

**4-Benzoyl-5-ethoxy-2-methyl-7,8-methylenedioxy-4,5-dihydro-
1H-1,3,4-benzotriazepine. CH₃OH. H₂O**

BY LÁSZLÓ PÁRKÁNYI AND GYULA ARGAY

Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1525-Budapest, P.O.B. 17, Hungary

AND JÓZSEF FETTER

Department of Organic Chemistry, Technical University, H-1521-Budapest, Hungary

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Abstract. C₁₉H₁₉N₃O₄.CH₃OH.H₂O, monoclinic, $P2_1/c$, $a=8.989$ (3), $b=11.886$ (4), $c=19.161$ (4) Å, $\beta=91.28$ (2)°, $V=2046.71$ Å³, $Z=4$, $D_m=1.302$, $D_x=1.309$ g cm⁻³, $F(000)=856$, $\mu(\text{Mo } K\alpha, \lambda=0.71069 \text{ \AA})=0.55$ cm⁻¹. The structure was solved by direct methods and Fourier techniques. An R of 0.055 was obtained for 1723 observed reflexions after least-squares refinement. The solvent molecules are linked to each other and to the title molecule by hydrogen bonding.

Introduction. Intensities were collected on a Syntex $P2_1$ four-circle automatic diffractometer with Mo $K\alpha$ radiation from a graphite monochromator. The intensity of 818 reflexions was lower than a preset limit and these were skipped rather than measured with the

lowest scanning speed (4.99° min⁻¹). 2092 reflexions were retained in the final set, 1731 of which had $I-2.5\sigma(I)>0$ and were taken as observed. The phase problem for 241 reflexions with $E\geq 1.7$ was solved with an XTL version of $MULTAN$ (Main, Woolfson & Germain, 1971). An E map computed from the solution with the best consistency revealed the positions of 22 non-H atoms ($R=0.35$). The remaining four non-H atoms of the molecule were located in a successive Fourier map and those of the solvent molecules in a difference map ($R=0.24$). H atoms [except H(N), H(O), H(W1) and H(W2)] were introduced at the beginning of the refinement with C-H distances of 1.08 Å. The C(14)···C(19) phenyl group was converted into a regular hexagon with C-C 1.395 and C-H 1.08 Å. This ring and the methyl groups of the

Table 1. Atomic parameters ($\times 10^4$) for the non-hydrogen atoms with their e.s.d.'s in parentheses

The thermal parameters are of the form: $T=\exp(-2\pi^2 \sum_i \sum_j a_i^* a_j^* h_i h_j U_{ij})$ with U in Å².

