C15—C16—C17	120.9 (5)	O8″A—S7″A—O9″A	112.2 (3)
C16—C17—C18	119.8 (5)	C1″—S7″B—O10″B	106.2 (6)
C17—C18—C21	119.9 (5)	C1″—S7″B—O9″B	109.5 (5)
C17—C18—C19	119.9 (5)	C1″—S7″B—O8″B	103.7 (6)
C19—C18—C21	120.2 (5)	O9″B—S7″B—O10″B	112.4 (7)
C18—C19—C20	119.9 (5)	O8″B—S7″B—O10″B	112.2 (6)
C15—C20—C19	120.6 (5)	O8″B—S7″B—O9″B	112.2 (7)
C18—C21—N22	178.8 (7)		

C9A—N1—C2—C11	133.5 (5)	N4—C5—C5A—C9A	37.4 (7)
C9A—N1—C2—C3	6.9 (6)	C5—C5A—C9A—N1	−0.4 (7)
N1—C2—C11—N12	167.1 (4)	C2—C11—N12—C13	−80.2 (6)
N1—C2—C3—N4	65.8 (5)	C11—N12—C13—O14	3.8 (9)
C2—C3—N4—C5	−78.6 (5)	C11—N12—C13—C15	−175.8 (5)
C3—N4—C5—C5A	8.4 (7)	N12—C13—C15—C16	155.0 (5)
N4—C5—C1′A—C2′A	−164 (1)	N12—C13—C15—C20	−26.2 (8)

Data were collected with a variable scan speed of 0.6–2.4° min^{-1} and a scan width of 1.4° in steps of 0.02° with extra steps for α_1–α_2 dispersion. The structure was solved by direct methods and refined by full-matrix least-squares techniques. Difference Fourier maps showed an 180° rotational disorder of the thienyl ring and a 60° rotational disorder of the sulfonate group. These disordered positions were modelled as idealized rigid groups. In the first instance, the complementary occupancy, positional and rotational parameters were refined, while keeping the isotropic displacement parameters fixed, then the positional, rotational and individual anisotropic parameters were refined with fixed population parameters. H-atom positions were calculated, except those of the methyl groups which were obtained from a difference Fourier synthesis. Data collection and cell refinement: *DIF*4 (Stoe & Cie, 1988*a*). Data reduction: *REDU*4 (Stoe & Cie, 1992*a*). Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

The authors thank Dr H. Zeugner, Kali-Chemie Pharma GmbH, Hannover, for providing the title compound.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1089). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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5-(2,4-Dichlorophenyl)-2-[(3-furoyl)aminomethyl]-8-methoxy-1-methyl-2,3-dihydro-1*H*-1,4-benzodiazepin-4-ium *p*-Toluenesulfonate

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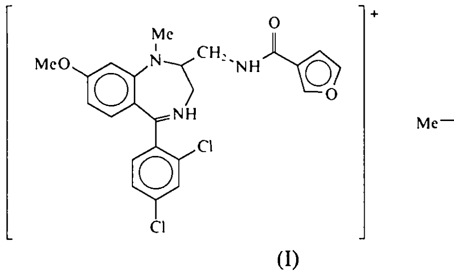
Abstract

The seven-membered ring of the title compound, $C_{23}H_{22}Cl_2N_3O_3^+.C_7H_7O_3S^-$, adopts a conformation halfway between a distorted boat and a distorted sofa. The 3-furoylaminomethyl moiety is in an extended conformation with the furan ring nearly parallel to the benzo part of the benzodiazepine ring. Two intermolecular hydrogen bonds to the *p*-toluenesulfonate anion stabilize the observed conformation.

Comment

The structure of the title compound (I) was determined as part of a structure–activity study of benzodiazepine derivatives with opioid activity.



(I)

Bond lengths and angles are in the same range as in other protonated 2-acylaminomethylbenzodiazepines (Meurisse, Blaton, Peeters & De Ranter, 1992, and references therein). The global conformation is practically the same in all these compounds. The seven-

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membered ring has a conformation halfway between a distorted boat and a distorted sofa [puckering parameters q_2 = 0.693 (8), q_3 = 0.282 (8) Å, φ_2 = −33.6 (6), φ_3 = −136 (2)°] with the 2-substituent axial and a mirror plane through C3 and the centre of the C5*A*—C9*A* bond [asymmetry parameter ΔC_s(C3) = 0.049 (3)]. The furan ring is nearly parallel to the benzo part of the benzodiazepine ring [dihedral angle 3.4 (2)°], which in turn is almost perpendicular to the 2,4-dichlorophenyl moiety [dihedral angle 78.1 (3)°]. The observed conformation of the furoylaminomethyl side chain is stabilized by hydrogen bonds from N4 and N12 to two O atoms of the *p*-toluenesulfonate anion [N4···O9″ = 2.69 (1), H4···O9″ = 1.62 Å, N4—H4···O9″ = 172°; N12···O10″ = 2.894 (8), H12···O10″ = 1.82 Å, N12—H12···O10″ = 164°].

