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Reaction of 5-Substituted 2-(3-Chloropropanoylamino)benzophenone *syn*- and *anti*-Oximes with Sodium Hydroxide

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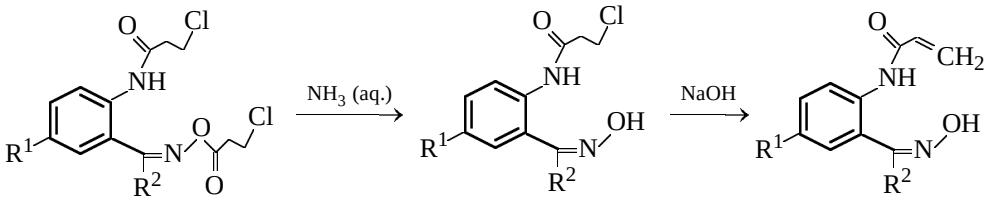
Abstract — Treatment of *syn*-oximes of 5-substituted 2-(3-chloropropanoylamino)benzophenones with equimolar amount of sodium hydroxide results in formation of *syn*-oximes of 5-substituted 2-propenoylaminobenzophenones. The corresponding *anti* isomers under the same conditions give a mixture of *anti*-oximes of 5-substituted 2-(propenoylamino)benzophenones and 18-membered 11,22-disubstituted 7,8,18,19-tetrahydrodibenzo[*d*,*m*][1,10,2,6,11,15]dioxatetraazacyclooctadecine-6,17(5*H*,16*H*)-diones.

The chemistry of oxaza macroheterocycles has attracted a wide researchers' attention [1–8]. Previously we reported the synthesis and structure of the *syn* and *anti* isomers of 2-(3-chloropropanoylamino)-5-methylbenzophenone (3-chloropropanoyl)oximines, possible building blocks for 18-membered dibenzodioxatetraaza macrocycles [9]. Proceeding with this research, we synthesized a series of *syn* and *anti* isomers of 3-(chloropropanoyl)oximines of 5-substituted 2-(3-chloropropanoylamino)benzophenones **I**–**V** whose aminolysis gave the corresponding *syn* and *anti*-oximes of 5-substituted 2-(3-chloropropanoylamino)benzophenones **VI**–**X**. *Syn*-oximes **VI** and **VII** give *syn*-oximes **XI** and **XII** in almost quantitative yields, whereas *anti*-oximes **VIII**–**X** under the same conditions form a mixture of competitive α,β-dehydrohalogenation and intermolecular O-alkylation reactions, specifically 5-substituted 2-propenoylaminobenzophenone *anti*-oximes **XIII**–**XV** and 18-membered 11,22-disubstituted 7,8,18,19-tetrahydrodibenzo[*d*,*m*][1,10,2,6,11,15]dioxatetraazacyclooctadecine-6,17(5*H*,16*H*)-diones **XVI**–**XVIII**, respectively (see Scheme 1).

The yields of compounds **XIII**–**XV** increase when stronger bases are used (MeONa, *t*-BuOK, NaH), whereas the yields of compounds **XVI**–**XVIII** much decrease. Macrocycles **XVI**–**XVIII** can be synthesized in an alternative way, via cyclization of compounds **XIII**–**XV** under the action of NaOH.

To confirm the structure of compound **XII**, we proposed an independent synthesis involving reaction of 2-amino-5-bromobenzophenone (**XIX**) with 3-chloropropanoyl chloride to obtain 5-bromo-2-(3-chloropropanoylamino)benzophenone (**XX**) in 72% yield. The latter was dehydrochlorinated with NaOH to form 5-bromo-2-(propenoylamino)benzophenone (**XXI**) that was converted into *syn*-oxime **XII** (Scheme 2).

Scheme 1.



I, **II** → **VI, VII** (96–98%) → **XI, XII** (59–93%)