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	4066 (3)	987 (3)	567 (1)	633 (26)	958 (31)	420 (21)	-142 (20)	116 (19)	75 (22)
O(2)	5576 (3)	624 (3)	1530 (1)	497 (22)	962 (32)	555 (25)	78 (22)	72 (18)	193 (21)
O(3)	1614 (3)	2853 (3)	3314 (1)	536 (19)	420 (19)	376 (18)	-24 (15)	39 (14)	-65 (16)
O(4)	1083 (3)	-205 (3)	3951 (1)	482 (19)	523 (19)	471 (18)	126 (16)	-85 (15)	79 (17)
O(5)	-2654 (4)	2747 (3)	4195 (2)	708 (25)	913 (27)	502 (20)	-3 (20)	-10 (17)	8 (21)
O(W)	-1372 (5)	2639 (4)	524 (2)	116 (32)	492 (27)	587 (26)	75 (22)	-245 (22)	-21 (24)
N(1)	-158 (4)	2070 (3)	1927 (2)	410 (21)	582 (25)	340 (20)	65 (18)	-48 (17)	31 (18)
N(2)	-1051 (4)	1853 (3)	3087 (2)	400 (20)	476 (23)	392 (22)	88 (18)	13 (16)	80 (17)
N(3)	206 (3)	1188 (3)	3268 (2)	346 (19)	420 (21)	344 (18)	112 (17)	-1 (15)	16 (17)
C(1)	5544 (7)	705 (6)	797 (3)	576 (39)	1189 (58)	598 (41)	-236 (39)	88 (31)	94 (39)
C(2)	4180 (3)	974 (3)	1740 (1)	379 (28)	441 (33)	547 (34)	-39 (27)	54 (25)	31 (25)
C(3)	3696 (5)	1130 (4)	2397 (2)	427 (31)	569 (34)	391 (30)	2 (27)	25 (23)	50 (27)
C(4)	2238 (5)	1491 (4)	2475 (2)	405 (29)	387 (30)	360 (27)	16 (23)	-5 (22)	19 (23)
C(5)	1316 (5)	1682 (4)	1890 (2)	362 (27)	362 (29)	419 (29)	39 (23)	36 (22)	-16 (22)
C(6)	1859 (5)	1524 (4)	1223 (2)	454 (32)	546 (35)	352 (30)	0 (25)	-20 (23)	-31 (26)
C(7)	3293 (3)	1187 (3)	1166 (1)	506 (34)	430 (32)	413 (30)	-104 (25)	67 (26)	-55 (26)
C(8)	1681 (5)	1694 (4)	3195 (2)	366 (27)	499 (32)	322 (26)	57 (23)	10 (21)	0 (24)
C(9)	-1106 (4)	2228 (4)	2456 (2)	346 (23)	420 (27)	441 (25)	49 (21)	11 (19)	3 (20)
C(10)	-2444 (5)	2917 (4)	2265 (2)	447 (27)	673 (33)	541 (27)	200 (25)	7 (22)	192 (24)
C(11)	1405 (6)	3135 (5)	4035 (2)	597 (35)	646 (39)	426 (29)	-129 (26)	9 (24)	1 (29)
C(12)	861 (7)	4334 (5)	4062 (4)	912 (41)	736 (43)	813 (48)	-264 (38)	73 (35)	105 (35)
C(13)	3 (5)	272 (2)	3665 (2)	466 (28)	394 (26)	239 (21)	22 (19)	4 (19)	60 (23)
C(14)	-1534 (5)	-169 (4)	3738 (2)	442 (27)	359 (27)	317 (25)	-31 (21)	-13 (20)	-6 (22)
C(15)	-2040 (5)	-355 (4)	4406 (2)	508 (31)	489 (31)	464 (30)	6 (26)	15 (23)	-67 (26)
C(16)	-3456 (6)	-779 (5)	4501 (3)	597 (38)	691 (41)	671 (39)	46 (32)	124 (31)	-76 (32)
C(17)	-4356 (6)	-1019 (5)	3925 (3)	488 (34)	576 (38)	882 (46)	130 (34)	13 (33)	-75 (29)
C(18)	-3841 (6)	-879 (4)	3265 (3)	601 (36)	427 (33)	719 (39)	2 (29)	-202 (29)	-64 (27)
C(19)	-2433 (6)	-430 (4)	3163 (2)	596 (34)	408 (30)	425 (30)	-18 (24)	-69 (25)	7 (26)
C(20)	-4137 (6)	2457 (7)	4102 (3)	631 (41)	1439 (61)	711 (38)	-201 (40)	78 (31)	-6 (42)

molecule and methanol have been treated as rigid groups during the isotropic refinement. Ten blocked cycles of isotropic refinement with 1608 reflexions reduced R to 0.089. The reflexion set was then expanded to the 1731 observed reflexions. At this stage the missing H(N), H(W1) and H(W2) atoms were located in a difference map. In the next step the geometric constraint applied to the phenyl ring was freed (all the C-H distances in the structure were fixed at 1.08 Å) and eight blocked cycles with anisotropic thermal parameters for the non-H atoms were performed. Common isotropic temperature factors were refined for different groups of H atoms. Another difference map was then computed which revealed the position of the still missing H(O) atom. In the last four cycles eight reflexions with low Miller indices (severely affected by secondary extinction) were eliminated. The final R was 0.055 [$R_G = (\sum w\Delta^2 / \sum w|F_o|^2)^{1/2} = 0.060$] for the 1723 observed reflexions and $R_{tot} = 0.070$ for all 2084 reflexions. The weights were given by $w = k / [\sigma^2(F_o) + gF_o^2]$ where k and g refined to 0.1725 and 0.015737 respectively. A bonded H atom scattering factor was employed (Stewart, Davidson & Simpson, 1965) with complex neutral atom scattering factors for the remaining atoms (Cromer & Mann, 1968; Cromer & Liberman, 1970). The refinement was performed with *SHELX* (Sheldrick, 1975) adapted to a CDC 3300 computer. The final atomic parameters for the non-H atoms are given in Table 1, the parameters for the H atoms and the X-H distances in Table 2, bond distances and angles in Table 3.* A perspective view of the mole-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31957 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

cule and the solvent molecules (indicating the numbering of atoms) is shown in Fig. 1.

