

References

GLINKA, R., GRZYWACZ, M., KOTELKO, B., MAJCHRZAK, M., MALINOWSKI, H., MIKOLAJEWSKA, H., MIKICIUK-OLASIK, E. & SZKUDLINSKI, J. (1980). *Pol. J. Pharmacol. Pharm.* **32**, 773.
 GLINKA, R., KAMIŃSKA, A. L., KOTELKO, B. & SZADOWSKA, A. (1977). *Acta Pol. Pharm.* **34**, 621.

GLINKA, R., KOTELKO, B., MIKOLAJEWSKA, H. & MIKICIUK-OLASIK, E. (1979). *Pol. J. Pharmacol. Pharm.* **31**, 65.
 GLINKA, R., SZADOWSKA, A. & PAKULSKA, W. (1982). *Pol. J. Pharmacol. Pharm.* **34**, 275–281.
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1987). **C43**, 2164–2165

Crystal Studies of Heterocyclic Compounds Containing One Oxygen and Two Nitrogen Atoms. II. N,N'-Ditosyltetrahydrobenzo[*b,h*][1,4,7]oxadiazonine

BY A. STĘPIEŃ, E. WAJSMAN AND M. J. GRABOWSKI

Department of Crystallography, Institute of Chemistry, University of Łódź, Nowotki 18, 91-416 Łódź, Poland

R. GLINKA

Institute of Chemistry and Technology of Drugs, School of Medicine, Narutowicza 120a, 90-145 Łódź, Poland

AND M. PERRIN

Laboratoire de Minéralogie-Cristallographie associé au CNRS (UA 805), Université Claude Bernard Lyon I, 43 boulevard du 11 novembre 1918, 69622 Villeurbanne CEDEX, France

(Received 5 September 1985; accepted 29 June 1987)

Abstract. C₂₈H₂₆N₂O₅S₂, *M_r* = 534.7, orthorhombic, *Pbcn*, *a* = 21.602 (4), *b* = 13.325 (2), *c* = 9.100 (1) Å, *V* = 2619.4 (9) Å³, *Z* = 4, *D_x* = 1.355 g cm⁻³, *μ* = 20.7 cm⁻¹, 1092 independent reflections with *I* > 3σ(*I*) were measured on a single-crystal diffractometer at room temperature [*λ*(Cu Kα) = 1.54178 Å]. *F*(000) = 1120; final *R* = 0.0485. The molecule is in a special position and the nine-membered ring is in a twist-crown conformation. The tosyl substituents are axial; centres of the aromatic rings in the tosyl substituents are 3.44 Å apart. There are no unusual bond lengths or angles.

Introduction. Within the group of nine-membered heterocyclic systems with two nitrogens and one oxygen and two fused aromatic rings, only derivatives of tetrahydrobenzo[*b,h*][1,4,7]oxadiazonine are known (Glinka, 1980). In particular, 3,4,5-trimethoxybenzoyl derivatives of this system show a neuroleptic activity (Glinka, Szadowska & Pakulska, 1982). It seems interesting to study the relationship between the pharmacological activity and the conformation of this system. Among compounds with heterocyclic systems of this type, nine-membered systems are the least known. For non-fused nine-membered rings, X-ray (Hamor, Paul, Robertson & Sim, 1963; Quin, Leimert, Middelmas, Miller & McPhail, 1979) and dynamic NMR (Anet & Vavari, 1977) studies show preference for existence in the boat-chair form. Dynamic NMR

studies (Ollis & Stoddart, 1976) indicate that the interconversion energy of a system containing only one heteroatom and fused with two aromatic rings is lower than the non-fused compound. Only in alkaloids (Ferris, 1971; Uprety, 1975) have similar systems been subjected to X-ray studies so far. A study of the structure of cyclooctane (Hendrickson, 1967) shows that the preferred form is twist-crown, which has the highest symmetry. In the ¹H NMR spectra of tetrahydrobenzo[*b,h*][1,4,7]oxadiazonine we observed a single signal for the methylene groups in the central ring (highest symmetry for this compound). We now report the X-ray crystal structure of the title compound.

