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Crystal Studies of Heterocyclic Compounds Containing One Oxygen and Two Nitrogen Atoms. VI. *N*,*N*′-Bis(methylsulfonyl)perhydro-1,4,7-oxadiazecine. VII. *N*,*N*′-Bis(phenylsulfonyl)perhydro-1,5,7-oxadiazecine

By A. Stępień, A. M. Brzozowski and M. J. Grabowski

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

K. Krakowiak

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

and C. Bavoux

Laboratoire de Minéralogie–Cristallographie associé au CNRS (*UA* 805), *Université Claude Bernard Lyon* I,
43 *Boulevard du* 11 *Novembre* 1918, 69622 *Villeurbanne CEDEX, France*

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Abstract. (VI) $C_9H_{20}N_2O_5S_2$, $M_r = 300·4$, orthorhombic, *Pbca*, $a = 9·866\,(2)$, $b = 14·838\,(4)$, $c = 18·865\,(5)$ Å, $V = 2762\,(1)$ Å^3, $Z = 8$, $D_x = 1·445\,(1)$ g cm^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0·71069$ Å, $\mu = 3·45$ cm^{-1}, $F(000) = 1280$, room temperature, $R = 0·0322$ for 2428 reflections with $I > 3\sigma(I)$. The perhydrooxadiazecine ring is in a crown conformation. Both methylsulfonyl groups are equatorial. (VII) $C_{19}H_{24}N_2O_5S_2$, $M_r = 424·5$, triclinic, $P\bar{1}$, $a = 10·919\,(2)$, $b = 11·692\,(2)$, $c = 9·542\,(3)$ Å, $\alpha = 107·69\,(2)$, $\beta = 79·45\,(2)$, $\gamma = 119·06\,(1)°$, $V = 1013·5\,(5)$ Å^3, $Z = 2$, $D_x = 1·391\,(1)$ g cm^{-3}, $\lambda(\text{Cu}\,K\alpha) = 1·54178$ Å, $\mu = 25·37$ cm^{-1}, $F(000) = 448$, room temperature, $R = 0·0481$ for 2911 reflections with $I > 3\sigma(I)$. The perhydrooxadiazecine ring is in a boat–chair–boat conformation. Both phenylsulfonyl groups are axial. The benzene-ring planes form angles of 22 and 20° with the plane of the heterocycle.

Introduction. The investigation of heterocyclic systems containing two N and one O atoms was extended to perhydrooxadiazecine derivatives, substituted at 4,7 or 5,7 positions. They show neuroleptic activity (Brzezińska, Glinka & Szadowska, 1988). This paper is the first report of the structural studies of these derivatives.

Experimental. Colourless crystals of (VI) and (VII) from ethanol at room temperature. Crystal size: 0·2 × 0·2 × 0·25 (VI), 0·2 × 0·2 × 0·2 mm (VII). Diffraction data measured on a CAD-4 diffractometer using θ–2θ scan technique, graphite-monochromatized Mo $K\alpha$ (VI) and Cu $K\alpha$ (VII). Data collected to $[(\sin\theta)/\lambda]_{\max} = 0·66$ (VI) and 0·62 Å^{-1} (VII). Ranges of h,k,l: 0 to 13, 0 to 19, 0 to 24 (VI) and −13 to 13, −14 to 13, 0 to 11 (VII), respectively. Data not corrected for absorption. Lattice parameters by least-squares method using 25 reflections within the θ range 7·1–19·2 (VI) and 11–47·2° (VII). For (VI), standard reflection 714, counts variation 0·44%; for (VII), $R_{\text{int}} = 0·022$, standard reflection 213, counts variation 0·8%. Of 3801 (VI) and 3587 (VII) independent reflections 2428 (VI) and 2911 (VII) were considered observed by the criterion $I \geq 3\sigma(I)$. The structures were solved by Patterson and direct methods using *SHELX*76 (Sheldrick, 1976); the refinement was carried out by full-matrix least squares using F magnitudes, 243 (VI) and 349 (VII) parameters. All H atoms were located on a difference map. Final $R = 0·0322$ (VI) and 0·0481 (VII). For (VI), unit weights, for (VII), $wR = 0·0536$, where $w = k/[\sigma^2(F) + pF^2]$ with $k = 0·0124$ and $p = 0·3647$. Max. shift/e.s.d. = 0·09 (VI) and 0·8 (VII); the largest peak on the final difference map was 0·28 (VI) and 0·45 e Å^{-3} (VII). Atomic scattering factors from *SHELX*76.

