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7-BROMO-5-PHENYL-1,2-DIHYDRO-3H-1,3,5-BENZTRIAZEPIN-2-ONE

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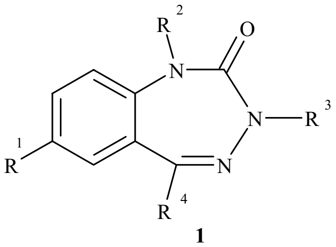
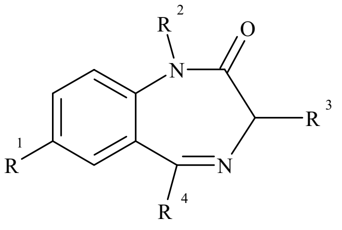
7-Bromo-5-phenyl-1,2-dihydro-3H-1,4-benztriazepin-2-one was obtained by thermolysis of the syn-4-phenylsemicarbazone of 2-aminobenzophenone. Its molecular and crystal structure were established by X-ray crystallography. The nature of the hydrogen bonds between molecules of the compound in solution and in the crystalline state was determined by IR spectroscopy and X-ray crystallography.

Keywords: benztriazepine, semicarbazone of 2-aminobenzophenone, hydrogen bonds, IR spectroscopy, UV spectroscopy, X-ray crystallography.

1,2-Dihydro-3H-1,3,4-benztriazepin-2-ones **1** have been less well studied than their heteroanalogs 1,2-dihydro-3H-1,4-benzdiazepin-2-ones **2** which include compounds with valuable pharmacological properties [1].



1



2

The potential of 1,3,4-benztriazepine derivatives as biologically active compounds, including anticonvulsants and antithrombotic compounds, has been discussed [2, 3].

One of the methods for the preparation of 1,2-dihydro-3H-1,3,4-benztriazepin-2-ones is to heat the semicarbazones of 2-aminobnezophenones **3** in solution or in the melt (at 190-195°C) [1, 4], however at a temperature of 230-240°C only the quinazolines-2 **5** were formed and not the dihydrobenztriazepinones **4**.

At 240-250°C compounds **3** cyclized into dihydrobenztriazepinones **4** [5,6]. However the authors did not state the configuration of compound **3** (Scheme 1).

We obtained three compounds when the *syn*-4-phenylsemicarbazone of 2-amino-5-bromobenzophenone **6** was thermolyzed in the molten phase (190-200°C). One was identified as 7-bromo-5-phenyl-1,2-dihydro-3H-1,3,4-benztriazepin-2-one, **4a**. The second, according to its elemental analysis, IR and mass spectra, was assigned as 7,16-dibromo-5,14-diphenyl-1,2,3,10,11,12-hexahydrodibenzo[*f,m*]-1,3,4,10,12,13-hexaazacyclotetradecin-2,11-dione (**7**). The third product of the reaction was aniline, which condensed on the cold finger of the reaction vessel (Scheme 2).