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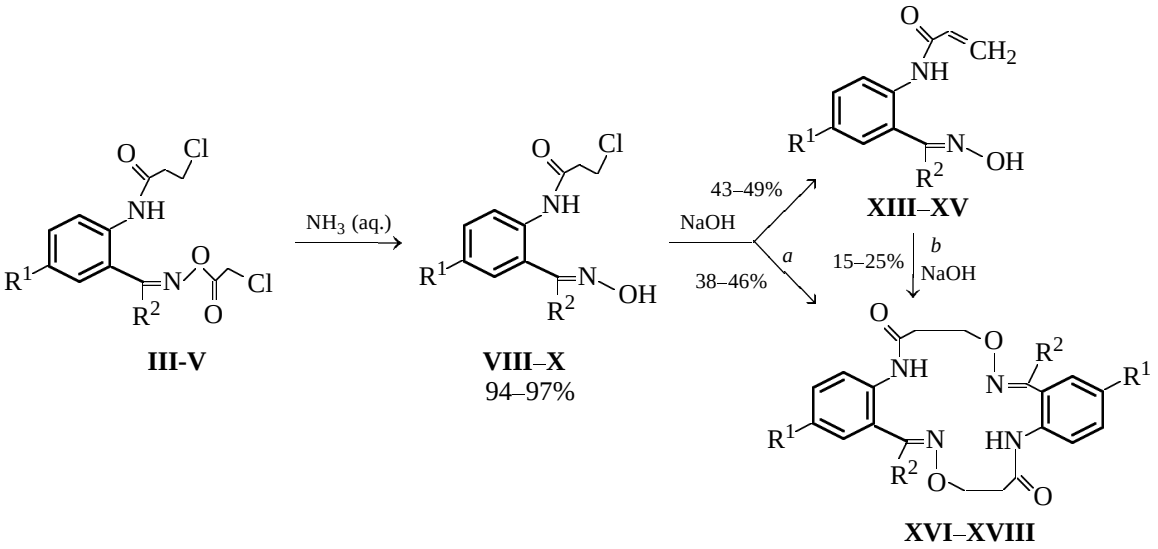


R^1 = Me, R^2 = Ph (**I, III, VI, VIII, XI, XIII, XVI**); R^1 = Br, R^2 = Ph (**II, IV, VII, IX, XII, XIV, XVII**); R^1 = Br, R^2 = *o*-ClC_6H_4 (**V, X, XV, XVIII**).

The synthesized compounds all (Table 1) were characterized by elemental analysis, IR and UV spectroscopy, and mass spectrometry (suggested fragmentation patterns were discussed).

The IR spectra of *syn* isomers **I** and **II** contain stretching absorption bands of the NH bond of the free (3390–3395 cm^{-1}) and associated (3330–3355 cm^{-1}) amido group, ester (1745–1760 cm^{-1}) and amide (1685 cm^{-1}) carbonyls, and azomethine bond (1575–1585 cm^{-1}). The respective bands in the spectra of *anti* isomers **III**–**V** are at 3265–3270, 3225–3235, 1755–1765, 1680–1685, and 1580–1600 cm^{-1}.

The IR spectra of *syn* isomers **VI** and **VII** contain stretching absorption bands of the hydroxy group (3545 cm^{-1}), amide N–H bond (3395–3400 cm^{-1}), amide carbonyl group (1680–1685 cm^{-1}), and azomethine bond (1585–1590 cm^{-1}); the respective bands of *anti* isomers **VIII**–**X** are at 3545–3555, 3245–3270, 1675–1680, and 1595–1605 cm^{-1}.

The IR spectra of *syn* isomers **XI** and **XII** contain stretching absorption bands of the hydroxyl group (3545–3550 cm^{-1}), amide N–H bond (3395–3405, 3275–3285 cm^{-1}), amide carbonyl group (1680–1685 cm^{-1}), and azomethine bond (1605 cm^{-1}); the respective bands of *anti* isomers **XIII**–**XV** are at 3545, 3245–3255, 1675–1685, and 1600–1605 cm^{-1}. Relying on data in [9, 10], we can suggest that *anti* isomers **XIII**–**XV** have an intramolecular hydrogen bond

Scheme 2.

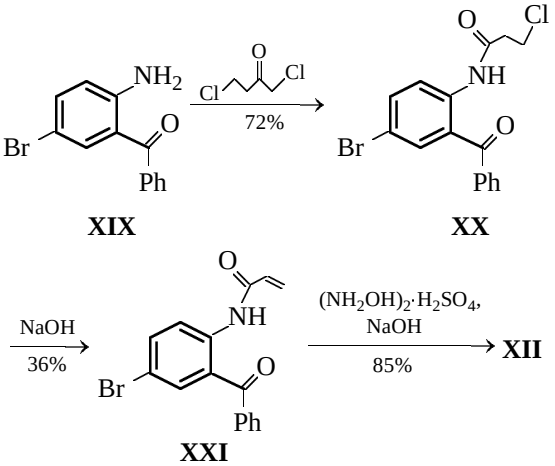


Table 1. Yields, melting points, and elemental analyses of the *syn* and *anti* isomers of 5-substituted 2-(3-chloropropanoylamino)benzophenone 3-(chloropropanoyl)oximines **I**–**V**, 5-substituted 2-(3-chloropropanoylamino)benzophenone *syn*- and *anti*-oximes **VI**–**X**, 5-substituted 2-(propenoylamino)benzophenone *syn*- and *anti*-oximes **XI**–**XV**, and 11,22-disubstituted 7,8,18,19-tetrahydrodibenzo[*d*,*m*][1,10,2,6,11,15]dioxatetraazacyclooctadecine-6,17(5*H*,16*H*)-diones **XVI**–**XVIII**