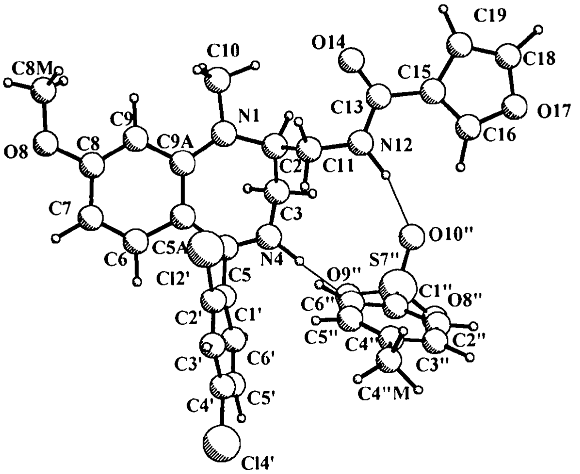

Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) drawing with atomic numbering scheme.

Experimental

Crystal data

$C_{23}H_{22}Cl_2N_3O_3^+.C_7H_7O_3S^-$
M_r = 630.54
Triclinic
$P\bar{1}$
a = 9.857 (1) Å
b = 12.048 (1) Å
c = 18.6205 (6) Å
α = 81.893 (7)°
β = 130.239 (1)°
γ = 115.938 (8)°
V = 1485.4 (2) Å^3
Z = 2
D_x = 1.410 Mg m^{-3}
D_m = 1.406 Mg m^{-3}
D_m measured by flotation in *n*-heptane/CCl$_4$

Cu $K\alpha$ radiation
λ = 1.54184 Å
Cell parameters from 24 reflections
θ = 15–23°
μ = 3.041 mm^{-1}
T = 293 K
Needle
0.40 × 0.08 × 0.07 mm
Pale orange
Crystal source: methanol/amyl acetate solution

Data collection

Hilger & Watts four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (North, Phillips & Mathews, 1968)
$T_{\min}$ = 0.908, $T_{\max}$ = 0.996
4786 measured reflections
4502 independent reflections
2304 observed reflections [$I > 3.0\sigma(I)$]

$R_{\rm int}$ = 0.0188
$\theta_{\max}$ = 64.88°
h = −12 → 0
k = −14 → 14
l = −22 → 22
4 standard reflections monitored every 50 reflections intensity variation: <3.0%

Refinement

Refinement on F
R = 0.0589
wR = 0.0738
S = 1.67
2304 reflections
379 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.00100F^2]$

$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.91 e Å^{-3}
$\Delta\rho_{\min}$ = −0.34 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