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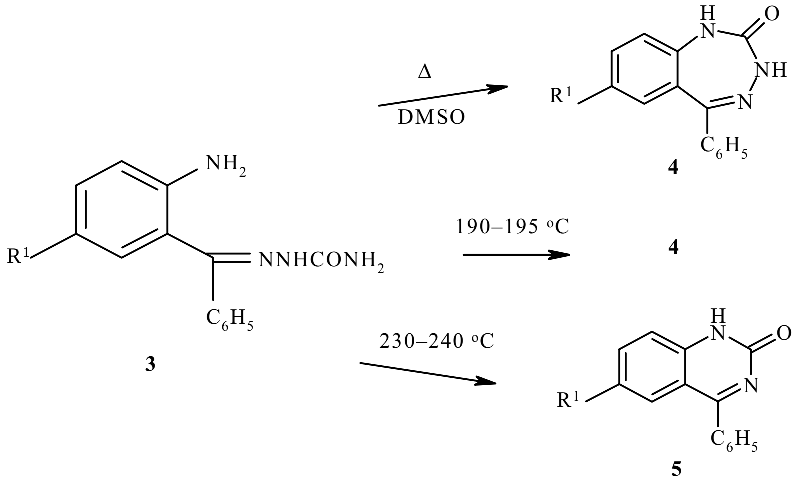
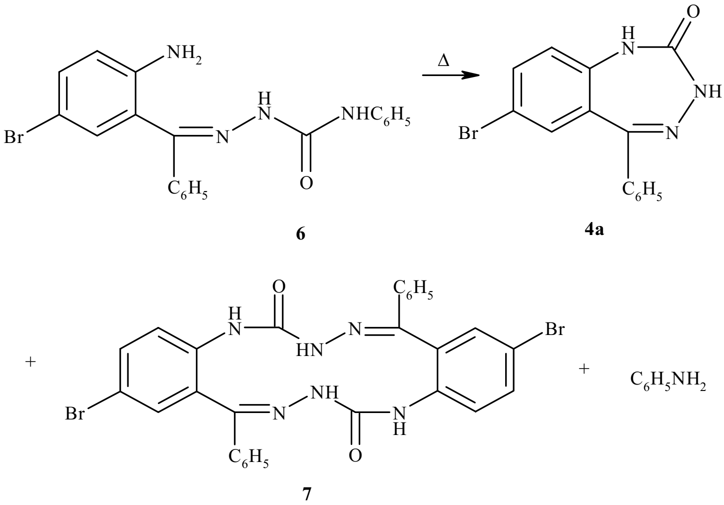
Scheme 1



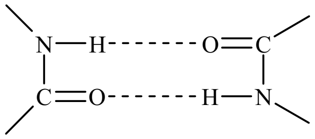
Scheme 2



This paper is concerned with the structure of the benztriazepinone **4a**. The structure and properties of the dibenzohexaazaheterocycle **7** will be the subject of a later publication.

The UV spectra of compound **4a** consists of three bands with maxima at 224, 250, and 302 nm. The first (most intense) and second may be assigned to the aromatic chromophore, and the third to the azomethine bond conjugated with the benzo group.

1,2-Dihydro-3H-1,4-benzdiazepin-2-ones form cyclic dimers in the crystalline state and in relatively concentrated solutions in CCl_4 *via* hydrogen bonds between the secondary amide groups [7]:



