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Crystal Studies of Heterocyclic Compounds Containing One Oxygen and Two Nitrogen Atoms. I. *N,N'*-Dibenzoylperhydro-1,4,5-oxadiazepine

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Abstract. C₁₈H₁₈N₂O₃, $M_r = 310.4$, monoclinic, $P2_1$, $a = 13.000$ (4), $b = 6.271$ (2), $c = 10.240$ (3) Å, $\beta = 111.29$ (2)°, $V = 777.8$ (6) Å³, $Z = 2$, $D_x = 1.325$ g cm⁻³, $\mu = 6.56$ cm⁻¹. Diffractometer data collected at room temperature [$\lambda(\text{Cu K}\alpha) = 1.54178$ Å] consisted of 1651 independent reflections with $I > 3\sigma(I)$. $F(000) = 328$; final $R = 0.0435$. The oxadiazepine ring is in the intermediate state between the chair and twist conformations. The benzoyl substituents are in equatorial configurations. There are no unusual bond lengths or angles.

Introduction. With the intention of searching for new substances with better therapeutic properties a series of new heterocyclic compounds containing five and more members and among them one O and two N atoms in the ring were obtained. The investigation of some of these compounds showed their neuroleptic and antiparasitic activity (Glinka, Kamińska, Kotelko & Szadowska, 1977; Glinka, Kotelko, Mikołajewska & Mikiciuk-

Olasik, 1979; Glinka, Grzywacz, Kotelko, Majchrzak, Malinowski, Mikołajewska, Mikiciuk-Olasik & Szkudlinski, 1980; Glinka, Szadowska & Pakulska, 1982). Some of the derivatives are under examination at the National Cancer Institute, Bethesda, Maryland, USA.

It is the aim of our X-ray structure investigation to find the three-dimensional structure of these compounds and to try to elucidate the structural dependence of their biological activity. The title compound has been investigated as the first of the series. It has been obtained by condensation of 2,2'-dichlorodiethyl ether with dibenzoylhydrazine. The formula was confirmed on the basis of IR, NMR and MS studies. The NMR spectrum of the compound seems to suggest that there are rotating conformers in solution.

Experimental. Colourless crystals grown from ethanol at room temperature, $\mu_r = 0.13$; CAD-4 diffractometer, using θ - 2θ scan technique; lattice parameters by least squares using 25 reflections with $\theta_{\text{max}} = 72.1^\circ$;

total of 1776 unique reflections measured to $(\sin\theta)/\lambda = 0.63 \text{ \AA}^{-1}$, 1651 reflections with $I > 3\sigma(I)$, data not corrected for absorption; ranges of h, k, l were 0 to 15, 0 to 7, -12 to 12 respectively, standard reflection $13\bar{1}$, mean variation 0.24%; solution by direct methods using *SHELX76* (Sheldrick, 1976), all non-H atoms found on *E* map; after initial anisotropic refinement difference map revealed positions of all H atoms at $R = 0.1303$, refinement by full-matrix least squares (F magnitudes, 279 parameters) to final $R = 0.0435$, $wR = 0.0463$ with $w = 19.3746/[\sigma^2(F) + 0.000157F^2]$; max. shift/e.s.d. = 0.43; largest peak on final difference map was 0.20 e \AA^{-3} . Atomic scattering factors those of *SHELX*.

Discussion. The final positional parameters are listed in Table 1 and bond lengths, valence angles and selected torsion angles in Table 2.* The molecules of the title compound are in a general position (the numbering of the atoms is shown in Fig. 1). In the crystal, the oxadiazepine ring is in the intermediate state between chair and twist conformations. The asymmetry coefficients are $\Delta C_2 = 10.3^\circ$ (the twofold axis passes through the C6 atom and the middle of the C2-C3 distance) and $\Delta C_m = 18.1^\circ$ (the mirror plane passes through the C2 atom and the middle of the N5-C6 distance). This result seems to be in accordance with the conclusion based on the NMR spectrum.

Both benzoyl substituents are in equatorial configurations. The phenyl rings are planar (max. deviation is 0.01 Å) and form an angle of 60.3°. The O atoms do not lie in the phenyl planes. The angles between the C=O bonds and the planes of the phenyl rings are 42.8 and 57.5°. The molecules are linked by van der Waals forces only.

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* 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 44144 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

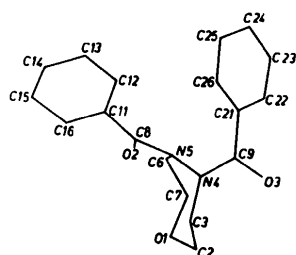


Fig. 1. Structure of the molecule with the atom-numbering scheme.