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

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

	x	y	z	$U_{\rm eq}$
N1	0.2814 (8)	0.2432 (4)	0.6495 (4)	0.064 (5)
C2	0.1585 (9)	0.3092 (6)	0.6064 (4)	0.060 (5)
C3	0.2486 (9)	0.4327 (6)	0.5857 (4)	0.064 (5)
N4	0.4200 (8)	0.5294 (4)	0.6735 (4)	0.055 (4)
C5	0.589 (1)	0.5238 (5)	0.7381 (5)	0.052 (5)
C5*A*	0.6228 (9)	0.4235 (5)	0.7330 (4)	0.057 (5)
C6	0.825 (1)	0.4568 (6)	0.7804 (5)	0.067 (5)
C7	0.886 (1)	0.3727 (6)	0.7839 (5)	0.072 (6)
C8	0.739 (1)	0.2447 (6)	0.7417 (5)	0.075 (7)
O8	0.8093 (7)	0.1647 (5)	0.7473 (4)	0.097 (5)
C8*M*	0.667 (1)	0.0341 (7)	0.7012 (6)	0.104 (8)
C9	0.544 (1)	0.2051 (6)	0.6974 (5)	0.064 (6)
C9*A*	0.477 (1)	0.2924 (6)	0.6904 (4)	0.061 (5)
C10	0.160 (1)	0.1049 (6)	0.6256 (6)	0.092 (7)
C11	0.1079 (9)	0.3219 (6)	0.6653 (5)	0.064 (6)
N12	−0.0673 (8)	0.3412 (4)	0.6102 (4)	0.060 (5)
C13	−0.249 (1)	0.2399 (6)	0.5560 (5)	0.055 (6)
O14	−0.2702 (6)	0.1347 (4)	0.5437 (4)	0.075 (4)
C15	−0.421 (1)	0.2611 (5)	0.5137 (5)	0.054 (5)
C16	−0.422 (1)	0.3705 (6)	0.5234 (5)	0.067 (7)
O17	−0.6115 (8)	0.3488 (4)	0.4766 (4)	0.083 (5)
C18	−0.733 (1)	0.2211 (7)	0.4369 (5)	0.074 (7)
C19	−0.626 (1)	0.1646 (6)	0.4566 (5)	0.069 (6)
C1′	0.7516 (9)	0.6355 (6)	0.8203 (5)	0.056 (6)
C2′	0.833 (1)	0.6219 (6)	0.9144 (5)	0.064 (6)
Cl2′	0.7441 (4)	0.4775 (2)	0.9375 (2)	0.104 (2)
C3′	0.980 (1)	0.7236 (7)	0.9909 (5)	0.072 (6)
C4′	1.042 (1)	0.8407 (7)	0.9732 (6)	0.079 (7)
Cl4′	1.2249 (3)	0.9698 (2)	1.0666 (2)	0.126 (2)
C5′	0.965 (1)	0.8593 (6)	0.8819 (6)	0.077 (7)
C6′	0.819 (1)	0.7567 (6)	0.8045 (5)	0.069 (7)
C1″	0.332 (1)	0.7452 (6)	0.8163 (5)	0.066 (6)
C2″	0.282 (1)	0.8071 (8)	0.8466 (6)	0.103 (8)
C3″	0.376 (2)	0.8295 (9)	0.9419 (8)	0.123 (9)
C4″	0.516 (2)	0.788 (1)	1.0088 (7)	0.10 (1)
C4″*M*	0.625 (2)	0.821 (1)	1.1142 (7)	0.15 (1)
C5″	0.558 (2)	0.723 (1)	0.9768 (8)	0.14 (1)
C6″	0.471 (1)	0.7020 (8)	0.8832 (7)	0.119 (9)
S7″	0.2204 (3)	0.7229 (2)	0.6941 (1)	0.074 (2)
O8″	0.1811 (7)	0.8293 (4)	0.6585 (3)	0.081 (5)
O9″	0.3666 (8)	0.7191 (5)	0.6948 (4)	0.104 (6)
O10″	0.0399 (8)	0.6044 (4)	0.6463 (4)	0.100 (5)