Discussion. The photolysis of *N*-(3-quinazolino)amides in primary alcohols furnishes six types of heterocyclic transformation products (Fetter, Lempert,

Table 2. *Positional parameters, isotropic temperature factors ($\times 10^3$) with their e.s.d.'s in parentheses and X-H distances for the hydrogen atoms*

All C-H distances are 1.08 Å.

	x	y	z	U (Å ²)
H(N)	-49	226	146	84 (15)
H(W1)	-183	249	6	128 (8)
H(W2)	-111	343	39	128 (8)
H(O)	-200	242	378	128 (8)
H(1A)	630	134	62	70 (13)
H(1B)	587	-10	59	70 (13)
H(3)	439	91	285	52 (8)
H(6)	117	173	77	52 (8)
H(8)	244	135	358	52 (8)
H(10A)	-251	319	173	194 (10)
H(10B)	-236	364	260	194 (10)
H(10C)	-343	244	239	194 (10)
H(11A)	57	258	424	70 (18)
H(11B)	248	290	425	70 (18)
H(12A)	172	479	380	128 (8)
H(12B)	82	461	460	128 (8)
H(12C)	-20	449	380	128 (8)
H(15)	-126	18	483	86 (12)
H(16)	-391	-89	501	128 (17)
H(17)	-535	-149	404	128 (17)
H(18)	-458	-102	282	128 (17)
H(19)	-193	-29	266	86 (12)
H(20A)	-476	274	455	194 (10)
H(20B)	-420	155	406	194 (10)
H(20C)	-460	283	363	194 (10)

H(N)—N(1)	0.97 Å
H(W1)—O(W)	1.00
H(W2)—O(W)	1.00
H(O)—O(5)	1.08

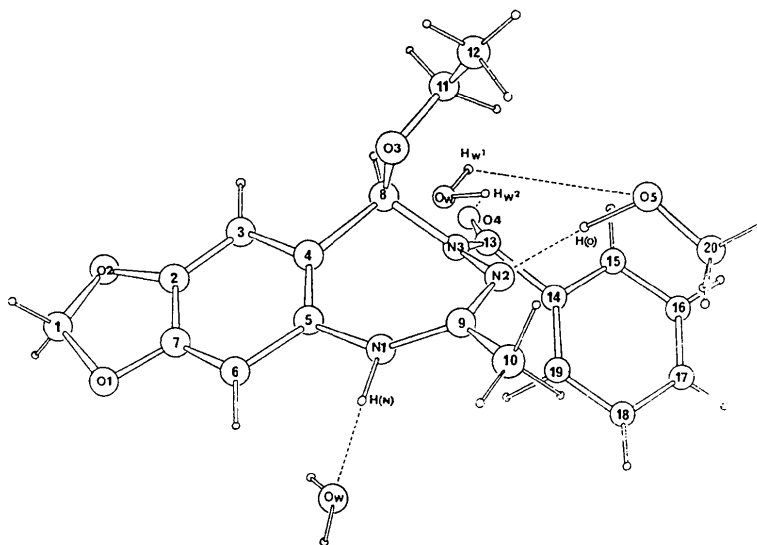


Fig. 1. A perspective view of the molecule indicating the numbering of the atoms.

