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

$B_{eq} = (8\pi^2/3)[(aa^*)^2U_{11} + (bb^*)^2U_{22} + (cc^*)^2U_{33} + (2aa^*bb^*\cos\gamma)U_{12} + (2aa^*cc^*\cos\beta)U_{13} + (2bb^*cc^*\cos\alpha)U_{23}]$.

	x	y	z	B_{eq}
Br	−0.0747 (1)	0.3478 (1)	0.2192 (1)	0.0405 (4)
Si	0.2622 (2)	0.8764 (1)	0.2976 (2)	0.028 (1)
O(1)	0.6436 (5)	0.5627 (2)	0.2602 (5)	0.031 (2)
O(2)	0.4188 (5)	0.6344 (2)	0.3208 (5)	0.024 (2)
O(3)	0.5209 (5)	0.7036 (2)	0.1153 (5)	0.026 (2)
O(4)	0.3812 (5)	0.7850 (2)	−0.0984 (5)	0.035 (3)
C(1)	0.0930 (8)	0.4189 (3)	0.2263 (7)	0.025 (4)
C(2)	0.0399 (8)	0.4824 (3)	0.2661 (8)	0.024 (3)
C(3)	0.1642 (8)	0.5348 (3)	0.2815 (8)	0.023 (4)
C(4)	0.3447 (7)	0.5196 (3)	0.2575 (7)	0.020 (3)
C(5)	0.3925 (8)	0.4543 (3)	0.2127 (8)	0.026 (4)
C(6)	0.2681 (9)	0.4025 (3)	0.1948 (8)	0.029 (4)
C(7)	0.4865 (8)	0.5727 (3)	0.2780 (7)	0.024 (4)
C(8)	0.5384 (8)	0.6891 (3)	0.3255 (9)	0.030 (4)
C(9)	0.4639 (7)	0.7501 (3)	0.4129 (8)	0.023 (3)
C(10)	0.3936 (7)	0.7950 (3)	0.2696 (8)	0.024 (3)
C(11)	0.4241 (7)	0.7639 (3)	0.0747 (8)	0.022 (4)
C(12)	0.3853 (10)	0.9129 (3)	0.5655 (10)	0.035 (4)
C(13)	0.2723 (9)	0.9342 (3)	0.1005 (10)	0.039 (4)
C(14)	0.0030 (7)	0.8550 (3)	0.2581 (9)	0.035 (4)
C(15)	−0.1001 (10)	0.9171 (4)	0.3215 (13)	0.057 (6)
C(16)	−0.0978 (10)	0.8343 (4)	0.0286 (12)	0.061 (6)
C(17)	−0.0033 (10)	0.7982 (4)	0.3969 (13)	0.055 (5)

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

Br—C(1)	1.904 (6)	Si—C(10)	1.881 (6)
Si—C(12)	1.845 (7)	Si—C(13)	1.836 (7)
Si—C(14)	1.898 (6)	O(1)—C(7)	1.206 (6)
O(2)—C(7)	1.355 (6)	O(2)—C(8)	1.420 (6)
O(3)—C(8)	1.426 (6)	O(3)—C(11)	1.368 (6)
O(4)—C(11)	1.202 (6)	C(1)—C(2)	1.343 (7)
C(1)—C(6)	1.393 (9)	C(2)—C(3)	1.391 (9)
C(3)—C(4)	1.406 (7)	C(4)—C(5)	1.372 (7)
C(4)—C(7)	1.484 (7)	C(5)—C(6)	1.380 (8)
C(8)—C(9)	1.476 (7)	C(9)—C(10)	1.321 (7)
C(10)—C(11)	1.490 (7)	C(14)—C(15)	1.531 (9)
C(14)—C(16)	1.513 (9)	C(14)—C(17)	1.526 (11)
C(10)—Si—C(12)	106.4 (3)	C(10)—Si—C(13)	110.5 (3)
C(10)—Si—C(14)	107.2 (3)	C(12)—Si—C(13)	110.1 (3)
C(12)—Si—C(14)	112.1 (3)	C(13)—Si—C(14)	110.3 (3)
C(7)—O(2)—C(8)	115.6 (4)	C(8)—O(3)—C(11)	107.6 (4)
Br—C(1)—C(2)	118.8 (5)	Br—C(1)—C(6)	118.4 (5)
C(2)—C(1)—C(6)	122.8 (6)	C(1)—C(2)—C(3)	119.7 (6)
C(2)—C(3)—C(4)	118.8 (5)	C(3)—C(4)—C(5)	119.9 (5)
C(3)—C(4)—C(7)	121.7 (5)	C(5)—C(4)—C(7)	118.4 (5)
C(4)—C(5)—C(6)	121.2 (5)	C(1)—C(6)—C(5)	117.5 (6)
O(1)—C(7)—O(2)	123.5 (6)	O(1)—C(7)—C(4)	124.8 (6)
O(2)—C(7)—C(4)	111.7 (5)	O(2)—C(8)—O(3)	109.4 (5)
O(2)—C(8)—C(9)	108.6 (5)	O(3)—C(8)—C(9)	105.1 (5)
C(8)—C(9)—C(10)	111.8 (5)	Si—C(10)—C(9)	127.5 (4)
Si—C(10)—C(11)	127.3 (4)	C(9)—C(10)—C(11)	104.9 (5)
O(3)—C(11)—O(4)	120.0 (5)	O(3)—C(11)—C(10)	110.2 (5)
O(4)—C(11)—C(10)	129.8 (5)	Si—C(14)—C(15)	109.2 (5)
Si—C(14)—C(16)	109.6 (5)	Si—C(14)—C(17)	110.1 (4)
C(15)—C(14)—C(16)	109.3 (6)	C(15)—C(14)—C(17)	108.4 (6)
C(16)—C(14)—C(17)	110.2 (6)		