Comp. no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %			M^+, [a] *m/z*
			C	H	N		C	H	N	
I	60	113–115	58.99	4.97	6.87	$C_{20}H_{20}Cl_2N_2O_3$	58.98	4.95	6.88	406
II	36	126–128	48.31	3.69	6.00	$C_{19}H_{17}BrCl_2N_2O_3$	48.33	3.63	5.93	470
III	30	82–87	58.94	4.91	6.89	$C_{20}H_{20}Cl_2N_2O_3$	58.98	4.95	6.88	406
IV	81	95–97	48.35	3.67	5.90	$C_{19}H_{17}BrCl_2N_2O_3$	48.33	3.63	5.93	470
V	62	115–117	45.08	3.16	5.58	$C_{19}H_{16}BrCl_3N_2O_3$	45.05	3.18	5.53	504
VI	98	146–148	64.50	5.46	8.89	$C_{17}H_{17}ClN_2O_2$	64.46	5.41	8.84	316
VII	96	133–136	50.39	3.67	7.31	$C_{16}H_{14}BrClN_2O_2$	50.35	3.70	7.34	380
VIII	97	96–98	64.40	5.38	8.87	$C_{17}H_{17}ClN_2O_2$	64.46	5.41	8.84	316
IX	96	102–104	50.30	3.68	7.37	$C_{16}H_{14}BrClN_2O_2$	50.35	3.70	7.34	380
X	94	183–185	46.20	3.19	6.81	$C_{16}H_{13}BrCl_2N_2O_2$	46.18	3.15	6.73	414
XI	59	157–160	72.80	5.79	9.97	$C_{17}H_{16}N_2O_2$	72.84	5.75	9.99	280
XII	93	143–146	55.64	3.78	8.09	$C_{16}H_{13}BrN_2O_2$	55.67	3.80	8.12	344
XIII	45	164–165	72.80	5.76	9.96	$C_{17}H_{16}N_2O_2$	72.84	5.75	9.99	280
XIV	43	173–175	55.63	3.84	8.14	$C_{16}H_{13}BrN_2O_2$	55.67	3.80	8.12	344
XV	49	210–215	50.60	3.21	7.40	$C_{16}H_{12}BrClN_2O_2$	50.62	3.19	7.38	378
XVI	39 (*a*), 23 (*b*)	348–350	72.83	5.71	9.94	$C_{34}H_{32}N_4O_4$	72.84	5.75	9.99	560
XVII	38 (*a*), 15 (*b*)	330–335	55.61	3.83	8.15	$C_{32}H_{26}Br_2N_4O_4$	55.67	3.80	8.12	688
XVIII	46 (*a*), 25 (*b*)	327–330	50.64	3.22	7.39	$C_{32}H_{24}Br_2Cl_2N_4O_4$	50.62	3.19	7.38	756

[a] The molecular masses determined by mass spectrometry coincide with calculated.

between the amide hydrogen and azomethine nitrogen. This is evidenced by the long-wave shift of the NH band with respect to the band of the free NH group in *syn* isomers **XI** and **XII**. Further evidence is provided by the fact that the integral intensity of the absorption bands of the amide N–H bond (3250 cm^{-1} for compound **XIV**) remains invariable as the solution concentration is changed from 2.9×10^{-2} to 7.25×10^{-3} M. With *syn* isomer **XII**, the band at 3285 cm^{-1} is weaker than the free NH band at 3395 cm^{-1}. The latter observable suggests suggests that *syn* isomers **XI** and **XII** contain an intramolecular hydrogen bond that is cleaved on dilution. The IR spectra of macrocycles **XVI**–**XVIII** show stretching absorption bands of the amide NH bond (3255–3275 cm^{-1}), amide carbonyl group (1655–1680 cm^{-1}), and azomethine bond (1580–1595 cm^{-1}). The IR spectra of macrocycles **XVI**–**XVIII** suggest a lactam structure of the compounds.

As seen from the above data, *syn* isomers **I, II, VI, VII, XI**, and **XII** characteristically contain a band at 3390–3400 cm^{-1}, corresponding to the NH bond of a free amido group, whereas the IR spectra of *anti* isomers **III**–**V**, **VIII**–**X**, and **XIII**–**XV**, as well as 18-membered macrocycles **XVI**–**XVIII** lack bands in this region.

Earlier we showed that the cyclization of 2-chloroacetamidobenzophenone *syn*-oximes in the presence of NaOH provides 16-membered dibenzodioxatetraaza macrocycles [7], and, therewith, the *syn* configuration of the C=N–O fragment is preserved [8]. With this in mind, we can admit that 18-membered macrocycles **XVI**– **XVIII**, too, preserve the *anti* configuration of the starting monopropanoyl derivatives **VIII**–**X**.