Experimental. Light-yellow needles grown from ethanol at room temperature, crystal diameter 0.1 mm; CAD-4 diffractometer using *θ*-2*θ* scan technique; lattice parameters refined using 15 reflections with *θ*_{max} = 48.7°; total of 1654 independent reflections measured to (sin*θ*)/*λ* = 0.63 Å⁻¹, 2*θ*_{max} = 154°, maximum values of *h*, *k*, *l* were 23, 14, 9 respectively, no absorption correction was applied, standard reflection 411; solution by direct methods using *SHELX76* (Sheldrick, 1976), all non-H atoms found on *E* map based on 180 reflections with *E* > 1.2; refinement by full-matrix least squares, *F* magnitudes, 220 parameters; a difference synthesis revealed positions of all H atoms which were refined isotropically; final *R* = 0.0485 for 1092 reflections with *I* > 3σ(*I*); max.

shift/e.s.d. = 0.38; max. peak on final difference map was $0.2 \text{ e } \text{Å}^{-3}$. Atomic scattering factors those of *SHELX*.

Table 1. Final fractional coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\times 10^4$) with e.s.d.'s in parentheses

$$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$$

	x	y	z	$U_{\text{eq}}(\text{Å}^2)$
C1	4704 (2)	7954 (4)	1357 (6)	680 (36)
C2	4379 (2)	7062 (4)	1478 (5)	558 (31)
C3	4083 (3)	6652 (6)	266 (6)	811 (43)
C4	4104 (4)	7177 (7)	-1045 (8)	1152 (67)
C5	4408 (4)	8072 (7)	-1158 (10)	1233 (75)
C6	4720 (4)	8464 (6)	35 (9)	1056 (60)
C7	4699 (3)	5572 (5)	2940 (7)	684 (40)
C11	3129 (2)	6252 (4)	3263 (5)	583 (31)
C12	2766 (2)	6802 (4)	2315 (7)	742 (33)
C13	2233 (3)	6375 (5)	1743 (7)	826 (44)
C14	2071 (2)	5406 (4)	2066 (6)	742 (39)
C15	2432 (3)	4873 (5)	3031 (7)	912 (46)
C16	2965 (3)	5293 (4)	3624 (7)	873 (46)
C141	1492 (4)	4953 (8)	1410 (11)	1042 (57)
S1	3811 (1)	6778 (1)	3988 (1)	646 (8)
O1	5000	8437 (4)	2500	808 (40)
O2	3734 (2)	7841 (3)	3994 (4)	807 (25)
O3	3956 (2)	6249 (3)	5311 (4)	863 (27)
N1	4373 (2)	6536 (3)	2830 (4)	537 (24)

Table 2. Selected bond lengths (Å), angles (°) and torsion angles (°)

