ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 6, pp. 1163–1170. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © V.M. Berestovitskaya, R.I. Baichurin, N.I. Aboskalova, K.A. Lysenko, I.V. Anan'ev, 2011, published in Zhurnal Obshchei Khimii, 2011, Vol. 81, No. 6, pp. 970–977.

Geminal Acylnitrostyrenes in the Reaction with *ortho*-Aminothiophenol

V. M. Berestovitskaya[a], R. I. Baichurin[a], N. I. Aboskalova[a], K. A. Lysenko[b], and I. V. Anan'ev[b]

[a] *Herzen Russian State Pedagogical University, nab. r. Moiki 48, St. Petersburg, 191186 Russia*
e-mail: kohrgpu@yandex.ru

[b] *Nesmeyanov Institute of Organoelemental Compounds, Russian Academy of Sciences, Moscow, Russia*

Received December 28, 2009

Abstract—The synthesis of previously unknown 2,3- and 2,5-dihydro-1,5-benzothiazepines sontaining nitro group was performed by the easy sondensation of geminal acylnitrostyrenes with the *o*-aminothiophenol. The structure of the obtained sompounds was studied by physicochemical methods. By X-ray diffraction analysis the geometry and structural parameters of 4-methyl-3-nitro-2-phenyl-2,3-dihydro-1,5-benzothiazepine were determined.

DOI: 10.1134/S1070363211060156

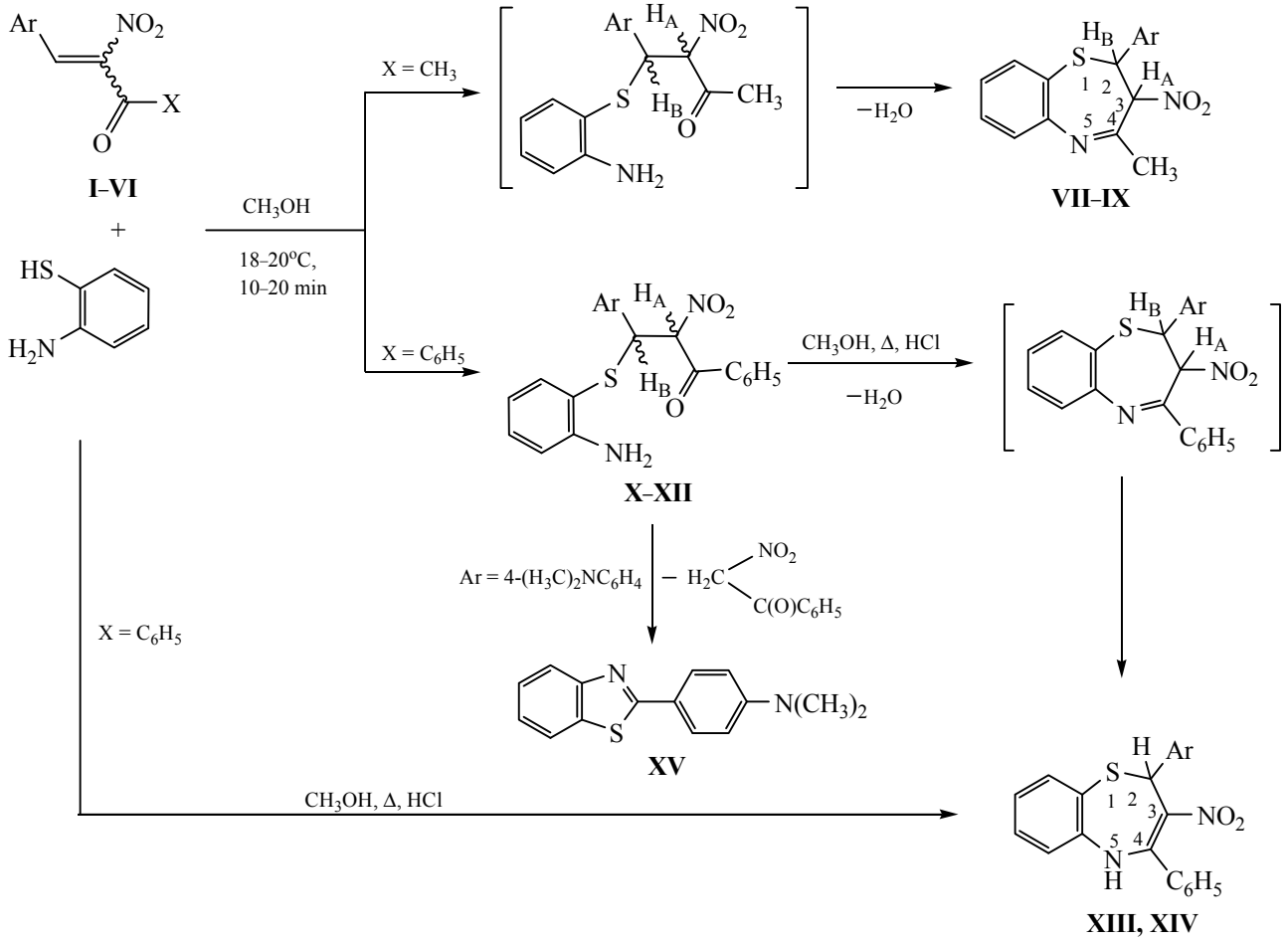
α,β-Conjugated enketones are known to possess high reactivity. They are convenient precursors for the synthesis of a wide range of various carbocyclic and heterocyclic compounds. Of particular interest are the reactions where the enketones act as bielectrophiles, interacting with binucleophilic reagents to form five-, six- and seven-membered cyclic structures [1–4].