Discussion. The final positional parameters are listed in Table 1, interatomic distances and bond angles in Table 2.* Figs. 1 and 2 show the structure of the molecule of (VI) and (VII) with the atom-numbering scheme. The geometry of the molecule was calculated using *ORFFE*3 (Busing, Martin & Levy, 1971).

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* Lists of structure factors, thermal parameters, H-atom coordinates, bonds and angles involving H atoms and torsion angles for both compounds have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51164 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final fractional coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^4$) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	U_{eq}
(VI)				
O1	1597 (2)	1527 (1)	−1248 (1)	573 (10)
C2	1240 (4)	1500 (2)	−1982 (1)	735 (19)
C3	1889 (4)	2300 (2)	−2327 (1)	664 (17)
N4	1305 (2)	3157 (1)	−2069 (1)	494 (10)
C5	1665 (2)	3448 (1)	−1345 (1)	410 (11)
C6	505 (2)	3273 (1)	825 (1)	374 (10)
N7	967 (2)	2917 (1)	−137 (1)	375 (8)
C8	320 (3)	2080 (2)	132 (1)	484 (12)
C9	1050 (3)	1214 (2)	−64 (1)	622 (16)
C10	864 (4)	918 (2)	−817 (1)	662 (16)
S1	805 (1)	3880 (0)	−2648 (0)	443 (2)
O11	356 (2)	4656 (1)	−2267 (1)	666 (11)
O12	−120 (2)	3443 (1)	−3118 (1)	713 (12)
C11	2212 (3)	4176 (3)	−3165 (2)	651 (17)
S2	1417 (1)	3637 (0)	461 (0)	405 (3)
O21	1990 (2)	4392 (1)	95 (1)	587 (10)
O22	2233 (2)	3174 (1)	971 (1)	594 (10)
C21	−58 (3)	4000 (2)	897 (2)	617 (16)
(VII)				
N1	1603 (2)	3480 (2)	6596 (2)	470 (9)
C2	1441 (3)	2527 (3)	7433 (4)	576 (13)
C3	2664 (3)	3017 (3)	8353 (4)	619 (13)
C4	4013 (4)	3133 (4)	7486 (4)	720 (16)
O5	4668 (2)	4217 (2)	6783 (2)	697 (10)
C6	5429 (3)	5506 (4)	7732 (4)	726 (16)
C7	5422 (3)	6577 (4)	7193 (5)	741 (16)
C8	3968 (3)	6310 (3)	6928 (4)	596 (13)
N9	2876 (2)	5755 (2)	8057 (2)	483 (9)
C10	1501 (3)	4695 (2)	7475 (3)	596 (10)
S1	862 (1)	2815 (1)	5001 (1)	483 (3)
O1	1162 (2)	1714 (2)	4262 (2)	627 (9)
O2	1306 (2)	3899 (2)	4329 (2)	603 (9)
C11	−957 (2)	2160 (2)	5406 (3)	498 (11)
C12	−1702 (3)	917 (3)	5741 (4)	660 (14)
C13	−3096 (4)	470 (4)	6157 (5)	814 (18)
C14	−3752 (3)	1245 (4)	6255 (4)	789 (17)
C15	−3015 (3)	2474 (4)	5922 (4)	717 (15)
C16	−1609 (3)	2953 (3)	5492 (3)	586 (13)
S2	2799 (1)	6795 (1)	9628 (1)	499 (3)
O3	1785 (2)	5991 (2)	10561 (2)	621 (9)
O4	4213 (2)	7663 (2)	10074 (2)	641 (9)
C21	2152 (2)	7783 (2)	9255 (3)	507 (10)
C22	732 (3)	7248 (3)	9065 (3)	552 (12)
C23	236 (3)	8018 (3)	8728 (3)	613 (13)
C24	1147 (4)	9311 (4)	8608 (4)	749 (17)
C25	2566 (4)	9843 (3)	8798 (5)	835 (20)
C26	3071 (3)	9086 (3)	9113 (4)	696 (16)

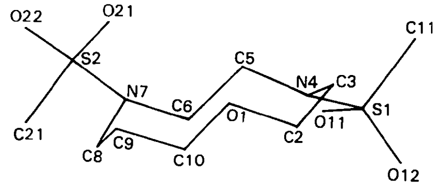

Fig. 1. The structure of the molecule of (VI) with the atom-numbering scheme.