The mass spectra of the *syn* (**XI**, **XII**) and *anti* (**XIII**–**XV**) isomers are identical to each other. They contain molecular ion peaks whose intensity depends on the nature of the 5-substituent. Bromo derivatives have considerably less stable molecular ions than methyl derivatives **XI** and **XIII** (63%). The main fragmentation pathway involves simultaneous elimination of the hydroxy and propenoyl groups to form ions of the indazole structure. The presence of 5-Br favors preferential localization of the positive charge on the propenoyl fragment, as a result of which the base ions (100%) in the mass spectra of compounds **XII** and **XIV** are at *m/z* 55. By contrast, methyl (compounds

Table 2. Bond lengths (*d*) and bond angles (ω) in compound **XII** and benzene solvate of compound **XIV**

Bond	*d*, Å		Angle	ω, deg	
	XII	solvate **XIV**		**XII**	solvate **XIV**
C^1–C^6	1.390(4)	1.401(3)	$C^6C^1C^7$	118.8(3)	118.07(17)
C^1–C^2	1.401(4)	1.424(3)	$C^2C^1C^7$	118.2(2)	117.75(16)
C^1–C^7	1.490(4)	1.491(3)	$C^3C^2C^1$	122.9(2)	124.17(16)
C^2–C^3	1.385(4)	1.400(3)	$C^3C^2N^2$	119.8(3)	119.89(17)
C^2–N^2	1.404(4)	1.405(2)	$C^1C^2N^2$	121.1(3)	120.96(17)
N^2–C^{21}	1.345(4)	1.354(2)	$C^{21}N^2C^2$	119.0(2)	119.12(16)
C^{21}–O^{21}	1.226(3)	1.231(2)	$O^{21}C^{21}N^2$	128.1(3)	129.13(17)
C^{21}–C^{22}	1.479(4)	1.486(3)	$O^{21}C^{21}C^{22}$	122.4(3)	123.55(18)
C^{22}–C^{23}	1.299(4)	1.316(3)	$N^2C^{21}C^{22}$	123.9(3)	123.43(17)
C^3–C^4	1.377(4)	1.385(3)	$C^{23}C^{22}C^{21}$	113.6(3)	113.02(17)
C^4–C^5	1.384(4)	1.382(3)	$C^4C^3C^2$	122.9(3)	122.6(2)
C^5–C^6	1.374(4)	1.384(3)	$C^3C^4C^5$	121.2(3)	120.67(18)
C^5–Br	1.889(3)	1.900(2)	$C^6C^5C^4$	118.6(3)	119.42(18)
C^7–N^7	1.284(3)	1.287(2)	C^6C^5Br	121.3(3)	121.25(18)
C^7–C^8	1.478(4)	1.496(2)	C^4C^5Br	119.5(2)	119.42(15)
N^7–O^{71}	1.401(3)	1.391(2)	$C^5C^6C^1$	119.2(2)	119.32(14)
C^8–C^{13}	1.386(4)	1.392(3)	$N^7C^7C^8$	120.3(3)	120.69(18)
C^8–C^9	1.394(4)	1.393(3)	$N^7C^7C^1$	114.6(2)	122.78(16)
C^9–C^{10}	1.363(5)	1.391(3)	$C^8C^7C^1$	119.1(2)	117.30(16)
C^{10}–C^{11}	1.377(5)	1.392(4)	$C^7N^7O^{71}$	119.1(2)	119.92(15)
C^{11}–C^{12}	1.373(5)	1.373(4)	$C^{13}C^8C^9$	113.1(2)	114.40(15)
C^{12}–C^{13}	1.375(4)	1.398(3)	$C^{13}C^8C^7$	118.1(3)	119.63(18)
C^{2A}–C^{3A}	–	1.358(5)	$C^9C^8C^7$	121.4(3)	120.85(18)
C^{2A}–C^{1A}	–	1.373(5)	$C^{10}C^9C^8$	120.5(3)	119.50(17)
C^{3A}–C^{1A} [a]	–	1.369(5)	$C^9C^{10}C^{11}$	120.4(3)	120.3(2)
C^{1A}–C^{3A} [a]	–	1.369(5)	$C^{12}C^{11}C^{10}$	121.0(3)	119.5(2)
			$C^{11}C^{12}C^{13}$	119.4(3)	120.5(2)
			$C^{12}C^{13}C^8$	120.0(3)	120.2(2)
			$C^{2A}C^{3A}C^{1A}$ [a]	121.1(3)	119.8(2)
			$C^{3A1}C^{1A}C^{2A}$ [a]	–	119.3(3)
				–	120.9(3)

[a] The C^{1A} and C^{3A} are related as $1 - x$, $2 - y$, $-z$.

XI and **XIII**) effectively stabilizes the indazole fragments whose ions are the most abundant.

