Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

4-(2-Benzylamino-1-oxoethyl)-1,2,3,4-tetrahydro-6,7-dimethylquinoxalin-2-one

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Key indicators

Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.008 Å
R factor = 0.088
wR factor = 0.273
Data-to-parameter ratio = 17.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 12 March 2002
Accepted 18 March 2002
Online 28 March 2002

All interatomic distances in the title compound, $C_{19}H_{21}N_3O_2$, are normal. The heterocycle of the quinoxalinone system exhibits a half-chair conformation. The value of the total puckering amplitude Q_T is 0.391 (5) Å. The benzylaminomethyl part of the side branch is close to planar. This weighted-least-squares plane makes a dihedral angle of 67.45 (14)° with the quinoxalinone plane. In the structure, there are C—H···N and C—H···O intramolecular hydrogen bonds. The molecules are held together by N—H···O intramolecular hydrogen bonds, resulting in a dimeric structure. The dimers are linked by weak C—H···O intermolecular hydrogen bonds, resulting in a three-dimensional layered hydrogen-bonded network.

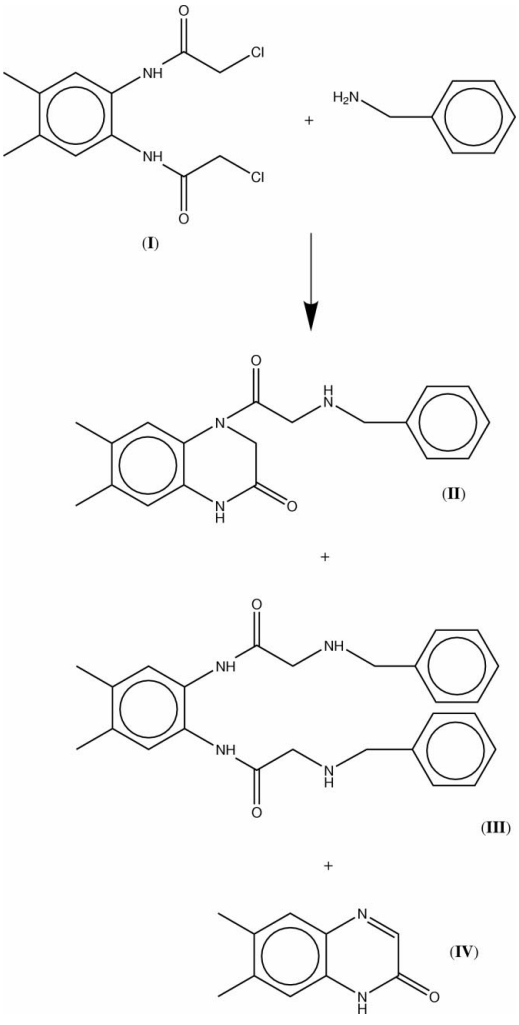
Comment

Great efforts have been made in recent years in the synthesis of new multimembered heterocyclic systems. Upon introduction of pharmacophoric substituents for a desired activity into those systems, it is expected that the resulting derivatives will exhibit numerous favourable properties, such as analeptic activity, possible anticancer and anti-HIV activities, and will form potential radiopharmaceuticals (Bartczak *et al.*, 1995). Fused ten-membered heterocycles with pendant arms are expected to possess catalytic properties comparable with the activity of enzymes, as observed by Hanson & Jakubke (1973) and Ivanov (1975). The possibility of linking metal ions to form stable complexes permits the utilization of heterocyclic systems with pendant arms for modelling cation receptors in proteins, as reported by Ovchinnikov (1974) and Müller (1974). Many similar systems are also useful in environmental protection, in medicinal therapies using complexones, and in the treatment of poisoning with heavy and radioactive metals, as reported by Bandot & Jacque (1977) and Num *et al.* (1983).