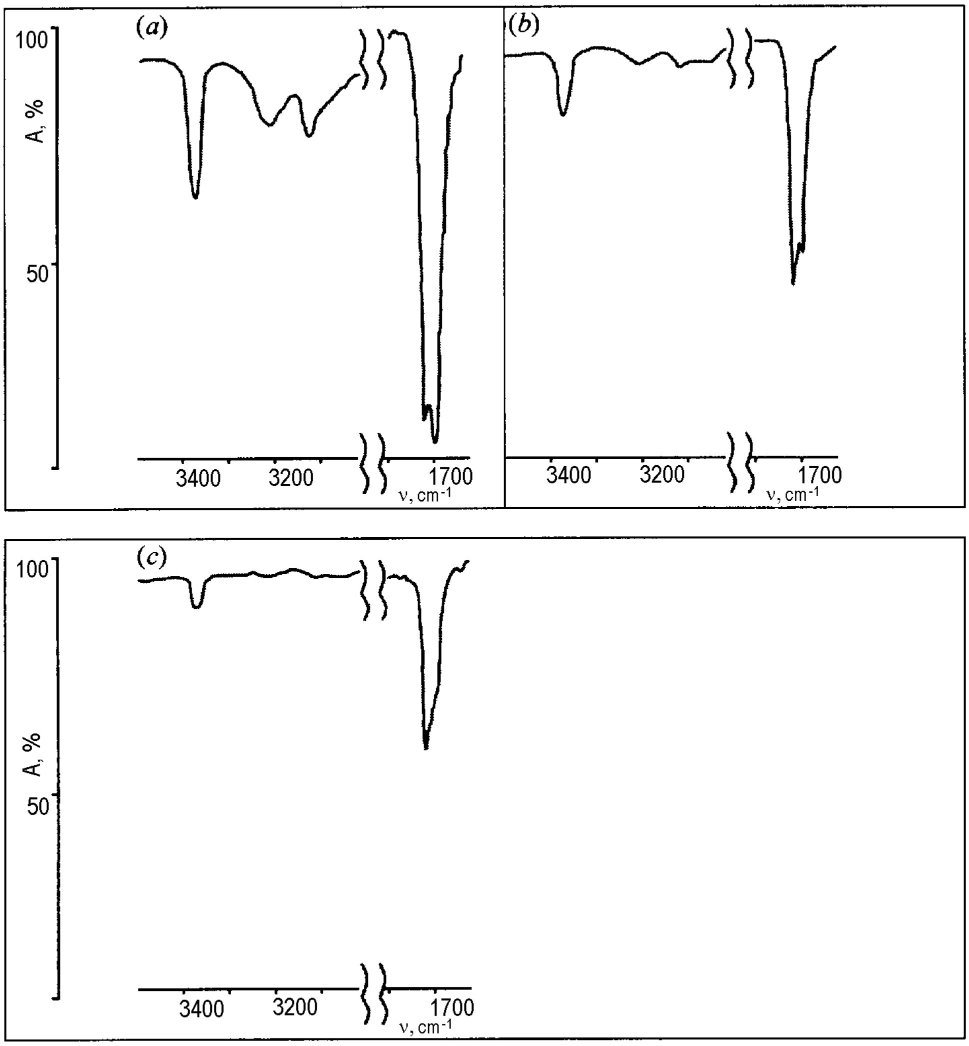


Fig. 1. IR spectra of 7-bromo-5-phenyl-1,2-dihydro-3H-1,3,4-benztriazepin-2-one at different concentrations in CCl_4: *a*) C = $3\cdot10^{-3}$ mol/l; *b*) C = $3\cdot10^{-3}$ mol/l; *c*) C = $5\cdot10^{-5}$ mol/l.

The features of the IR spectra for compounds **4** suggest that hydrogen bonds are formed in molecules of compound **4a**. At a concentration of $3\cdot10^{-3}$ mol/l the IR spectrum of a CCl_4 solution has two carbonyl absorption bands at 1725 and 1700 cm^{-1} and bands of free and hydrogen bonded NH groups at 3370, 3210, and 3125 cm^{-1} (Fig. 1). When the solution was diluted to $5\cdot10^{-1}$ mol/l the intensities of the bands at 1725 and 3370 cm^{-1} increased while the bands at 3125, 3210, and 1700 cm^{-1} practically disappeared. The observed changes in principle echo the changes in the spectra of 1,2-dihydro-3H-1,4-benzdiazepin-2-ones when their solutions in CCl_4 are diluted [7].

The mass spectrum of compound **4a** corresponds to that reported [4]; its crystal and molecular structure were studied by X-ray crystallography.

A fragment of the molecular packing in the crystal is shown in Fig. 2. A characteristic of the packing is the formation of dimers connected by hydrogen bonds of the $N_{(1)}$–H···$O_{(1)}$ type. The parameters of the hydrogen bonds are $N_{(1)}\cdots O_{(1)}$* = 2.931 Å. H···$O_{(1)}$ = 2.09 Å, and the angle at the hydrogen atom is 168° (an eight membered pseudoring is formed). A similar system of hydrogen bonds in the crystal is also characteristic for 1,2-dihydro-3H-1,4-benzdiazepin-2-ones and is called type *A* by Gilli et al. [8]. The same type of bond is observed in nitrazepam [9], phenazepam [10], and also in 7-chloro-3,5-diphenyl-1,2-dihydro-3H-1,3,4-benztriazepin-2-one **1a** [11].

Only van der Waals interactions exist between the dimers formed in the crystal. The $N_{(3)}$–H group does not participate in the system of hydrogen bonds because it is screened by the phenyl ring of the neighboring molecule.