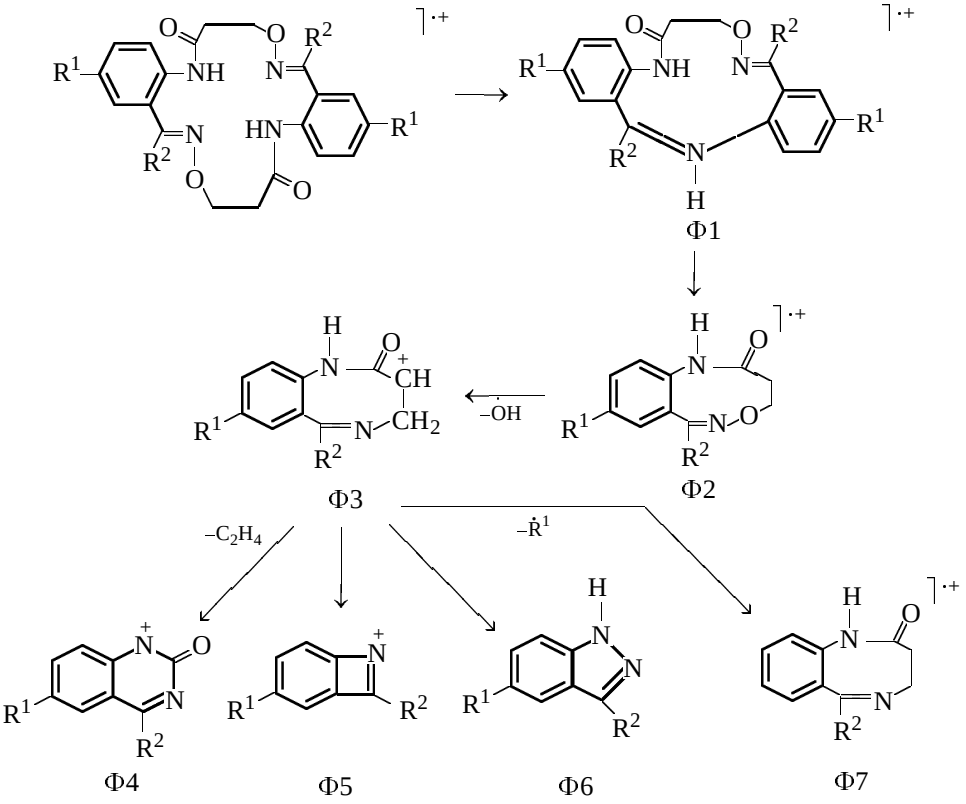
The molecular ion peaks in the mass spectra of macrocyclic compounds **XVI**–**XVIII** decrease in intensity in going from 2,13-dimethyl to 2,13-dibromo derivatives. The main fragmentation pathway of compounds **XVI**–**XVIII** is presented in Scheme 3.

The primary fragmentation act involves opening of the macrocycle and elimination of the $C_3H_4NO_2$ fragment, which is probably associated with cleavage of the amide and azomethine bond to form the molecular ion of divenzooxatriaza macrocycle Φ1. Further fragmentation involves formation of benzoxadiazonine Φ2, benzodiazocine Φ3, quinazolone Φ4, benzazete Φ5, and indazole Φ6 ions, of which the latter being the most abundant.

We performed a full X-ray analysis of compounds **XII** and **XIV** and obtained a model of structure **XVIII**. Selected interatomic distances and bond angles in structures **XII** and **XIV** are listed in Table 2.

The X-ray diffraction analysis gave evidence to show that compounds **XII** and **XIV** the *syn* and *anti* isomers, respectively. Figure 1 presents the molecular structure of compound **XII**. The molecular conformation is stabilized by the intramolecular hydrogen bond N^2–H···O^{71} with the donor–acceptor distance of 2.689(4) Å; the angle at the H atom is 148(2)°, and the HO^{71} distance is 1.98(3) Å. Therewith, a seven-

Scheme 3.



R^1 = Me, Br; R^2 = Ph, *o*-ClC_6H_4.

membered ring is formed in the molecule. The dihedral angle between the fuzed aromatic nucleus and Br and Ph is 66.2°, which is characteristic of 1,4-benzodiazepines [11, 12]. In the substituent at C^2, there is π-electron delocalization, and the N^2–C^2, C^{21}–O^{21}, and C^{22}–C^{23} distances are 1.345, 1.226, and 1.299 Å (Table 2). Molecules in the crystal form chains due to the intramolecular hydrogen bond O^{71}–H···O^{21} [2.629(3) Å]. The chains are held together by van der Waals contacts.