Within this area of research, a series of derivatives has been obtained (Mikiciuk-Olasik, 1990; Mikiciuk-Olasik *et al.*, 1993, 1994; Szadowska *et al.*, 1991). The preliminary results on the crystal structures of derivatives of 2,3,4,5,6,7-hexahydro-1*H*-1,4,7-benzotriazone-2,5-dione have been published (Mikiciuk–Olasik *et al.*, 1993), but only two complete structures of these compounds have been previously determined, namely *N,N′*-bis[2-(4-ethoxyphenyl)amino]-4,5-dimethyl-*o*-phenylenediamine (Kruszynski *et al.*, 2001) and 4-[2-acetyl-2-(4-ethoxyphenyl)amino-1-oxoethyl]-1,2,3,4-tetrahydro-2-quinoxalinone, hereafter (II*A*) (Kruszynski *et al.*, 2002).

A perspective view of the title compound, (II), together with the atom-numbering scheme, is shown in Fig. 1. All interatomic distances can be considered normal. The molecular geometry of the main skeleton of (II) is similar to that of (II*A*). The weighted r.m.s. deviation for all atoms of the 4-(2-

amino-1-oxoethyl)-1,2,3,4-tetrahydroquinoxalin-2-one part in (II) and in inverted molecule (II*A*) is 0.099 (4) Å. The superposition of the two molecules, (II) and (II*A*), is shown in Fig. 2. Conformational analysis of the puckered heteroatom



ring of the quinoxalinone system shows a half-chair conformation, with a local pseudo-twofold axis through the midpoints of the N1—C8 and N2—C6 bonds (Duax & Norton, 1975; Duax *et al.*, 1976). The value of the asymmetry parameter is ΔC_2(N1—C8) = 7.60 (2). The value of the total puckering amplitude (Cremer & Pople, 1975) Q_T = 0.391 (5) Å, which is close to the value, Q_T = 0.435 (3) Å, in (II*A*). In the case of the weighted-least-squares plane calculated through all the quinoxalinone atoms, the maximum deviation of 0.345 (4) Å occurs for atom C8. Atoms O1, C9 and C10 deviate by 0.123 (6), 0.228 (8) and 0.059 (7) Å, respectively, from the above plane. The benzylaminomethyl part of the side branch is close to planarity. The maximum deviation of 0.131 (4) Å occurs for atom N12. This weighted-least-squares plane makes a dihedral angle of 67.45 (14)° with the quinoxalinone plane. The side-branch conformation (best described by the torsion angles, for details see Table 1) is distinctly different from that of (II*A*). This may be explained

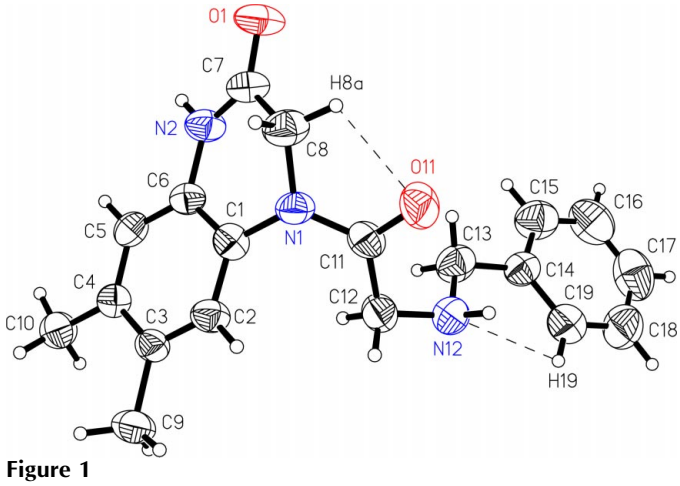


Figure 1
The molecular structure of the title compound, (II). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are indicated by dashed lines.

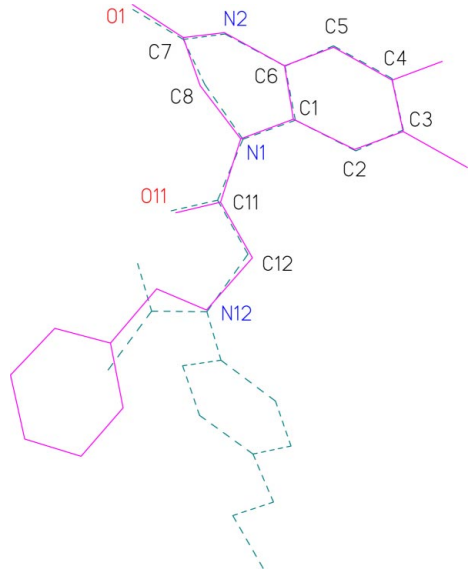


Figure 2
Superposition of (II) and inverted (II*A*). Molecule (II*A*) is indicated by dashed lines. H atoms have been omitted for clarity. Superimposed atoms are labelled.