Table 3. Bond lengths (Å) and angles (°) with their *e.s.d.*'s in parentheses

C(1)—O(1)	1.430 (7)	N(3)—C(13)	1.344 (6)
C(1)—O(2)	1.408 (7)	C(13)—O(4)	1.240 (5)
O(1)—C(7)	1.376 (4)	C(13)—C(14)	1.487 (6)
O(2)—C(2)	1.390 (4)	C(14)—C(15)	1.386 (6)
C(2)—C(7)	1.367 (4)	C(15)—C(16)	1.385 (8)
C(2)—C(3)	1.354 (5)	C(16)—C(17)	1.384 (8)
C(7)—C(6)	1.357 (6)	C(17)—C(18)	1.367 (9)
C(3)—C(4)	1.390 (7)	C(18)—C(19)	1.392 (7)
C(6)—C(5)	1.391 (6)	C(19)—C(14)	1.387 (6)
C(4)—C(5)	1.397 (6)	N(3)—N(2)	1.416 (5)
C(4)—C(8)	1.499 (6)	N(2)—C(9)	1.288 (5)
C(8)—N(3)	1.465 (6)	C(9)—C(10)	1.494 (6)
C(8)—O(3)	1.397 (6)	C(9)—N(1)	1.352 (5)
O(3)—C(11)	1.437 (6)	N(1)—C(5)	1.406 (6)
C(11)—C(12)	1.508 (8)	O(5)—C(20)	1.384 (7)
O(1)—C(1)—O(2)	108.8 (4)	C(8)—N(3)—C(13)	121.4 (4)
C(1)—O(1)—C(7)	105.4 (3)	N(2)—N(3)—C(13)	118.3 (3)
C(1)—O(2)—C(2)	105.6 (3)	N(3)—C(13)—O(4)	120.4 (5)
O(1)—C(7)—C(2)	110.1 (3)	N(3)—C(13)—C(14)	118.5 (4)
O(2)—C(2)—C(7)	109.7 (3)	O(4)—C(13)—C(14)	121.1 (4)
O(1)—C(7)—C(6)	128.0 (3)	C(13)—C(14)—C(15)	117.9 (4)
O(2)—C(2)—C(3)	128.3 (3)	C(13)—C(14)—C(19)	122.0 (4)
C(3)—C(2)—C(7)	122.0 (3)	C(14)—C(15)—C(16)	120.1 (5)
C(6)—C(7)—C(2)	121.9 (3)	C(15)—C(16)—C(17)	119.5 (5)
C(2)—C(3)—C(4)	117.7 (4)	C(16)—C(17)—C(18)	120.6 (5)
C(5)—C(6)—C(7)	117.8 (4)	C(17)—C(18)—C(19)	120.3 (5)
C(3)—C(4)—C(5)	120.6 (4)	C(18)—C(19)—C(14)	119.3 (4)
C(6)—C(5)—C(4)	120.0 (4)	C(19)—C(14)—C(15)	120.1 (4)
C(3)—C(4)—C(8)	118.9 (4)	N(3)—N(2)—C(9)	115.9 (3)
C(5)—C(4)—C(8)	120.5 (4)	N(2)—C(9)—N(1)	130.1 (4)
C(4)—C(8)—N(3)	110.1 (4)	N(2)—C(9)—C(10)	15.6 (4)
C(4)—C(8)—O(3)	109.0 (4)	C(10)—C(9)—N(1)	114.2 (4)
O(3)—C(8)—N(3)	110.3 (3)	C(9)—N(1)—C(5)	133.9 (4)
C(8)—O(3)—C(11)	113.2 (3)	N(1)—C(5)—C(4)	123.8 (4)
O(3)—C(11)—C(12)	107.7 (4)	N(1)—C(5)—C(6)	116.1 (4)
C(8)—N(3)—N(2)	117.8 (3)		

Barta-Szalai, Møller & Párkányi, 1976). The title compound is a ring-expansion type photoisomer obtained by the irradiation of *N*-(2-methyl-6,7-methylene-dioxy-3-quinazolino)benzamide in ethanol. X-ray structure determination was carried out in order to corroborate the molecular structure which had been deduced from spectroscopic data.

The tautomeric structure in the solid state is different from that in solution as shown by the UV spectra (Fetter *et al.*, 1976). A double bond is found between N(2) and C(9) rather than between N(1) and C(9). The H atom is attached to N(1). The solvent molecules (H₂O and MeOH) forming a hydrogen-bond system

(Fig. 1) may also be of importance in fixing this tautomer. The solvent molecules are linked to each other and to the triazepine ring by the hydrogen bonds described in Table 4.

Table 4. Hydrogen bonds

Bond X—H···Y	X···Y	H···Y	∠X—H···Y
N(1)—H···O(W)	2.96 Å	1.99 Å	180.0°
O(5)—H(methanol)···N(2)	2.80	1.81	180.0
O(W)—H*···O(5)	(methanol) 2.81	1.73	170.1
O(W)—H*···O(4)	(carbonyl) 2.76	2.06	125.1

* Water molecule at (\bar{x} , $\frac{1}{2}$ + y , $\frac{1}{2}$ - z).

Table 5. Torsion angles in the triazepine ring (°)

C(4)—C(5)—N(1)—C(9)	9.1
C(5)—N(1)—C(9)—N(2)	16.0
N(1)—C(9)—N(2)—N(3)	-1.3
C(9)—N(2)—N(3)—C(8)	-58.3
N(2)—N(3)—C(8)—C(4)	89.0
N(3)—C(8)—C(4)—C(5)	-46.8
C(8)—C(4)—C(5)—N(1)	-0.2

C(1), O(1), O(2), C(3), C(4), C(5), C(6), C(7), C(8) and N(1) form a least-squares plane with a mean deviation of 0.025 Å. The torsion angles for the triazepine ring are given in Table 5.

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