O1—C1	1.380 (6)	N1—S1	1.639 (4)
C1—C2	1.384 (7)	S1—O2	1.426 (4)
C2—N1	1.417 (6)	S1—O3	1.430 (4)
N1—C7	1.467 (7)	S1—C11	1.761 (5)
C7—C7 ⁱ	1.528 (12)	C11—C12	1.376 (7)
C2—C3	1.387 (7)	C12—C13	1.386 (8)
C3—C4	1.383 (10)	C13—C14	1.370 (8)
C4—C5	1.366 (13)	C14—C15	1.372 (9)
C5—C6	1.379 (12)	C15—C16	1.388 (8)
C6—C1	1.382 (10)	C16—C11	1.367 (8)
		C14—C141	1.511 (10)
C1—O1—C1 ⁱ	124.4 (6)	N1—S1—O2	106.6 (2)
O1—C1—C2	125.1 (5)	N1—S1—O3	106.4 (2)
O1—C1—C6	114.5 (5)	O2—S1—O3	120.8 (2)
C2—C1—C6	120.2 (5)	O2—S1—C11	107.4 (2)
C1—C2—C3	120.6 (5)	O3—S1—C11	107.6 (2)
C2—C3—C4	118.1 (6)	N1—S1—C11	107.5 (2)
C3—C4—C5	121.5 (7)	S1—C11—C12	120.0 (4)
C4—C5—C6	120.4 (8)	S1—C11—C16	119.9 (4)
C5—C6—C1	119.2 (7)	C12—C11—C16	120.1 (5)
C3—C2—N1	119.5 (5)	C11—C12—C13	119.3 (5)
C1—C2—N1	119.9 (4)	C12—C13—C14	121.2 (6)
C2—N1—S1	117.8 (3)	C13—C14—C15	118.6 (5)
C2—N1—C7	119.3 (4)	C14—C15—C16	120.8 (6)
C7—N1—S1	118.9 (3)	C15—C16—C11	119.9 (6)
N1—C7—C7 ⁱ	109.4 (3)	C13—C14—C141	120.2 (6)
		C15—C14—C141	121.1 (6)
C1 ⁱ —O1—C1—C2	35.4 (6)	C2—N1—C7—C7 ⁱ	37.2 (7)
O1—C1—C2—N1	-4.9 (7)	N1—C7—C7 ⁱ —N1 ⁱ	39.0 (7)
C1—C2—N1—C7	-110.9 (6)		

Symmetry code (i) $1-x, y, \frac{1}{2}-z$.

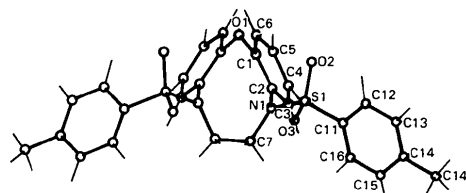


Fig. 1. Structure of the molecule with the atom-numbering scheme.

Discussion. The final positional parameters are listed in Table 1, bond lengths, bond angles and torsion angles in Table 2.*

The molecule of the title compound lies in a special position: a twofold axis passes through atom O1 and the centre of the C7—C7ⁱ bond [the numbering of the atoms is given in Fig. 1; symmetry code: (i) $1-x, y, \frac{1}{2}-z$]. The nine-membered heterocyclic ring is in a twist-crown conformation. The mean torsion angle is $\alpha = 46.2^\circ$. The fused benzene rings are planar, the average distance of the C atoms from the plane is 0.02 Å . The value of the dihedral angle formed by two benzene-ring planes is 120.6° . The N1 atom lies in the benzene-ring plane (the distance from the plane is 0.025 Å). The C1—O1 distance [$1.380(6) \text{ Å}$] and C1—O1—C1ⁱ angle [$124.4(6)^\circ$] are typical.

The tosyl substituents are axial. The distance between the centres of their rings is 3.44 Å . Both this distance and the coloured crystals suggest an intermolecular charge-transfer interaction.

The support of this work by grant M.R.I.9 from the Polish Academy of Sciences is gratefully acknowledged.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44145 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- ANET, A. & VAVARI, J. (1977). *J. Am. Chem. Soc.* **99**, 6496.
 FERRIS, J. (1971). *J. Am. Chem. Soc.* **93**, 2963.
 GLINKA, R. (1980). *Pol. J. Chem.* **54**, 1275.
 GLINKA, R., SZADOWSKA, A. & PAKULSKA, W. (1982). *Pol. J. Pharmacol. Pharm.* **34**, 275–281.
 HAMOR, A., PAUL, J., ROBERTSON, J. & SIM, G. (1963). *J. Am. Chem. Soc.* **85**, 5502.
 HENDRICKSON, B. (1967). *J. Am. Chem. Soc.* **89**, 7047.
 OLLIS, D. & STODDART, J. (1976). *J. Chem. Soc. Perkin Trans. 1*, p. 926.
 QUIN, L., LEIMERT, J., MIDDELMAS, E., MILLER, R. & MCPHAIL, T. (1979). *J. Org. Chem.* **44**, 3499–3502.
 SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
 UPRETY, H. (1975). *Tetrahedron Lett.* **14**, 1201–1205.