Space group $P\bar{1}$ or $P1$; the former was assumed and confirmed by successful analysis. Lorentz-polarization corrections were applied but not extinction corrections. The structure was solved by the heavy-atom method and refined by full-matrix least squares with the non-H atoms anisotropic. The H atoms were located from the ΔF map and allowed to refine with fixed isotropic temperature factors. The scattering factors were taken from Cromer & Waber (1974) and Stewart, Davidson & Simpson (1965); allowance was made for anomalous dispersion (Ibers & Hamilton, 1964). All calculations were performed using *TEXSAN* (Molecular Structure Corporation, 1992) on a Silicongraphics Personal Iris D/35 computer. A search of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) yielded only one hit of a similar compound, a diphenylmethylsilylbenzofuran (de Perez, Fuentes, Larson, Barnes & Heeg, 1986).

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55823 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1021]

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Structure of Methyl 2-(Nitrooxy)ethyl 1,4-Dihydro-2,6-dimethyl-4-(3-nitrophenyl)-3,5-pyridinedicarboxylate

T. Ogawa, K. Matsumoto,* C. Yokoo, K. Hatayama and K. Kitamura

Research Center, Taisho Pharmaceutical Co., Ltd, 1-403 Yoshino-cho, Ohmiya 330, Japan

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Abstract

The orientations of the carbonyl groups at C3 and C5 are different. The phenyl ring linked to C4 is perpendicular to the dihydropyridine ring. Some other structural features have also been elucidated.

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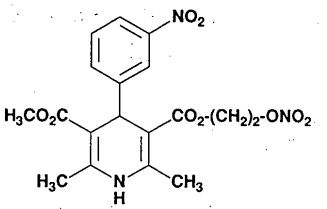
Comment

In the last decade, synthetic studies on Hantzsch-type 1,4-dihydropyridines (Bossert, Meyer & Wehinger, 1981) have been carried out in many research institutes all over the world because of their vasodilator properties as calcium antagonists. When this work was initiated, nifedipine was the only known compound used clinically for the treatment of anginia pectoris (Ellrodt, Chew & Singh, 1980; Leonard & Talbert, 1982; Spivack, Ocken & Frishman, 1983; Theroux, Taeymans & Waters, 1983; Vater *et al.*, 1972), and it was also known that nicardipine had been developed in preclinical studies for the treatment of hypertension (Iwanami *et al.*, 1979; Seki & Takenaka, 1977; Takenaka, Miyazaki, Asano, Higuchi & Maeno, 1982; Takenaka, Usuda, Nomura, Maeno & Sado, 1976). The aim of our work was to produce a drug comparable in overall pharmacological profile to nifedipine and with an extended duration of action. In commencing our program, we found it of interest that organic nitrate compounds, including nitroglycerine and nicorandil, increase the level of cyclic GMP (guanosine monophosphate) produced in various vascular smooth muscle tissues and promote relaxation (Holzmann, 1983; Waldman & Murad, 1988). So the combination of a nitro-like action and a calcium-blocking action in a single molecule was expected to have a vasodilating activity. Therefore, we synthesized novel dihydropyridine derivatives having a nitrate moiety in one of the ester chains. One compound, methyl 2-(nitrooxy)ethyl 1,4-dihydro-2,6-dimethyl-4-(3-nitrophenyl)-3,5-pyridinedicarboxylate (I) (Hatayama, Nakazato, Ogawa, Ito & Sawada, 1983; Ogawa, Nakazato, Sato & Hatayama 1990; Ogawa, Nakazato, Tsuchida & Hatayama, 1993; Ogawa, Matsumoto, Yokoo, Hatayama & Kitamura, 1993), was found to be comparable in potency and duration to nifedipine.