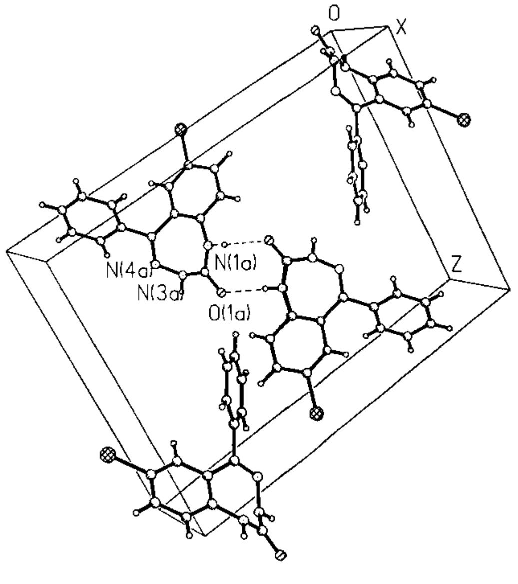


Fig. 2. Fragment of the packing of the 7-bromo-5-phenyl-1,2-dihydro-3H-1,3,4-benztriazepin-2-one in the crystal.

The molecular structure of compound **4a** is shown in Fig. 3. The characteristic parts of the skeleton of this molecule are a nonplanar seven membered heterocycle (B), conjugated with a bromobenzo group (A) and a phenyl radical (C) at position 5 of the heterocycle. The heterocycle B has a pseudoboat conformation with three mutually intersecting planes: $N_{(1)}C_{(2)}N_{(4)}C_{(5)}$, $N_{(1)}C_{(5)}C_{(10)}C_{(11)}$, and $C_{(2)}N_{(3)}N_{(4)}$. The second and third fragments lie on the same side of the first. Some characteristic parameters of molecule **4a** are presented in Table 1 and compared with data for the 3-phenyl analog **1a** [11] and nitrazepam **2b** [9].

TABLE 1. Comparative Geometric Parameters of Compounds **4a**, 7-Chloro-3,5-diphenyl-1,2-dihydro-3H-1,3,4-benztriazepin-2-one **1a** [11], and Nitrazepam **2b** [9]

Dihedral angle between planes, deg	4a	1a	2b
Rings A and C	116.5	116.8	118.2
$N_{(1)}–C_{(2)}–N_{(4)}–C_{(5)}$ and $N_{(1)}–C_{(5)}–C_{(10)}–C_{(11)}$	35.6	35.9	32.3
$N_{(1)}–C_{(2)}–N_{(4)}–C_{(5)}$ and $C_{(2)}–N_{(3)}–N_{(4)}$	42.8	55.8	60.3

Torsion Angles and ΔC_S Values (deg) in the 7-membered Ring

	4a	1a	2b
$C_{(10)}–N_{(1)}–C_{(2)}–N_{(3)}$	-31.6	-25.7	-0.9
$N_{(1)}–C_{(2)}–N_{(3)}–N_{(4)}$	-41.1	-56.7	-71.2
$C_{(2)}–N_{(3)}–C_{(4)}–C_{(5)}$	60.4	75.0	72.9
$N_{(3)}–N_{(4)}–C_{(5)}–C_{(6)}$	-1.5	-2.7	-2.2
$N_{(4)}–C_{(5)}–C_{(11)}–C_{(10)}$	-36.0	-45.0	-40.0
$C_{(5)}–C_{(11)}–C_{(10)}–N_{(1)}$	0.6	5.5	0.1
$C_{(11)}–C_{(10)}–N_{(1)}–C_{(2)}$	51.5	53.0	40.1
ΔC_S	20.67	17.6	1.8

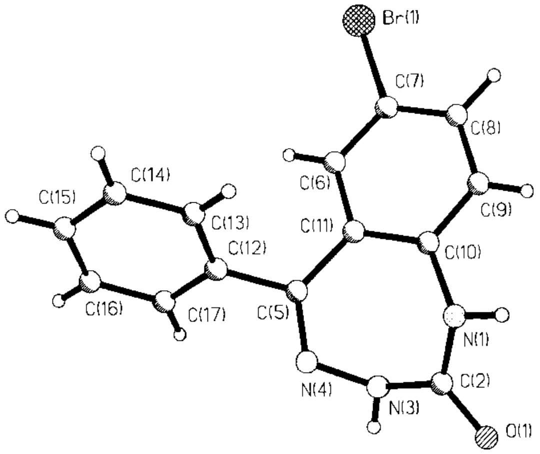


Fig. 3. Molecular structure of 7-bromo-5-phenyl-1,2-dihydro-3H-1,3,4-benztriazepin-2-one.