The introduction of another acceptor, the nitro group, to the enketone molecule in the *gem*-position to the carbonyl function increases electrophilicity of the unsaturated compound and significantly expands the range of its synthetic performance. Previously, based on the preparatively available *gem*-acylnitroethenes, carbocyclic and heterocyclic structures were obtained with potentially useful properties, namely, *gem*-acylnitrocyclohexenes, pyrimidines, 1,2,3-triazoles, pyrazoles, dihydrofurans, and others [5–11].

Aiming to study further the chemical behavior of nitroenketones we investigated a reaction of *gem*-acetyl- and *gem*-benzoylnitrostyrenes **I–VI** with *o*-aminothiophenol. These reactions proceed successfully at equimolar ratio of reagents under very mild conditions: At 18–20ºC in methanol, in the absence of a catalyst, in 10–20 min, to form new compounds **VII–XII,** respectively, immediately precipitating from the reaction solution as crystalline substances. However, while the *gem*-acetylnitrostyrenes **I–III** afford 2-aryl-4-methyl-3-nitro-2,3-dihydro-1,5-benzothiazepines **VII–IX**, from the *gem*-benzoylnitrostyrenes **IV–VI** linear S-adducts **X–XII** were obtained in 80–98% yield.

Apparently, the reaction of *o*-aminothiophenol with *gem*-acylnitrostyrenes **I–VI** leads initially to the formation of an adduct at the multiple C=C bond (Ad_N), which is isolated in the case of a compound with the benzoyl group **X–XII**, but the S-adduct obtained from the *gem*-acetylnitrostyrene **I–III** immediately suffers heterocyclizaton. This difference may be due to the difference in activity of carbonyl groups in the benzoyl and acetyl functions of the addition products. Probably the attack of amino group on the bezoyl carbonyl group in the adducts **X–XII** is difficult compared to the acetyl analogs due to steric and electronic factors [12–14].

Note that the enketones without nitro group react with *o*-aminothiophenol to form the seven-membered benzothiazepine ring under fairly rigid conditions (at boiling in methanol for several hours in the presence of acid [15] or basic [16] catalyst, or at boiling without a catalyst, but in a high-boiling solvent such as toluene [17]) and, depending on conditions, either linear S-adducts, or substituted 2,3-dihydrobenzothiazepines are isolated [18–20]. Recently information appeared on the reaction of activated geminal enketones like arylidenacetylacetones and arylidenacetoacetic esters with *o*-aminothiophenol and its derivatives in methanol at room temperature, but the reaction proceeded over at least



X = CH_3: Ar = C_6H_5 (**I**), 4-$H_3COC_6H_4$ (**II**), 4-$(H_3C)_2NC_6H_4$ (**III**); X = C_6H_5: Ar = C_6H_5 (**IV**), 4-$H_3COC_6H_4$ (**V**), 4-$(H_3C)_2NC_6H_4$ (**VI**); Ar = C_6H_5 (**VII, X, XIII**), 4-$H_3COC_6H_4$ (**VIII, XI, XIV**), 4-$(H_3C)_2NC_6H_4$ (**IX, XII**).

