Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1218). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1-(4-Chlorophenyl)-3a-methyl-5-phenyl-3a,4-dihydro-1,2,4-oxadiazolo[4,5-*a*][1,5]-benzodiazepine

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(*Received 14 February 1996; accepted 20 March 1996*)

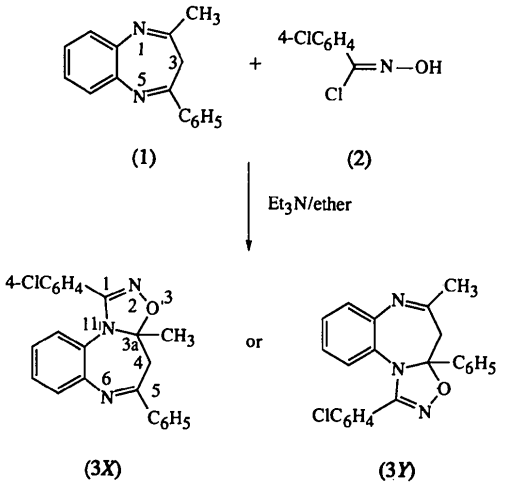
Abstract

We report here the peri- and regioselectivity experienced in the 1,3-dipolar cycloaddition of 1,5-benzodiazepine to a nitrile oxide. The crystal structure of the title cycloadduct, $C_{23}H_{18}ClN_3O$, shows that the condensation occurs at the N=C double bond at the 1 and 2 positions of the benzodiazepine.

Comment

Several benzodiazepine derivatives containing additional rings are of pharmacological interest (Sternbach, 1978). In connection with investigations on possible approaches to novel benzodiazepine derivatives with an additional fused heterocyclic ring (Aversa, Giannetto, Ferlazzo & Romeo, 1982), we have tested the C=N double bond of the 1,5-benzodiazepine system as a dipolarophile in the 1,3-dipolar cycloadditions of nitrile oxides.

The condensation of 2-methyl-4-phenyl-1,5-benzodiazepine [(1); Barltrop, Richards, Russel & Ryback, 1959] with a slight excess of 4-chlorobenzonitrile oxide, generated *in situ* from 4-chlorobenzohydroxamoyl chloride [(2); Grundmann & Dean, 1965; Liu, Shelton & Howe, 1980), gives the title 1,2,4-oxadiazolo[4,5-*a*][1,5]-benzodiazepine, (3) (*X* or *Y*), as indicated below.



The structure of cycloadduct (3) was assigned by X-ray crystallographic analysis which shows it to be adduct (3*X*), *i.e.* the N=C double bond at the 1 and 2 positions of the benzodiazepine is the site of addition (Fig. 1). The reaction is periselective as only one C=N double bond is affected. The O atom of the dipole is linked to the C atom of the C=N dipolarophile making the reaction regioselective.

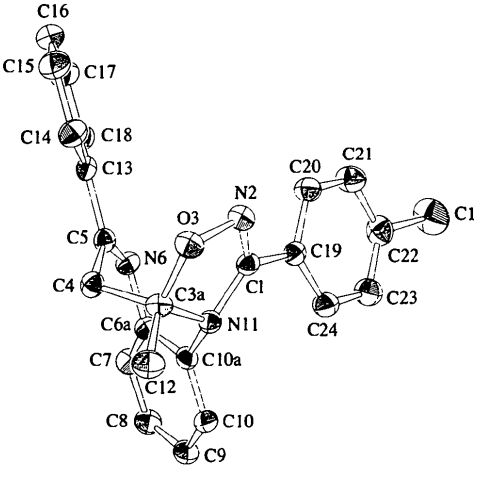


Fig. 1. *ORTEP*II (Johnson, 1976) view of the title molecule with displacement ellipsoids at the 50% probability level and the atomic numbering scheme. H atoms have been omitted for clarity.

As usual, the seven-membered diazepine ring has a fragment (N6—C6a—C10a—N11) which is conjugated with the adjacent benzene ring. The five-membered oxadiazolo ring has an envelope conformation, the bending angle between the O3, C3a, N11 and N11, C1, N2, O3 planes being equal to 17.9 (4)°. The N11—C1—N2—O3 fragment, while almost perpendicular to the benzodiazepine moiety, makes an angle of 29.6 (2)° with the 4-chlorobenzene ring. The phenyl ring (C13–C18) makes an angle of only 12.5 (2)° with the C5=N6 double bond.