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

$$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta).$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
N4	1068 (1)	679	8371 (2)	448 (8)
N5	1547 (1)	-280 (4)	7499 (2)	391 (7)
O1	-776 (1)	-496 (4)	5898 (2)	495 (8)
C7	-192 (2)	-2362 (5)	6536 (2)	469 (10)
C2	-896 (2)	982 (6)	6904 (3)	540 (11)
C3	157 (2)	2154 (5)	7685 (2)	503 (11)
C6	1029 (2)	-2246 (5)	6779 (2)	443 (10)
C12	3328 (2)	-2218 (5)	6636 (2)	502 (11)
C13	3880 (2)	-3095 (6)	5826 (3)	622 (14)
C14	3939 (2)	-1978 (7)	4689 (3)	708 (17)
C15	3484 (2)	31 (7)	4375 (3)	690 (15)
C16	2962 (2)	965 (6)	5213 (3)	528 (11)
C11	2879 (1)	-185 (5)	6328 (2)	410 (9)
C8	2334 (2)	885 (5)	7215 (2)	407 (9)
O2	2595 (2)	2677 (4)	7677 (2)	608 (10)
C22	2221 (3)	-3287 (6)	10569 (3)	592 (13)
C23	3081 (3)	-4720 (7)	11108 (3)	756 (19)
C24	4144 (3)	-4095 (8)	11341 (3)	763 (19)
C25	4368 (3)	-2009 (8)	11044 (3)	732 (20)
C26	3507 (2)	-564 (7)	10506 (3)	607 (14)
C21	2435 (2)	-1212 (5)	10274 (2)	466 (10)
C9	1475 (2)	299 (5)	9760 (2)	489 (10)
O3	1049 (2)	1072 (6)	10527 (2)	899 (15)

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

N5-C8	1.372 (3)	N4-C9	1.346 (3)
C8-O2	1.219 (3)	C9-O3	1.214 (3)
C8-C11	1.498 (3)	C9-C21	1.502 (3)
C11-C12	1.390 (3)	C21-C22	1.387 (4)
C12-C13	1.391 (3)	C22-C23	1.383 (4)
C13-C14	1.384 (5)	C23-C24	1.372 (6)
C14-C15	1.379 (6)	C24-C25	1.397 (7)
C15-C16	1.400 (4)	C25-C26	1.389 (4)
C11-C16	1.387 (3)	C21-C26	1.387 (4)
O1-C2	1.436 (3)	O1-C7	1.418 (3)
C2-C3	1.503 (4)	C6-C7	1.516 (3)
C3-N4	1.465 (3)	N5-C6	1.469 (3)
N4-N5	1.397 (2)		
C8-N5-N4	116.5 (2)	C9-N4-N5	120.3 (2)
C8-N5-C6	125.6 (2)	C9-N4-C3	123.9 (2)
N5-C8-O2	122.2 (2)	N4-C9-O3	121.1 (2)
N5-C8-C11	116.3 (2)	N4-C9-C21	116.1 (2)
O2-C8-C11	121.5 (2)	O3-C9-C21	122.8 (2)
C8-C11-C12	121.7 (2)	C9-C21-C22	117.5 (2)
C8-C11-C16	117.5 (2)	C9-C21-C26	122.1 (2)
C12-C11-C16	120.8 (2)	C22-C21-C26	120.4 (2)
C11-C12-C13	119.5 (2)	C21-C22-C23	120.0 (3)
C12-C13-C14	119.9 (3)	C22-C23-C24	120.0 (4)
C13-C14-C15	120.5 (3)	C23-C24-C25	120.4 (3)
C14-C15-C16	120.1 (3)	C24-C25-C26	119.7 (3)
C11-C16-C15	119.1 (3)	C21-C26-C25	119.4 (3)
O1-C2-C3	112.5 (2)	O1-C7-C6	112.9 (2)
C2-C3-N4	111.6 (2)	N5-C6-C7	112.7 (2)
C3-N4-N5	115.8 (2)	N4-N5-C6	116.9 (2)
C2-O1-C7	112.4 (2)		
C7-O1-C2-C3	75.1 (3)	C3-N4-N5-C6	-86.3 (3)
C6-C7-O1-C2	-95.6 (2)	C2-C3-N4-N5	77.6 (2)
N5-C6-C7-O1	50.6 (2)	O1-C2-C3-N4	-55.8 (3)
N4-N5-C6-C7	27.3 (3)		

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

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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.