(I)

As can be seen in Fig. 1, the phenyl ring is perpendicular to the dihydropyridine ring owing to the steric hindrance of the nitrooxyethyl ester group in the molecule. The torsion angle C8—C9—N13—O15 of −14.6 (2)° indicates that the nitro group is not on the same plane as the phenyl ring. This conformation is also considered to result from interactions between the nitrooxyethyl ester group and the phenyl ring. The orientations of the carbonyl groups at C3 and C5 are synperiplanar to the C2=C3 double bond and antiperiplanar to the C5=C6 double bond. Furthermore, the torsion angles C6—C5—C25—O26 of 171.8 (2)° and C2—C3—C16—O17 of 3.4 (2)°, indicate that the C25—O26 carbonyl group is slightly declined to the dihydropyridine ring compared to the C16—O17 carbonyl group. The torsion angles of the intra 1,4-dihydropyridine ring, along bonds N1—C2, C2—C3, C3—C4, C4—C5, C5—C6 and C6—N1, are −11.7 (1), −3.1 (1), 17.3 (2), −17.8 (2), 5.7 (1) and 10.3 (1)°, respectively. The large ring distortion is seen at C4 and N1. This is in agreement with other dihydropyridine derivatives reported previously (Tamazawa *et al.*, 1986).

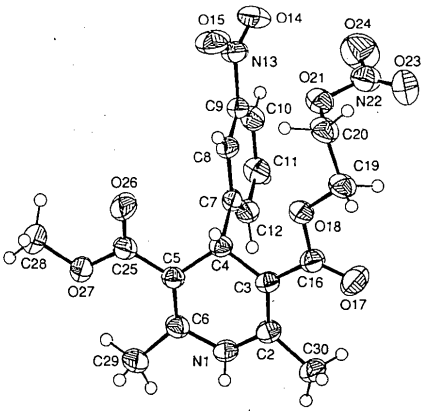


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title compound showing the atomic numbering.

Experimental

Crystal data

$C_{18}H_{19}N_3O_9$
M_r = 421.00
Orthorhombic
$P2_12_12_1$
a = 11.962 (2) Å
b = 20.917 (4) Å
c = 7.624 (2) Å
V = 1907.6 (6) Å^3
Z = 4
D_x = 1.47 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 20 reflections
θ = 27.5–30°
μ = 0.92 mm^{-1}
T = 288 K
Plate
0.60 × 0.50 × 0.40 mm
Light yellow

Data collection

Mac-Science MXC18 diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical (Katayama, 1986)
T_{min} = 0.541, T_{max} = 0.584
1934 measured reflections
1854 independent reflections
1851 observed reflections
R_{int} = 0.00
θ_{max} = 65°
h = 0 → 14
k = 0 → 24
l = 0 → 8
3 standard reflections monitored every 100 reflections
intensity variation: 2%

Refinement

Refinement on F
Final $R = 0.031$
$wR = 0.052$
$S = 2.55$
1851 reflections
337 parameters
Only coordinates of H atoms refined
$w = [\sigma^2(F_o) + (0.020F_o)^2]^{-1}$
$(\Delta/\sigma)_{max} = 0.21$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.14$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV), including anomalous-dispersion corrections