Experimental

Crystal data

$C_{23}H_{18}ClN_3O$
M_r = 387.87
Monoclinic
$P2_1/c$
a = 19.685 (1) Å
b = 11.023 (2) Å
c = 8.881 (3) Å
β = 98.4 (3)°
V = 1907 (2) Å^3
Z = 4
D_x = 1.35 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 14–17°
μ = 0.216 mm^{-1}
T = 294 K
Cube
0.50 × 0.50 × 0.50 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3008 measured reflections
2752 independent reflections
1995 observed reflections [$I > 3\sigma(I)$]

R_{int} = 0.020
θ_{max} = 23.96°
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 17$
3 standard reflections
frequency: 60 min
intensity decay: 0.92%

Refinement

Refinement on F
R = 0.045
wR = 0.056
S = 1.941
1995 reflections
253 parameters
H atoms included but not refined
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.50 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 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)*

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

	x	y	z	U_{eq}
Cl	0.98072 (4)	0.2467 (1)	0.0485 (1)	0.0912 (3)
O3	1.34408 (9)	−0.0883 (2)	0.2441 (2)	0.0434 (5)
N2	1.2891 (1)	−0.0133 (2)	0.1713 (2)	0.0402 (6)
N6	1.2894 (1)	0.1202 (2)	0.5546 (2)	0.0380 (6)
N11	1.2555 (1)	−0.0964 (2)	0.3798 (2)	0.0338 (5)
C1	1.2415 (1)	−0.0193 (2)	0.2563 (3)	0.0342 (6)
C3a	1.3293 (1)	−0.1225 (2)	0.3926 (3)	0.0375 (7)
C4	1.3709 (1)	−0.0408 (2)	0.5142 (3)	0.0397 (7)
C5	1.3455 (1)	0.0892 (2)	0.5081 (2)	0.0350 (7)
C6a	1.2474 (1)	0.0294 (2)	0.6057 (3)	0.0363 (7)
C7	1.2202 (1)	0.0477 (2)	0.7392 (3)	0.0478 (8)
C8	1.1766 (1)	−0.0375 (3)	0.7885 (3)	0.0510 (8)
C9	1.1593 (1)	−0.1412 (3)	0.7051 (3)	0.0507 (8)
C10	1.1864 (1)	−0.1609 (2)	0.5713 (3)	0.0424 (7)
C10a	1.2290 (1)	−0.0754 (2)	0.5207 (2)	0.0355 (7)
C12	1.3463 (1)	−0.2555 (2)	0.4181 (3)	0.0492 (8)
C13	1.3880 (1)	0.1866 (2)	0.4508 (3)	0.0362 (7)
C14	1.4406 (1)	0.1608 (3)	0.3686 (3)	0.0496 (8)
C15	1.4796 (2)	0.2534 (3)	0.3192 (3)	0.062 (1)
C16	1.4663 (2)	0.3727 (3)	0.3529 (3)	0.0634 (9)
C17	1.4137 (2)	0.3998 (3)	0.4327 (3)	0.0586 (9)
C18	1.3747 (1)	0.3073 (2)	0.4822 (3)	0.0476 (8)
C19	1.1767 (1)	0.0460 (2)	0.2119 (3)	0.0378 (7)
C20	1.1776 (1)	0.1535 (2)	0.1304 (3)	0.0481 (8)
C21	1.1176 (2)	0.2153 (3)	0.0795 (3)	0.0565 (9)
C22	1.0562 (1)	0.1694 (3)	0.1130 (3)	0.0571 (9)
C23	1.0539 (2)	0.0636 (3)	0.1943 (4)	0.064 (1)
C24	1.1142 (1)	0.0020 (3)	0.2448 (3)	0.0536 (8)

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

O3—N2	1.439 (3)	N6—C6a	1.415 (3)
O3—C3a	1.441 (3)	N11—C1	1.383 (3)
N2—C1	1.287 (3)	N11—C3a	1.469 (3)
N6—C5	1.281 (3)	N11—C10a	1.443 (3)
N2—O3—C3a	108.8 (2)	C3a—N11—C10a	116.3 (2)
O3—N2—C1	105.7 (2)	N2—C1—N11	114.7 (2)
C5—N6—C6a	119.1 (2)	N2—C1—C19	119.7 (2)
C1—N11—C3a	105.2 (2)	N11—C1—C19	125.4 (2)
C1—N11—C10a	122.2 (2)		

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *BEGIN* in *SDP-Plus* (Frenz, 1985). Program(s) used to solve structure: Direct methods *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *LSFM* in *SDP-Plus*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CIF VAX* in *MolEN* (Fair, 1990).

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