Compound **XIV** crystallizes as a 2:1 benzene solvate. The benzene molecule has an intrinsic crystallographic symmetry C_i. Figure 2 presents a fragment of the structure. The X-ray diffraction data give evidence to show that the *anti* isomers have an intramolecular hydrogen bond. The presence of the amido group of *E* configuration makes possible a strong intramolecular hydrogen bond N^2–H···N^7 of 2.638(5) Å with the H···N^7 distance of 2.00(5) Å and the NHN angle of 143(1)°. The molecule contains a pseudo ring that ensures coplanarity of the substituents and the benzene ring. The molecular conformation is further stabilized by the C^3–H···O^{21} contact with the H···O^{21} distance of 2.26 Å and the angle at

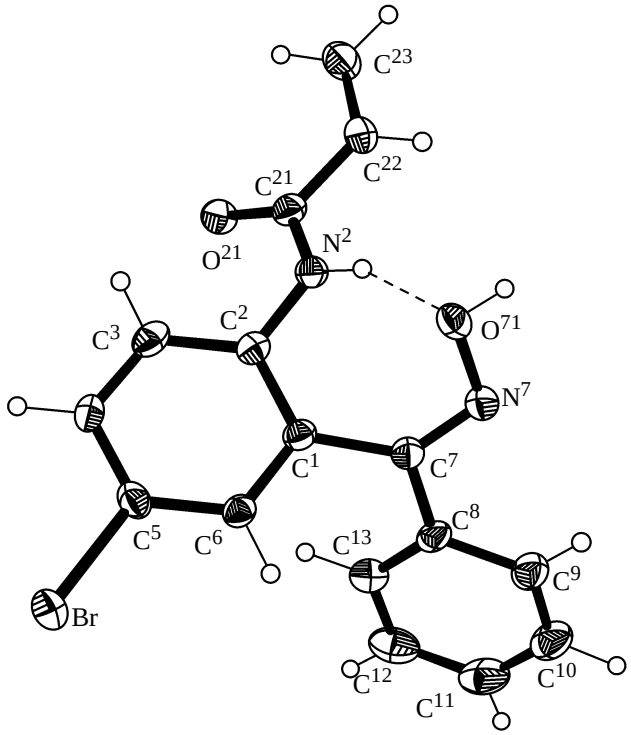


Fig. 1. Molecular structure of 5-bromo-2-(propenoylamino)benzophenone *sym*-oxime (**XII**).

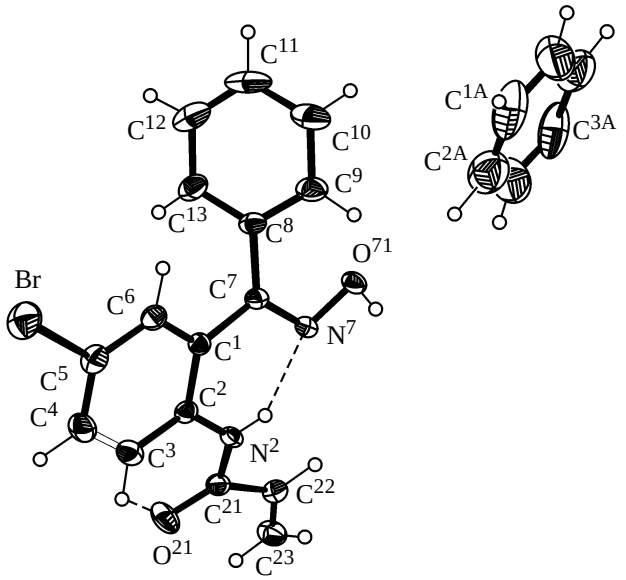


Fig. 2. Structure of the benzene solvate of 5-bromo-2-(propenoylamino)benzophenone *anti*-oxime (**XIV**).

the H atom of 120°. The dihedral angle between the fuzed aromatic ring and Br and Ph is 69.9°, like in compound **XII**. The interatomic distances are listed in Table 2. Note the π-electron delocalization in the C^2–N^2–C^{21}=O^{21}–C^{22}–C^{23} fragment [C^2–N^2 1.405(2), C^{21}–N^2 1.354(2), C^{21}–C^{22} 1.486(2) Å; the length of the terminal double bond is 1.316(2) Å]. The intermolecular hydrogen bond O^{71}–H···O^{21} [2.663(5) Å] combines molecules into a chain with a double screw axis (–*x* + 2, *y* + 1/2, –*z* – 1/2). The hydrogen bond has the H···O^{21} distance of 1.83(5) Å and the angle at the H atom of 179(1)°. The chains are held together by π–π interactions. The distance between the antiparallel phenyl planes is 3.59 Å. The interacting chains form cavities occupied by solvate benzene molecules. Previously in 1,4-benzodiazepines and their macrocyclic analogs we observed π–π or C–H···π interactions between the base molecules and solvate aromatic molecules [8, 11], like in [13, 14]. In the present case we found no such interactions. The contacts between the base and solvate molecules are van der Walls in nature. The latter feature renders the crystals unstable at room temperature.

Figure 3 presents the molecular structure of compound **XVIII**. The *anti* configuration of the C=N–O fragment in the macroring is confirmed by the X-ray diffraction data. This configuration is fixed by two intramolecular N–H···N hydrogen bonds. It should also be noted that the amido group has an *E* configuration, which maikes the NH hydrogens to point to the ring cavity, as described in [8].

