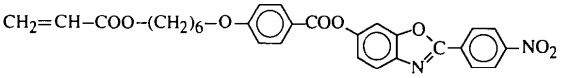
Abstract

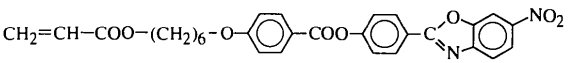
The crystal and molecular structures of two isomeric benzoxazoles, 2-(4-nitrophenyl)benzoxazol-6-yl 4-(acryloyloxyhexyloxy)benzoate, $C_{29}H_{26}N_2O_8$, (1), and 4-(6-nitro-2-benzoxazolyl)phenyl 4-(acryloyloxyhexyloxy)benzoate, $C_{29}H_{26}N_2O_8$, (2), are reported. Both compounds are mesogenic and are of potential interest for non-linear optics. Some differences in the molecular conformations of the two compounds are observed, mainly in the torsion angle around the bond from the aromatic C to ester O atoms and in the dihedral angle between the planes of the benzoxazole system and the phenyl group attached to it. The torsion angle is $-23.6(3)°$ for compound (1) and $32.2(7)$ and $-67.0(6)°$ for the two independent molecules of (2). These differences, which are probably due to packing effects, do not affect the pattern of bond lengths and angles within the molecules to any significant extent.

Comment

The title compounds, (1) and (2), are monomer precursors of comb-like polymers, the investigation of which is underway in our laboratory. Owing to the expected planarity and π-electron cojugation in the 2-phenylbenzoxazole moiety and to the strong electron-withdrawing effect of the nitro group, these polymers are likely to show non-linear optical properties of the second order (Williams, 1984). Compounds (1) and (2) were prepared by interfacial esterification of 4-(6-acryloyloxyhexyloxy)benzoyl chloride with 2-(4-nitrophenyl)-6-hydroxybenzoxazole and 2-(4-hydroxyphenyl)-6-nitrobenzoxazole, respectively. Detailed descriptions of both the syntheses of the nitrohydroxybenzoxazoles by intramolecular cyclization of parent Schiff bases and the esterification procedure are planned (Centore, Panunzi, Roviello & Sirigu, 1996).



(1)



(2)

Both compounds are mesogenic, but notwithstanding their closely related chemical natures, their mesophasic behaviours are quite different. Compound (1) is nematogenic and the interval of stability of the mesophase is rather small (melting point 407 K, isotropization temperature 415.1 K). Compound (2), on the other hand, melts at 375 K to a smectic A phase that trasforms, at 441 K, into a nematic phase; isotropization of this latter phase is at 463 K. Furthermore, both compounds are polymorphic in the solid state. The crystal structures reported in this paper refer to a low-temperature polymorph of (1) and to a high-temperature polymorph of (2). For compound (1), in particular, the low-temperature polymorph transforms, at 397 K, into another crystal phase that melts at 407 K.

Bond lengths and angles in the molecules of compounds (1) and (2) have close to expected values, with the exception of some bond lengths in the acryl-