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

N1—C2	1.47 (1)	C16—O17	1.36 (1)
N1—C9*A*	1.37 (1)	O17—C18	1.383 (7)
N1—C10	1.477 (7)	C18—C19	1.34 (1)
C2—C3	1.509 (9)	C1′—C2′	1.40 (1)
C2—C11	1.52 (1)	C1′—C6′	1.395 (9)
C3—N4	1.460 (6)	C2′—Cl2′	1.710 (7)
N4—C5	1.311 (9)	C2′—C3′	1.379 (8)
C5—C5*A*	1.42 (1)	C3′—C4′	1.36 (1)
C5—C1′	1.498 (7)	C4′—Cl4′	1.719 (7)
C5*A*—C6	1.43 (1)	C4′—C5′	1.37 (1)
C5*A*—C9*A*	1.444 (7)	C5′—C6′	1.394 (9)
C6—C7	1.36 (1)	C1″—C2″	1.38 (1)
C7—C8	1.420 (7)	C1″—C6″	1.39 (1)
C8—O8	1.37 (1)	C1″—S7″	1.771 (9)
C8—C9	1.37 (1)	C2″—C3″	1.37 (1)
O8—C8*M*	1.440 (7)	C3″—C4″	1.39 (1)
C9—C9*A*	1.42 (1)	C4″—C4″*M*	1.51 (1)
C11—N12	1.44 (1)	C4″—C5″	1.37 (2)
N12—C13	1.347 (6)	C5″—C6″	1.36 (1)
C13—O14	1.220 (9)	S7″—O8″	1.447 (5)
C13—C15	1.47 (1)	S7″—O9″	1.45 (1)
C15—C16	1.36 (1)	S7″—O10″	1.444 (4)
C15—C19	1.441 (8)		
C9*A*—N1—C10	119.2 (7)	C15—C16—O17	110.1 (6)
C2—N1—C10	112.2 (7)	C16—O17—C18	106.9 (7)
C2—N1—C9*A*	127.3 (5)	O17—C18—C19	110.2 (7)
N1—C2—C11	111.3 (5)	C15—C19—C18	106.7 (6)
N1—C2—C3	112.4 (7)	C5—C1′—C6′	120.8 (6)
C3—C2—C11	113.3 (6)	C5—C1′—C2′	121.0 (6)
C2—C3—N4	111.7 (5)	C2′—C1′—C6′	118.1 (6)
C3—N4—C5	122.0 (6)	C1′—C2′—C3′	122.1 (6)
N4—C5—C1′	114.2 (6)	C1′—C2′—Cl2′	120.5 (6)
N4—C5—C5*A*	124.6 (6)	Cl2′—C2′—C3′	117.4 (5)
C5*A*—C5—C1′	121.2 (7)	C2′—C3′—C4′	118.4 (6)
C5—C5*A*—C9*A*	126.5 (8)	C3′—C4′—C5′	121.8 (7)
C5—C5*A*—C6	115.3 (6)	C3′—C4′—Cl4′	119.9 (6)
C6—C5*A*—C9*A*	118.1 (7)	Cl4′—C4′—C5′	118.4 (6)
C5*A*—C6—C7	123.7 (6)	C4′—C5′—C6′	120.1 (7)
C6—C7—C8	116.4 (9)	C1′—C6′—C5′	119.6 (7)
C7—C8—C9	123.2 (7)	C6″—C1″—S7″	121.2 (8)
C7—C8—O8	113.6 (7)	C2″—C1″—S7″	120.0 (7)
O8—C8—C9	123.1 (6)	C2″—C1″—C6″	118.8 (8)
C8—O8—C8*M*	117.6 (8)	C1″—C2″—C3″	120
C8—C9—C9*A*	120.8 (6)	C2″—C3″—C4″	121 (1)
C5*A*—C9*A*—C9	117.7 (7)	C3″—C4″—C5″	118 (1)
N1—C9*A*—C9	116.7 (6)	C3″—C4″—C4″*M*	120 (1)
N1—C9*A*—C5*A*	125.5 (8)	C4″*M*—C4″—C5″	122 (1)
C2—C11—N12	112.7 (6)	C4″—C5″—C6″	122 (1)
C11—N12—C13	118.7 (6)	C1″—C6″—C5″	120 (1)
N12—C13—C15	116.9 (6)	C1″—S7″—O10″	106.3 (3)
N12—C13—O14	121.9 (8)	C1″—S7″—O9″	105.5 (4)
O14—C13—C15	121.2 (6)	C1″—S7″—O8″	106.7 (3)
C13—C15—C19	125.3 (6)	O9″—S7″—O10″	112.3 (3)
C13—C15—C16	128.5 (7)	O8″—S7″—O10″	112.7 (3)
C16—C15—C19	106.1 (7)	O8″—S7″—O9″	112.7 (4)
C2—N1—C9*A*—C5*A*	26 (1)	N4—C5—C1′—C6′	−58 (1)
C9*A*—N1—C2—C11	−112.5 (9)	N4—C5—C5*A*—C9*A*	−31 (1)
C9*A*—N1—C2—C3	16 (1)	C5—C5*A*—C9*A*—N1	−1 (1)
N1—C2—C11—N12	−158.1 (6)	C2—C11—N12—C13	83.3 (9)
N1—C2—C3—N4	−74.3 (8)	C11—N12—C13—O14	−7 (1)
C2—C3—N4—C5	69.4 (9)	C11—N12—C13—C15	170.4 (7)
C3—N4—C5—C5*A*	−2 (1)	N12—C13—C15—C19	−177.8 (8)

Data collection was performed with a fixed scan width and a 2:1 ratio of peak-counting time to background-counting time. The structure was solved by direct methods and refined by full-matrix least squares. H-atom positions were calculated where possible; others were obtained from a difference Fourier synthesis. The largest density of 0.91 e Å^{-3} in the final difference Fourier map is near the H6′ position, suggesting some partial occupancy of Cl2′ (180° rotational disorder of the 2,4-dichlorophenyl ring). Data collection and cell refinement: Hilger & Watts Y290 software. Data reduction: *REDU*4 (Stoe & Cie, 1992). Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1088). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4-Hydroxyacetophenone Oxime (I) and 4-Hydroxy-3-methylacetophenone Oxime (II)

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Abstract

The crystal structures of the two chemically similar compounds (I), $C_8H_9NO_2$, and (II), $C_9H_{11}NO_2$, have been determined at room temperature. Despite the