by additional intramolecular C—H···N hydrogen bonds in (II) (Table 2 and Fig. 1). This interaction forces the phenyl ring toward atom N12. In (II*A*), this atom is acetylated, and there exists only a C—H···O intramolecular hydrogen bond. The molecules of (II) are held together by N—H···O intermolecular hydrogen bonds (Jeffrey & Saenger, 1994), resulting in a dimeric structure. The dimers are linked by short intermolecular C—H···O interactions (Table 2 and Fig. 3), which can be considered as weak intermolecular hydrogen bonds (Taylor & Kennard, 1982; Desiraju & Steiner, 1999). In this way, a three-dimensional layered hydrogen-bonded network is created. There are no unusual intermolecular short contacts, apart from the hydrogen bonds described in Table 2.

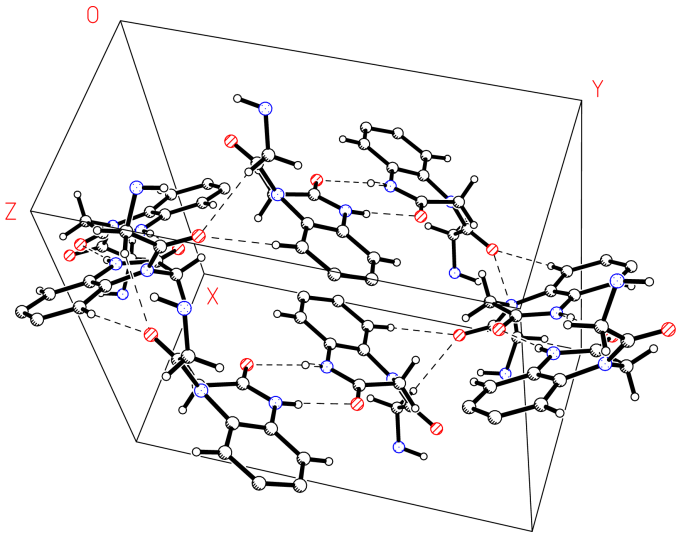


Figure 3
Part of the molecular packing of (II), showing the three-dimensional layered net structure created by intermolecular hydrogen bonds. Methyl and benzyl groups have been omitted for clarity. Hydrogen bonds are indicated by dashed lines.

Experimental

The title compound, (II), was prepared according to the method depicted in the Scheme. To a stirred solution of chloroacetyl chloride (9.04 g, 0.08 mol) in dry chloroform (300 ml) with anhydrous Na_2CO_3 (13.4 g, 0.16 mol) 4,5-dimethyl-*o*-phenylenediamine (3.5 g, 0.032 mol) was added in small portions at 277 K over a period of 2 h. On the next day, 20 ml of methyl alcohol was added. The reaction mixture was stirred, then filtered. The precipitate was dried, washed with water and filtered. The residue was recrystallized from ethyl alcohol. 6.3 g of the *N,N′*-bis(chloroacetyl)-4,5-dimethyl-*o*-phenylenediamine, (I), was obtained (74% yield), m.p. 472 K. Elemental analysis (calculated/found): C 49.84/50.16, H 4.88/5.259, N 9.69/9.56%. ^{1}H NMR (in DMSO/TMS, chemical shifts in p.p.m.): δ 2.35 (*s*, 6H, $2CH_3$), 4.45 (*s*, 4H, $2CH_2$), 7.45 (*s*, 2H, H_{ar}), 9.75 (*s*, 2H, 2NHCO). 3.0 g (0.01 mol) of (I) was dissolved in 500 ml of anhydrous ethanol with fine powdered sodium carbonate (6.00 g, 0.07 mol). Then 1.07 g (0.01 mol) of benzylamine was added. The reaction mixture was heated at boiling point under reflux for 10 h (Mikiciuk-Olasik *et al.*, 1994). The solvent was distilled off and the dry residue was recrystallized from ethanol. Compound (II), and small amounts of (III) and (IV) were isolated by fractional crystallization of the solid residue. Data for (II): yield 17%, m.p. 431.5 K. Elemental analysis (calculated/found): C 70.56/70.38, H 6.54/6.64, N 12.99/12.81%. ^{1}H NMR (in DMSO/TMS, chemical shifts in p.p.m.): 2.2 (*s*, 6H, $2CH_3$Ph), 3.4 (*broad*, 1H, NH_2CH_2), 3.6 (*s*, 6H, NCH_2CON), 3.73 (*s*, 2H, CH_2CO), 4.4 (*s*, 2H, NCH_2Ph), 7.0 (*m*, 7H, H_{ar}), 9.85 (*broad*, 1H, NHCO).