A measure of the boat distortion is the criterion

$$\Delta C_S = \{[T_o^2 + \Sigma\,(T_i + T_{i*})^2]/4\}^{1/2},$$

where T_o is the torsion angle at the $C_{(10)}$–$C_{(11)}$ bond. This criterion shows the extent to which the 7-membered ring diverges from C_s symmetry. In the molecule of compound **4a** $\Delta C = 20.67°$.

Analysis of the torsion angles shows that considerable distortion of the boat occurs for 1,2-dihydro-3H-1,3,4-benztriazepinones **1** (R^1 = Cl, R^2 = H, $R^3 = R^4 = C_6H_5$) [11] and **4a**. This arises from two circumstances: (1) considerable twisting of the $N_{(1)}C_{(2)}N_{(4)}C_{(5)}$ fragment (in compound **4a** the deviations of atoms from the mean plane lie between +0.090 and -0.076 Å, while in nitrazepam the deviations are practically zero; (2) deviation of the boat from C_S symmetry: in the case of nitrazepam ΔC_S is less than 2°, whereas in compound **4a** and its 3-phenyl derivative it is about 20°.

TABLE 2. Interatomic Distances *d* (Å) in the Molecules of Compound **4a** and 7-Chloro-3,5-diphenyl-1,2-dihydro-3H-1,3,4-benztriazepin-2-one **1a** [11]

Bond	**4a**	**1a**
$O_{(1)}$–$C_{(2)}$	1.221(3)	1.215(5)
$Cl_{(1)}$–$C_{(7)}$		1.739(4)
$Br_{(1)}$–$C_{(7)}$	1.899(3)	
$N_{(1)}$–$C_{(2)}$	1.368(3)	1.367(5)
$N_{(1)}$–$C_{(10)}$	1.413(3)	1.408(5)
$C_{(2)}$–$N_{(3)}$	1.376(4)	1.411(6)
$N_{(3)}$–$N_{(4)}$	1.408(3)	1.422(4)
$N_{(4)}$–$C_{(5)}$	1.283(3)	1.295(5)
$C_{(5)}$–$C_{(11)}$	1.481(3)	1.479(5)
$C_{(5)}$–$C_{(12)}$	1.488(4)	1.480(5)
$C_{(6)}$–$C_{(7)}$	1.377(4)	1.371(6)
$C_{(6)}$–$C_{(11)}$	1.403(4)	1.398(5)
$C_{(7)}$–$C_{(8)}$	1.379(4)	1.383(7)
$C_{(8)}$–$C_{(9)}$	1.379(4)	1.366(6)
$C_{(9)}$–$C_{(10)}$	1.387(4)	1.397(6)
$C_{(10)}$–$C_{(11)}$	1.393(4)	1.386(6)
$C_{(12}$–$C_{(13)}$	1.387(4)	
$C_{(12)}$–$C_{(17)}$	1.392(4)	
$C_{(13)}$–$C_{(14)}$	1.383(4)	
$C_{(14)}$–$C_{(15)}$	1.372(5)	
$C_{(15)}$–$C_{(16)}$	1.374(5)	
$C_{(16)}$–$C_{(17)}$	1.384(4)	

Tables 2 and 3 contain interatomic distances and bond angles for compound **4a** in comparison with compound **1a** [11]. In the plane of fragment A the mean C–C distance is 1.386(4) Å, the C–Br distance is 1.899(3) Å. All of these parameters are close to those found in structures of other 1,2-dihydro-3H-1,4-benzdiazepin-2-ones [9, 10] and 7-chloro-3,5-diphenyl-1,2-dihydro-3H-1,3,4-benztriazepin-2-one [11]. The deviation of the endocyclic angle in ring A from the average value of 120° for atoms $C_{(6)}$, $C_{(11)}$, and $C_{(10)}$ may be noted. This may be caused by the influence of the substituents on these atoms.