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

$B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
N1	0.4675 (2)	0.43539 (8)	−0.0130 (3)	3.28 (5)
C2	0.5682 (2)	0.46355 (9)	0.0288 (3)	2.96 (5)
C3	0.5774 (2)	0.52790 (9)	0.0279 (2)	2.71 (5)
C4	0.4803 (2)	0.57022 (9)	−0.0276 (2)	2.60 (5)
C5	0.3703 (2)	0.53301 (9)	−0.0270 (2)	2.73 (5)
C6	0.3679 (2)	0.46859 (9)	−0.0276 (3)	3.03 (5)
C7	0.5009 (1)	0.59977 (8)	−0.2074 (2)	2.45 (5)
C8	0.5017 (2)	0.66536 (9)	−0.2305 (3)	2.70 (5)
C9	0.5209 (2)	0.68995 (9)	−0.3960 (3)	2.93 (5)
C10	0.5384 (2)	0.6519 (1)	−0.5418 (3)	3.39 (6)
C11	0.5374 (2)	0.5867 (1)	−0.5170 (3)	3.52 (6)
C12	0.5198 (2)	0.5610 (1)	−0.3526 (3)	3.10 (6)
N13	0.5247 (2)	0.75965 (8)	−0.4174 (3)	3.62 (5)
O14	0.5634 (2)	0.78176 (8)	−0.5536 (2)	4.88 (6)
O15	0.4891 (2)	0.79306 (7)	−0.2995 (3)	5.18 (6)
C16	0.6826 (2)	0.55933 (9)	0.0726 (3)	3.26 (6)
O17	0.7710 (2)	0.53506 (8)	0.1066 (4)	6.02 (7)
O18	0.6700 (1)	0.62325 (7)	0.0745 (2)	3.51 (5)
C19	0.7670 (2)	0.6606 (1)	0.1171 (3)	3.94 (6)
C20	0.7388 (2)	0.7287 (1)	0.0754 (4)	4.13 (6)
O21	0.7210 (1)	0.73826 (8)	−0.1089 (2)	4.33 (5)
N22	0.8173 (2)	0.74818 (9)	−0.2056 (3)	4.45 (6)
O23	0.9063 (1)	0.7451 (1)	−0.1316 (3)	5.36 (6)
O24	0.7994 (2)	0.7590 (1)	−0.3571 (3)	7.09 (8)
C25	0.2725 (2)	0.5754 (1)	−0.0255 (3)	3.15 (5)
O26	0.2806 (1)	0.63208 (7)	−0.0060 (3)	5.25 (6)
O27	0.1726 (1)	0.54786 (7)	−0.0478 (3)	4.19 (5)
C28	0.0789 (2)	0.5912 (1)	−0.0467 (5)	5.00 (8)
C29	0.2678 (2)	0.4255 (1)	−0.0395 (4)	4.27 (7)
C30	0.6578 (2)	0.4169 (1)	0.0767 (4)	3.94 (6)

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

N1—C2	1.378 (3)	C10—C11	1.376 (3)
N1—C6	1.384 (3)	C11—C12	1.381 (3)
C2—C3	1.350 (3)	N13—O15	1.216 (3)
C2—C30	1.494 (3)	N13—O14	1.226 (3)
C3—C16	1.459 (3)	C16—O17	1.201 (3)
C3—C4	1.520 (3)	C16—O18	1.346 (2)
C4—C7	1.524 (2)	O18—C19	1.437 (3)
C4—C5	1.528 (3)	C19—C20	1.497 (3)
C5—C6	1.348 (3)	C20—O21	1.435 (3)
C5—C25	1.468 (3)	O21—N22	1.384 (3)
C6—C29	1.502 (3)	N22—O24	1.196 (3)
C7—C8	1.383 (2)	N22—O23	1.206 (3)
C7—C12	1.391 (3)	C25—O26	1.199 (2)
C8—C9	1.382 (3)	C25—O27	1.336 (2)
C9—C10	1.382 (3)	O27—C28	1.442 (3)
C9—N13	1.468 (2)		
C2—N1—C6	123.8 (2)	C10—C9—N13	118.5 (2)
C3—C2—N1	119.8 (2)	C11—C10—C9	117.3 (2)
C3—C2—C30	126.4 (2)	C10—C11—C12	120.8 (2)
N1—C2—C30	113.8 (2)	C11—C12—C7	121.3 (2)
C2—C3—C16	121.2 (2)	O15—N13—O14	122.8 (2)
C2—C3—C4	121.3 (2)	O15—N13—C9	118.5 (2)
C16—C3—C4	117.4 (2)	O14—N13—C9	118.7 (2)
C3—C4—C7	111.3 (2)	O17—C16—O18	121.0 (2)
C3—C4—C5	111.1 (2)	O17—C16—C3	128.2 (2)
C7—C4—C5	110.4 (2)	O18—C16—C3	110.7 (2)
C6—C5—C25	125.9 (2)	C16—O18—C19	116.9 (2)
C6—C5—C4	121.8 (2)	O18—C19—C20	106.7 (2)
C25—C5—C4	112.3 (2)	O21—C20—C19	112.0 (2)
C5—C6—N1	118.9 (2)	N22—O21—C20	114.7 (2)
C5—C6—C29	128.1 (2)	O24—N22—O23	128.3 (2)
N1—C6—C29	113.0 (2)	O24—N22—O21	113.1 (2)
C8—C7—C12	118.4 (2)	O23—N22—O21	118.5 (2)
C8—C7—C4	121.2 (2)	O26—C25—O27	121.0 (2)
C12—C7—C4	120.4 (2)	O26—C25—C5	122.2 (2)
C9—C8—C7	119.1 (2)	O27—C25—C5	116.8 (2)
C8—C9—C10	123.0 (2)	C25—O27—C28	115.0 (2)
C8—C9—N13	118.4 (2)		