The conformations of the oxadiazecine rings in (VI) and (VII) are different. In (VI) the ring is in a crown conformation with the mean value of the torsion angle $\langle\varphi\rangle = 108{\cdot}1°$. The ring is approximately symmetrical with respect to a pseudo-mirror plane running through atoms O1 and C6; the asymmetry parameter (Duax & Norton, 1975) $\Delta_m = 7{\cdot}44°$. In (VII) the oxadiazecine ring is in a boat–chair–boat conformation.

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

(VI)			
O1–C2	1·429 (3)	S1–N4	1·609 (2)
C2–C3	1·496 (4)	S1–O11	1·428 (2)
C3–N4	1·479 (3)	S1–O12	1·428 (2)
N4–C5	1·475 (2)	S1–C11	1·752 (3)
C5–C6	1·529 (3)	S2–N7	1·617 (2)
C6–N7	1·473 (2)	S2–O21	1·432 (2)
N7–C8	1·486 (2)	S2–O22	1·429 (2)
C8–C9	1·518 (3)	S2–C21	1·756 (3)
C9–C10	1·498 (4)		
C10–O1	1·415 (3)		
C2–O1–C10	114·4 (2)	N4–S1–O11	106·9 (1)
O1–C2–C3	107·1 (2)	N4–S1–O12	108·4 (1)
C2–C3–N4	111·9 (2)	N4–S1–C11	107·6 (1)
C3–N4–C5	117·5 (2)	C11–S1–O11	108·9 (2)
N4–C5–C6	111·4 (2)	C11–S1–O12	105·9 (1)
C5–C6–N7	113·2 (2)	O11–S1–O12	118·8 (1)
C6–N7–C8	117·9 (2)	N7–S2–O21	106·8 (1)
N7–C8–C9	114·9 (2)	N7–S2–O22	107·9 (1)
C8–C9–C10	114·9 (2)	N7–S2–C21	107·5 (1)
C9–C10–O1	107·2 (2)	C21–S2–O21	108·3 (1)
S1–N4–C3	118·0 (1)	C21–S2–O22	107·4 (1)
S1–N4–C5	120·5 (1)	O21–S2–O22	118·6 (1)
S2–N7–C6	117·5 (1)		
S2–N7–C8	115·6 (1)		
(VII)			
C10–N1	1·459 (3)	N9–C10	1·476 (3)
N1–C2	1·486 (3)	C8–N9	1·485 (3)
C2–C3	1·504 (4)	C7–C8	1·517 (4)
C3–C4	1·516 (4)	C6–C7	1·494 (5)
C4–O5	1·424 (4)	O5–C6	1·419 (4)
S1–N1	1·642 (2)	S2–N9	1·636 (2)
S1–O1	1·427 (2)	S2–O3	1·428 (2)
S1–O2	1·426 (2)	S2–O4	1·431 (2)
S1–C11	1·761 (2)	S2–C21	1·760 (2)
C11–C12	1·383 (3)	C21–C22	1·386 (3)
C12–C13	1·371 (4)	C22–C23	1·385 (4)
C13–C14	1·377 (5)	C23–C24	1·376 (4)
C14–C15	1·369 (5)	C24–C25	1·385 (4)
C15–C16	1·383 (4)	C25–C26	1·370 (4)
C16–C11	1·395 (3)	C26–C21	1·391 (3)
N1–C10–N9	110·5 (2)	C4–O5–C6	114·5 (3)
C10–N1–C2	115·6 (2)	C8–N9–C10	115·0 (2)
N1–C2–C3	114·4 (2)	C7–C8–N9	114·6 (2)
C2–C3–C4	115·0 (3)	C6–C7–C8	113·8 (2)
C3–C4–O5	114·2 (2)	O5–C6–C7	110·1 (3)
S1–N1–C2	117·0 (1)	S2–N9–C8	118·5 (2)
S1–N1–C10	115·0 (2)	S2–N9–C10	114·8 (1)
N1–S1–O1	106·8 (1)	N9–S2–O3	107·0 (1)
N1–S1–O2	106·7 (1)	N9–S2–O4	106·7 (1)
N1–S1–C11	106·0 (1)	N9–S2–C21	106·3 (1)
C11–S1–O1	108·3 (1)	C21–S2–O3	108·0 (1)
C11–S1–O2	108·8 (1)	C21–S2–O4	108·1 (1)
O1–S1–O2	119·4 (1)	O3–S2–O4	120·0 (1)
S1–C11–C12	120·0 (2)	S2–C21–C22	119·9 (2)
S1–C11–C16	119·1 (2)	S2–C21–C26	119·9 (2)
C11–C12–C13	119·0 (3)	C21–C22–C23	119·5 (2)
C12–C13–C14	120·9 (3)	C22–C23–C24	120·1 (3)
C13–C14–C15	120·0 (3)	C23–C24–C25	120·3 (3)
C14–C15–C16	120·6 (3)	C24–C25–C26	120·2 (3)
C15–C16–C11	118·7 (3)	C25–C26–C21	119·7 (3)
C16–C11–C12	120·7 (2)	C26–C21–C22	120·2 (2)