In ring C the mean C–C bond length is 1.382(4) Å, the mean value of the endocyclic angles is 120°, and the $C_{(5)}$–$C_{(12)}$ bond length is 1.488(4) Å.

We have already noted (Table 1) that the dihedral angle between cycles A and C is 116.5° which is characteristic of all the compounds cited in this table (116.8° [11], 118.2°[9]). In the 7-membered ring B distances are close to those found in the analog [11]. The length of the $C_{(5)}$=$N_{(4)}$ bond (1.283(3) Å) is typical of a double bond. Conjugation with ring A affects the $C_{(5)}$–$C_{(11)}$ bond length (1.481(2) Å) and also the shortening of the $N_{(1)}$–$C_{(10)}$ bond. The geometry of the amide group is standard [9, 11]. The lengths of bonds $N_{(3)}$–$C_{(2)}$ and $N_{(3)}$–$N_{(4)}$ are 1.376 and 1.408 Å respectively. The length of the first bond indicates participation of the unshared pair on $N_{(3)}$ in conjugation with the amide group.

Comparison of the parameters for 1,2-dihydro-3H-1,3,4-benztriazepin-2-ones described in this report and in paper [11] with dihydrobenzdiazepinones shows a large degree of the boat distortion for the 7-membered ring in first two compounds. It is probable that this can be explained by replacement of an sp^3-hybridized carbon at position 3 of the dihydrobenzdiazepins by a nitrogen atom which has a state between sp^2 and sp^3-hybridization.

TABLE 3. Bond Angles ω (deg) in the Molecules of Compound **4a** and 7-Chloro-3,5-diphenyl-1,2-dihydro-3H-1,3,4-benztriazepin-2-one **1a** [11]

Bond	**4a**	**1a**
$C_{(2)}$–$N_{(1)}$–$C_{(10)}$	123.7(2)	124.9(4)
$O_{(1)}$–$C_{(2)}$–$N_{(1)}$	122.2(2)	122.9(4)
$O_{(1)}$–$C_{(2)}$–$N_{(3)}$	120.0(2)	123.1(4)
$N_{(1)}$–$C_{(2)}$–$N_{(3)}$	117.8(2)	114.0(3)
$C_{(2)}$–$N_{(3)}$–$N_{(4)}$	125.0(2)	115.1(3)
$C_{(5)}$–$N_{(4)}$–$N_{(3)}$	119.3(2)	116.8(3)
$N_{(4)}$–$C_{(5)}$–$C_{(11)}$	126.6(2)	124.1(3)
$N_{(4)}$–$C_{(5)}$–$C_{(12)}$	114.6(2)	115.9(3)
$C_{(11)}$–$C_{(5)}$–$C_{(12)}$	118.7(2)	120.1(3)
$C_{(7)}$–$C_{(6)}$–$C_{(11)}$	120.1(3)	120.5(4)
$C_{(6)}$–$C_{(7)}$–$C_{(8)}$	121.4(2)	120.7(4)
$C_{(6)}$–$C_{(7)}$–$Br_{(1)}$	119.5(2)	
$C_{(6)}$–$C_{(7)}$–$Cl_{(1)}$		119.3(4)
$C_{(8)}$–$C_{(7)}$–$Br_{(1)}$	119.1(2)	
$C_{(8)}$–$C_{(7)}$–$Cl_{(1)}$		119.9(3)
$C_{(7)}$–$C_{(8)}$–$C_{(9)}$	118.8(2)	119.6(4)
$C_{(8)}$–$C_{(9)}$–$C_{(10)}$	121.0(3)	120.1(4)
$C_{(9)}$–$C_{(10)}$–$C_{(11)}$	120.2(2)	120.6(4)
$C_{(9)}$–$C_{(10)}$–$N_{(1)}$	117.7(2)	119.1(4)
$C_{(11)}$–$C_{(10)}$–$N_{(1)}$	122.1(2)	120.3(3)
$C_{(10)}$–$C_{(11)}$–$C_{(6)}$	118.5(2)	118.3(4)
$C_{(10)}$–$C_{(11)}$–$C_{(5)}$	122.3(2)	120.1(3)
$C_{(6)}$–$C_{(11)}$–$C_{(5)}$	119.2(2)	121.5(4)
$C_{(13)}$–$C_{(12)}$–$C_{(17)}$	118.9(3)	
$C_{(13)}$–$C_{(12)}$–$C_{(5)}$	120.9(2)	
$C_{(17)}$–$C_{(12)}$–$C_{(5)}$	120.2(2)	
$C_{(14)}$–$C_{(13)}$–$C_{(12)}$	120.6(3)	
$C_{(15)}$–$C_{(14)}$–$C_{(13)}$	120.0(3)	
$C_{(14)}$–$C_{(15)}$–$C_{(16)}$	119.9(3)	
$C_{(15)}$–$C_{(16)}$–$C_{(17)}$	120.7(3)	
$C_{(16)}$–$C_{(17)}$–$C_{(12)}$	119.8(3)	