Lorentz and polarization corrections were applied. Absorption correction was applied using an analytical function (Katayama, 1986). The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1986). All H atoms were located by difference Fourier synthesis. Anisotropic least-squares refinement was performed for non-H atoms, isotropic for H atoms (Katayama, 1986).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, and bond distances and angles involving H atoms, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55847 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1024]

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Structure of the Epoxide of a Tricyclic Lactone

JOEL T. MAGUE,* HARRY E. ENSLEY AND GUOQING CHEN

Department of Chemistry, Tulane University, New Orleans, Louisiana 70118, USA

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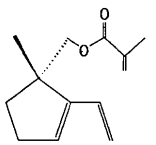
Abstract

The crystal structure of 1,5-dimethyl-3,9-dioxatetracyclo[8.3.0.0^{5,11}.0^{8,10}]tridecan-4-one, (4), obtained from the epoxidation of the olefin generated by the intramolecular Diels–Alder reaction of the methacrylate ester of 3-hydroxymethyl-3-methyl-2-vinylcyclopentene, demonstrates that the desired regioselectivity in the cycloaddition reaction has occurred. The five-membered carbocyclic ring is distinctly non-planar and there is significant strain in the portion of the lactone adjacent to this ring and at the junction with the six-membered ring adjacent to the epoxide moiety.

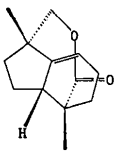
Comment

In connection with model studies directed towards the synthesis of cinncassiol D_1 (Nohara *et al.*, 1980, 1981) we were interested in the regioselectivity of the intramolecular Diels–Alder reaction of (1).

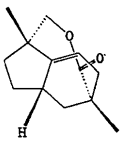


(1)

Previous work on related systems (Shea *et al.*, 1982; Shea, Lease & Ziller, 1990; Shea, Staab & Zandi, 1991) indicated that the length of the 'tether' between the 2-position of the diene and the dienophile influences the regioselectivity, with a five-atom tether preferentially giving the '*meta*' adduct (Shea *et al.*, 1991). Compound (1) has a four-atom tether and while a single low-melting product was obtained from its intramolecular cycloaddition, NMR could not distinguish between the desired '*meta*' isomer (2) and the '*para*' isomer (3) because of an accidental chemical-shift degeneracy of the allylic

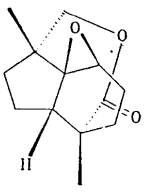


(2)



(3)

methine and methylene resonances. As suitable crystals of the product olefin could not be obtained, it was epoxidized to yield a single product, (4), which formed X-ray quality crystals when a concentrated ethanol solution was cooled at 278 K. The structure of (4) (Fig. 1) confirms that the product of the intramolecular cycloaddition is indeed the '*meta*' isomer (2).



(4)

Compound (4) crystallizes as a racemic mixture with no unusual intermolecular contacts. The five-membered ring is distinctly non-planar with C(2) lying nearly in the weighted least-squares plane and the remaining four atoms 0.138 (2)–0.202 (3) Å from it. Most bond distances and interbond angles are

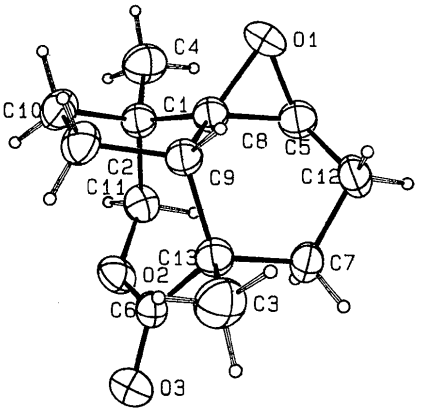


Fig. 1. A perspective view of (4). Thermal ellipsoids for non-H atoms are drawn at the 40% probability level. H atoms are drawn artificially small for clarity and are numbered to correspond to the attached C atoms.

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