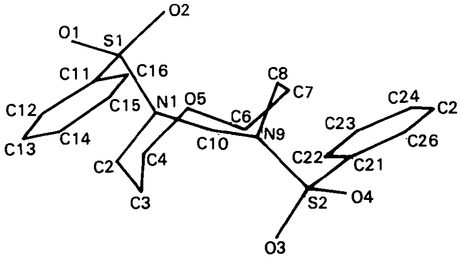

Fig. 2. The structure of the molecule of (VII) with the atom-numbering scheme.

It is approximately symmetrical with respect to a pseudo-twofold axis running through atoms C2 and C7; $\Delta_2 = 11{\cdot}0°$.

Both N atoms in (VI) and (VII) have sp^3 hybridization. In (VI), both methylsulfonyl groups are equatorial; in (VII), on the contrary, both phenylsulfonyl groups are axial.

In (VI) the conformations of the O11, O12, C11 and O21, O22, C21 atoms with respect to C3, N4, C5 and C6, N7, C8, respectively, are staggered. The weighted least-squares plane calculated for the heterocyclic ring atoms is nearly parallel to the (100) plane, the angle formed by the normal to the best plane and the X axis being 13·6°. The planes of the heterocyclic rings of all the molecules in the crystal are nearly parallel. In (VII) the planes of the two benzene rings form an angle of 23·1 (3)°. The deviations of the S atoms from the benzene-ring planes are 0·13 Å for S1 and 0·04 Å for S2. The angles formed by the plane through the oxadiazecine ring with the planes of the benzene rings attached to S1 and S2 are 22·2 (1) and 19·9 (1)°, respectively.

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Crystal Studies of Heterocyclic Compounds Containing One Oxygen and Two Nitrogen Atoms. VIII. *N,N'*-Ditosyl-7,8,9,14-tetrahydro-2*H*-dibenz[*c,h*][1,5,7]oxadiazecine

By A. Stępień, Tomasz A. Olszak 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 120*a*, 90-145 *Łódź, Poland*

and C. Bavoux

Laboratoire de Minéralogie–Cristallographie associé au CNRS (*UA* 805), *Université Claude Bernard Lyon* I, 43 *Boulevard du* 11 *Novembre* 1918, 69622 *Villeurbanne CEDEX, France*

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Abstract. $C_{29}H_{28}N_2O_5S_2$, $M_r = 548{\cdot}7$, tetragonal, $P4_12_12$ or $P4_32_12$, $a = 10{\cdot}229$ (2), $c = 26{\cdot}047$ (3) Å, $V = 2725$ (1) Å^3, $Z = 4$, $D_x = 1{\cdot}337$ (1) g cm^{-3}, $\lambda(\text{Cu }K\alpha) = 1{\cdot}54178$ Å, $\mu = 20{\cdot}01$ cm^{-1}, $F(000) = 1152$, room temperature, $R = 0{\cdot}0329$ for 1436 reflections with $I > 3\sigma(I)$. The molecule lies on a twofold axis. The oxadiazecine ring is in a chair conformation, and the tosyl substituents are axial. The two fused benzene rings are nearly parallel.

Introduction. The present paper is a continuation of the study of the relationship between the biological activity and the structure of heterocyclic compounds containing two N and one O atoms in a ring and, at the same time, the first study of a compound having two aromatic rings fused to this ten-membered heterocyclic ring. The title compound was obtained by condensation of *N,N'*-[oxybis(methylenedi-*o*-phenylene)]di-*p*-toluenesulfonamide with methylene bromide (Glinka & Walczyński, 1986). The structure was confirmed by elemental, IR, ^{1}H NMR and mass spectrometry analyses. The NMR spectrum displayed only one signal for the methylene group. The compound shows less neuroleptic activity than the nine-membered analogue, toxicity being much the same (Glinka, 1987).

Experimental. Colourless dipyramidal crystals were prepared by repeated recrystallization from ethanol at room temperature; crystal size 0·1 × 0·2 × 0·3 mm. Diffraction data measured on a CAD-4 diffractometer

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