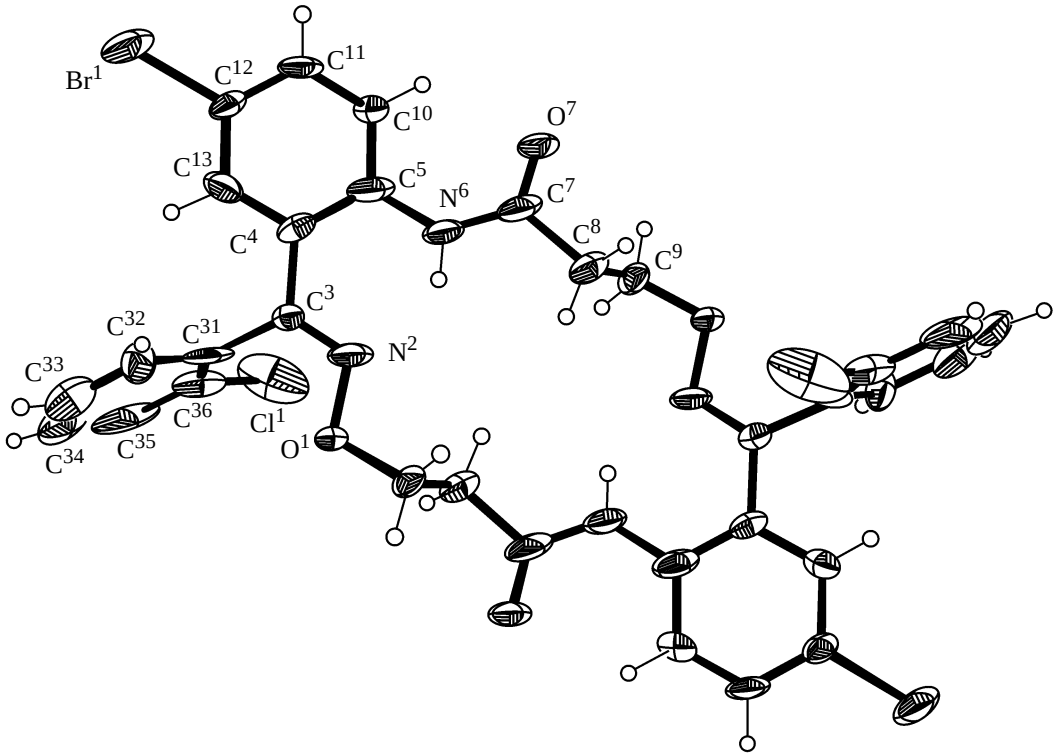


Fig. 3. Molecular structure of compound **XVIII**.

EXPERIMENTAL

The IR spectra were measured on a Specord IR-75 spectrophotometer in $CHCl_3$. The UV spectra were measured on an SF-56 spectrophotometer in EtOH. The mass spectra were registered on an MX-1321 instrument with direct sample admission into the ion source, ionizing energy 70 eV, batch temperature 150°C. The X-ray analysis of compound **XII** was performed on a KUMA-4CCD (MoK_α radiation) from a shapeless colorless sample with the linear dimensions $0.5 \times 0.5 \times 0.4$ mm at 130 K. The sample strongly fluoresced under X-ray irradiation. Monoclinic crystal, space group $P2_1/c_1$; *a* 12.615 (3), *b* 10.015(2), *c* 13.973(2) Å; α 100.40(3)°, *V* 1736.3(7) Å^3, Z 4, ρ_{calc} 1.470 g cm^{-3}. Intensities with 516 frames were registered; φ 0, 90, 180, and 270°; ω scanning, step 0.75°; frame measurement time 8 s. All intensities were corrected for absorption. A total of 6902 reflections were measured, 2556 of which were used for solving and refining the structure. The structure was solved and refined by the SHELX-97 program [15] anisotropically for non-hydrogen atoms and isotropically for hydrogen atoms. The latter were refined in terms of the solid body model. Final *R* factor 0.0352, wR_2 0.0894 on 2556 reflections with $I \geq 2\sigma(I)$. The X-ray analysis of compound **XIV** was performed using a colorless single crystal of prismatic habitus with the linear dimensions 0.6.0.25.0.25 mm. The crystal is a benzene solvate and decomposes in air. For conservation the solvate was cooled to 140 K. The crystal data were collected and treated as described for compound **XII**. Monoclinic crystal, space group $P2_1/c_1$; *a* 12.615 (3), *b* 10.015(2), *c* 13.973(2) Å; α 100.40(3)°, *V* 1736.3(7) Å^3, Z 4, ρ_{calc} 1.470 g cm^{-3}. The experimental data were corrected for absorption on the basis of ψ-scanning data. A total of 10341 reflections were measured, 4403 of which with $I \geq 2\sigma(I)$ were used in structure solving and refining. Final *R* factor 0.0344, wR_2 0.0841 on reflections with $I \geq 2\sigma(I)$. The structure was solved and refined using the SHELX-97 program package anisotropically for non-hydrogen atoms. The hydrogen atoms were refined in terms of the solid body model. Compound **XVIII** crystallizes as dimers with overlapping diffraction patters. We could determine unit cell parameters for an individual block. Monoclinic crystal, *a* 12.822(3), *b* 12.236(2), *c* 19.860 Å; α 100.09(3)°, space group *Cc*, *Z* 4, ρ_{calc} 1.644 g cm^{-3}. The structure model was obtained by direct methods using the SHELX-97 program package and refined isotropically to R_1 0.136.