TABLE 4. Crystallographic Data and Refinement for the Structure of Compound **4a**

Empirical formula	$C_{14}H_{10}BrN_3O$	
Molecular mass	316.16	
Temperature	293(2) K	
Wavelength	1.54178 Å	
Space group	$P2_1/c$	
Unit cell parameters	a = 5.140(1) Å	α = 90 deg.
	b = 18.314(4) Å	β = 91.14(3) deg.
	c = 13.645(3) Å	γ = 90 deg.
Volume, V	1284.2(5) Å^3	
Z	4	
Density (calculated)	1.635 mg/mm^3	
Absorption coefficient	4.326 mm^{-1}	
F(000)	632	
Range of θ for data set	from 4.04 to 65.05°	
Range of indexes	$-6 \le h \le 5$,	
	$-4 \le k \le 22$,	
	$0 \le l \le 16$	
Number of independent reflexions	2127 (R_{int} = 0.0182)	
Maximum and minimum transmission	0.979 and 0.435	
Refinement method	Full matrix least squares in F^2	
Quality of the refinement in F^2	1.092	
Final R-factors		
[$I>2\sigma(I)$]	R_1 = 0.0317, wR_2 = 0.0822	
R-factor (all data)	R_1 = 0.0352, wR_2 = 0.0893	
Extinction coefficient	0.0033(3)	
Maximum and minimum peaks in the difference synthesis		
$\Delta\rho_{max}$	0.586 e·Å^{-3}	
$\Delta\rho_{min}$	-0.581 e·Å^{-3}	

TABLE 5. Coordinates of the Main Non-hydrogen atoms (× 10^4) and Equivalent Isotropic Temperature Parameters U_{eq} (Å·10^{-3})

Atom	x	y	z	U_{eq}
$O_{(1)}$	8111(4)	5688(1)	5507(1)	45(1)
$Br_{(1)}$	1461(1)	3922(1)	686(1)	62(1)
$N_{(1)}$	7929(5)	5383(1)	3896(2)	37(1)
$C_{(2)}$	6957(5)	5705(1)	4717(2)	35(1)
$N_{(3)}$	4578(5)	6047(1)	4633(2)	42(1)
$N_{(4)}$	3762(4)	6484(1)	3836(2)	38(1)
$C_{(5)}$	3621(5)	6203(1)	2975(2)	34(1)
$C_{(6)}$	2840(5)	5092(2)	1961(2)	38(1)
$C_{(7)}$	3472(5)	4393(2)	1682(2)	41(1)
$C_{(8)}$	5547(6)	4027(2)	2109(2)	44(1)
$C_{(9)}$	6982(6)	4369(2)	2839(2)	41(1)
$C_{(10)}$	6359(5)	5068(1)	3147(2)	33(1)
$C_{(11)}$	4298(5)	5445(1)	2702(2)	33(1)
$C_{(12)}$	2589(5)	6703(1)	2201(2)	36(1)
$C_{(13)}$	3671(6)	6719(2)	1278(2)	41(1)
$C_{(14)}$	2735(7)	7195(2)	567(2)	47(1)
$C_{(15)}$	686(7)	7648(2)	765(2)	50(1)
$C_{(16)}$	-408(6)	7638(2)	1676(3)	51(1)
$C_{(17)}$	530(6)	7171(2)	2399(2)	44(1)