Crystal data

$C_{19}H_{21}N_3O_2$
M_r = 323.39
Monoclinic, $P2_1/c$
a = 15.523 (3) Å
b = 14.521 (3) Å
c = 7.520 (2) Å
β = 94.45 (3)°
V = 1690.0 (7) Å^3
Z = 4
D_x = 1.271 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 99 reflections
θ = 4–22°
μ = 0.08 mm^{-1}
T = 291 (1) K
Plate, colourless
0.35 × 0.11 × 0.07 mm

Data collection

Kuma KM-4 diffractometer
ω–2θ scans
Absorption correction: numerical (*X-RED*; Stoe & Cie, 1999)
T_{min} = 0.942, T_{max} = 0.997
4189 measured reflections
3892 independent reflections
1256 reflections with $I > 2\sigma(I)$
R_{int} = 0.059
θ_{max} = 27.6°
$h = -20 \rightarrow 20$
$k = -18 \rightarrow 0$
$l = -9 \rightarrow 0$
2 standard reflections every 100 reflections
intensity decay: 7.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.088
$wR(F^2)$ = 0.273
S = 0.97
3892 reflections
221 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1058P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Table 1
Selected torsion angles (°).

N1—C1—C6—N2	−1.9 (7)	C8—N1—C11—C12	−166.0 (5)
C1—C6—N2—C7	−19.1 (7)	C1—N1—C11—C12	4.9 (8)
C6—N2—C7—C8	5.5 (8)	N1—C11—C12—N12	145.6 (5)
N2—C7—C8—N1	26.3 (7)	C11—C12—N12—C13	−65.3 (6)
C7—C8—N1—C1	−45.7 (6)	C12—N12—C13—C14	−176.3 (4)
C8—N1—C1—C6	34.2 (7)	N12—C13—C14—C15	−169.5 (5)
C8—N1—C11—O11	12.0 (8)	N12—C13—C14—C19	12.9 (8)
C1—N1—C11—O11	−177.1 (5)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8A···O11	0.97	2.27	2.705 (7)	106
C19—H19···N12	0.93	2.51	2.857 (8)	102
N2—H2N···O1^{i}	0.85	2.07	2.913 (6)	171
C2—H2···O11^{ii}	0.93	2.39	3.255 (7)	154
C12—H12A···O11^{ii}	0.97	2.54	3.285 (7)	134

Symmetry codes: (i) $1-x, 2-y, 1-z$; (ii) $x, \frac{3}{2}-y, z-\frac{1}{2}$.

All H atoms, except those bonded to N atoms, were placed in calculated positions. The H atoms bonded to N atoms were located in a difference Fourier synthesis, calculated after four cycles of anisotropic refinement. All H atoms were treated as riding on the adjacent C atom. The methyl groups were allowed to rotate about their local threefold axis.

As the collected data were relatively weak, there are a large number of reflections with small intensities, and thus some reflections were marked as unobserved. This affects the fraction of unique reflections observed (out to θ = 27.56°), which is equal to 96%, and the weighted R factor which is equal to 0.273.

Data collection: *KM-4 Software* (Kuma, 1993); cell refinement: *KM-4 Software*; data reduction: *DATAPROC* (Gałdecki *et al.*, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1990*b*) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 1990).

This work was supported financially by statutory funds allocated by the State Committee for Scientific Research,

Warsaw, Poland, to the Institute of General and Ecological Chemistry, Technical University of Łódź.

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