Compounds **I**–**V** were synthesized as described in [9].

5-Methyl-2-(3-chloropropanoylamino)benzophenone *anti*-oxime (VIII). Aqueous ammonia, 5 ml, was added to a solution of 1.34 g of compound **III** in 15 ml of freshly distilled dioxane. The suspension that formed was stirred for 30 min and then poured into water. A colorless precipitate formed and was washed with water, dried in air, and recrystallized from a benzene–heptane mixture. Yield 1.01 g (97%), mp 96–98°C.

Compounds **VI**, **VII**, **IX**, and **X** were prepared in a similar way (Table 1).

5-Bromo-2-(propenoylamino)benzophenone *syn*-oxime (XII). A solution of 0.06 g of NaOH in 2 ml of water was added to a solution of 0.568 g of compound **VII** in 10 ml of freshly distilled dioxane. The suspension was stirred for 24 h, the colorless precipitate that formed was filtered off, washed with water, and recrystallized from benzene. Yield 0.477 g (93%), mp 143–146°C.

Compound **XI** was prepared in a similar way.

11,22-Dibromo-7,8,18,19-tetrahydrodibenzo[*d*,*m*][1,10,2,6,11,15]dioxatetraazacyclooctadecine-6,17(5*H*,16*H*)-dione (XVII) and 5-bromo-2-(propenoylamino)benzophenone *anti*-oxime (XIV). *a*. A solution of 2 g of NaOH in 10 ml of water was added to a solution of 6.627 g of compound **IX** in 40 ml of freshly distilled dioxane. The suspension was stirred for 24 h, the colorless precipitate that formed was filtered off, washed with water, dried in air, and washed hot dioxane to obtain 2.23 g (38%) of compound **XVII**. The mother solution was poured into water, the precipitate that formed was filtered off, washed with water, dried in air, and recrystallized from benzene to obtain 2.58 g (43%) of compound **XIV**. Compounds **XIII**, **XV**, **XVI**, and **XVIII** were prepared in a similar way (Table 1).

b. Sodium hydride, 0.418 g, was added to a solution of 6.627 g of compound **IX** in 40 ml of dry dioxane. The suspension was stirred for 24 h, the colorless precipitate that formed was filtered off, washed with water, dried in air, and washed hot dioxane to obtain 0.84 g (14%) of compound **XVII**. The mother solution was poured into water, the precipitate that formed was filtered off, washed with water, dried in air, and recrystallized from benzene to obtain 4.02 g (67%) of compound **XIV**. In a similar way, compounds **XIV** and **XVII** were synthesized with MeONa and *t*-BuOK as bases.

5-Bromo-2-(3-chloropropanoylamino)benzophenone (XX) was prepared from compound **XIX** according to [16].

5-Bromo-2-(propenoylamino)benzophenone (XXI). A solution of 0.2 g of NaOH in 2 ml of water was added to a solution of 0.3 g of compound **XX** in 10 ml of freshly distilled dioxane. The suspension was stirred for 2 h and poured into water, the yellowish precipitate was filtered off, dried in air, subjected to chromatography on silica gel (eluent benzene), and recrystallized from benzene–hexane. Yield 0.097 g (36%), mp 86–88°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 3300 (NH), 1675 (NH–C=O), 1630 (C=O), 1595 (C=N). UV spectrum (EtOH), λ_{max}, nm ($\log\varepsilon$): 249 (4.42), 324 (3.64). Mass spectrum, *m/z*: 329 [M^+].

5-Bromo-2-(propenoylamino)benzophenone *syn*-oxime (XII) from compound XXI. A solution of 0.08 g of NaOH in 2 ml of water and 0.149 g of hydroxylamine sulfate was added to a solution of 0.3 g of compound **XXI** in 10 ml of ethanol. The suspension was stirred for 2 h and poured into water, the colorless precipitate was filtered off, dried in air, and recrystallized from benzene–hexane. Yield 0.267 g (85%).

Synthesis of macrocycle XVII from compound XIV. A solution of 0.005 g of NaOH in 2 ml of water was added to a solution of 0.04 g of compound **XIV** in 5 ml of THF. The suspension was stirred for 24 h, the colorless precipitate that formed was filtered off, washed with water, dried in air, and washed with hot THF. Yield 0.006 g (15%).

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