EXPERIMENTAL

IR spectra of CCl_4 solutions were recorded with a Specord 75-IR spectrophotometer. UV spectra of ethanol solutions ($3\cdot10^{-5}$ mol/l, thickness 10 mm) were recorded with a Specord UV-vis spectrophotometer. Mass spectra were recorded with an MX-1321 mass spectrometer with direct injection of the sample into the ionizing chamber, ionizing electron energy of 70 eV, and an ionizing chamber temperature of 150°C.

Purity of compounds was monitored by TLC on Silufol UV-254 strips (Kavalier) using a 2:2:1 acetone–chloroform–hexane solvent system.

^{1}H NMR spectra of DMSO-d_6 (99.9%) solutions with TMS as internal standard were recorded with a Varian WXP-300 machine with a working frequency of 299.95 MHz.

A colorless monocrystalline platelet (0.6×0.2×0.2 mm) was used for X-ray crystallography. The unit cell parameters of the monoclinic crystal, which were determined by least squares analysis of 40 reflections in the range $8.5 < \theta < 35°$, are cited in Table 4. Parameters were determined with a KUMA (KM-4) diffractometer with graphite monochromated CuKα radiation using $\omega/2\theta$ scanning. Two control reflexions were monitored for each 100 reflexions measured to monitor the quality of the crystal. The difference in the controls did not exceed ±1%. 2298 Reflexions were measured of which 1978 had $I \geq 2\sigma(I)$. Solution and refinement used 2298 non-zero reflexions. During preparation of the data for calculation a correction for absorption, determined experimentally (ψ-scan) was introduced. The structure was solved by direct methods. Refinement was carried out using the anisotropic approximation for non-hydrogen atoms. The hydrogen atoms were found objectively and were refined isotropically within the solid sphere model for H atoms. The final coordinates for the principal atoms are cited in Table 5.

The SHELXG 86 [12] and SHELX-93 [13] set of programs were used for the calculations.

Thermolysis of 2-Amino-5-bromobenzophenone 4-Phenylsemicarbazone. The *syn*-isomer of of 2-amino-5-bromobenzophenone 4-phenylsemicarbazone (8.18 g, 0.02 mol) was placed in a flask and heated at 190-200°C for 2.5 h. A cold finger was attached to the upper part of the flask to collect sublimable products. Aniline was identified among the sublimable products which collected in the cold finger. The reaction mixture was cooled, ground up, and cold chloroform (15 ml) was added. The insoluble material was filtered off and recrystallized several times from chloroform to give compound **7** (3.9 g, 61.7%); mp 370-375°C (dec.) Found, %: C 53.2; H 3.1; Br 25.2; N 13.3. $C_{28}H_{20}Br_2N_6O_2$. Calculated, %: C 53.19; H 3.19; Br 25.27; N 13.29.

The mother liquor was evaporated, the precipitate was filtered off and crystallized from chloroform to give 7-bromo-5-phenyl-1,2-dihydro-3H-1,3,4-benztriazepin-2-one **4a** (1.7 g, 27%); mp 263-265°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 9.72 (1H, s, $N_{(1)}H$); 9.35 (1H, s, $N_{(3)}H$); 7.66-7.01 (8H, m, Ar). Found, %: C 53.3; H 3.31; Br 25.1; N 13.18. $C_{14}H_{10}BrN_3O$. Calculated, %: C 53.19; H 3.19; Br 25.27; N 13.29.

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