1 h. The S-adducts isolated were converted into the cyclic dihydro-1,5-benzothiazepine structures [21, 22].

In order to obtain nitrobenzothiazepine structures with phenyl substituent at the C^4 atom, the obtained linear S-adducts **X** and **XI** were heated in alcohol solution in the presence of an acidic agent (methanol, 10 drops of concentrated hydrochloric acid, 1–3 h of reflux). As a result, we isolated 2-aryl-3-nitro-4-phenyl-2,5-dihydro-1,5-benzothiazepines **XIII** and **XIV**, respectively, which can be regarded as the products of isomerization of initially formed 2,3-dihydro-1,5-benzothiazepines. This prototropic transformation is likely to be caused by the ability of the phenyl substituent, in contrast to the methyl group, to participate in conjugation with nitroenamine fragment. We were able to obtain the same compounds **XIII** and **XIV** in a one-pot reaction directly from the corresponding *gem*-benzoylnitrostyrenes **IV** and **V** and *o*-aminothiophenol by boiling the reagents in a methanol solutions for 1–3 h in the presence of hydrochloric acid.

Synthesized cyclic structures **VII–IX, XIII, XIV** and linear S-adducts **X, XI** are fairly stable, colorless or yellowish crystalline substances, with sharp melting points. Only the S-adduct **XII** derived from the *gem*-benzoylnitrostyrene containing dimethylamino group in the *para*-position of benzene ring is unstable, and gradually spontaneously undergoes an intramolecular transformation, which, however, does not lead to benzothiazepine. In this case, the process is accompanied by the release of benzoylnitromethane and the formation of a highly conjugated aromatic system of 2-(4-*N*,*N*-dimethylaminophenyl)benzothiazole (**XV**). In favor of assignment of this structure to compound **XV** speaks the close value of the melting point and spectral characteristics of the synthesized substance with the

Table 1. Yields, melting points, and the data of IR and ^{1}H NMR spectra of dihydro-1,5-benzothiazepines **VII–IX, XIII, XIV** and S-adducts **X–XII**

Comp. no.	Yield, %	mp, °C	IR spectra[a] ($CHCl_3$), ν, cm^{-1}			^{1}H NMR spectra ($CDCl_3$), δ, ppm (*J*, Hz)				
			NO_2 (NOO^-)	C=O (C=N) [C=C, $C=N^+$]	NH_2 (NH^+)	H_A (H)	H_B	CH_3 (OCH_3) [NCH_3]	Ar	NH_2 (NH^+)
VII	81	136–137	1560, 1360	(1645)	–	5.52 d Δδ 0.25 $^3J_{AB}$ 11.90	5.27 d	2.44 s	7.17–7.58 m	–
VIII	98	132–134	1560, 1360	(1645)	–	5.45 d Δδ 0.20 $^3J_{AB}$ 11.90	5.25 d	2.43 s (3.76 s)	6.79 d, 7.11 d, 7.20 t, 7.29 d, 7.52 t, 7.57 d	–
IX	98	144–146	1560, 1360	(1645)	–	5.46 d Δδ 0.23 $^3J_{AB}$ 11.90	5.23 d	2.43 s [2.91 s]	6.57 d, 7.03 d, 7.18 t, 7.28 d, 7.50 t, 7.58 d	–
X	98	124–126	1560, 1355	1695	3480, 3375	6.74 d Δδ 1.57 $^3J_{AB}$ 11.29	5.17 d	–	6.43 t, 6.61 d, 6.74 d, 7.06 t, 7.22 m, 7.59 t, 7.72 t, 8.18 d	4.08 s
XI	80	104–106	1560, 1355	1695	3480, 3375	6.67 d Δδ 1.54 $^3J_{AB}$ 11.29	5.13 d	(3.77 s)	6.44 t, 6.61 d, 6.77 d.d, 7.07 t, 7.14 d, 7.58 t, 7.71 t, 8.16 d	4.11 s
XII[b]	80	102–104	1560, 1360	1695	3480, 3375	6.68 d Δδ 1.58 $^3J_{AB}$ 11.29 6.66 d Δδ 1.62 $^3J_{AB}$ 11.29	5.10 d 5.04 d	[2.92 s] [2.81 s]	6.37–7.14 m, 6.57 m, 7.08 m, 7.38–8.17 m	4.10 s 4.18 s
XIII	57 (32[c])	161–163	(1125–1295)	[1630]	3330	(6.30 s)	–	–	6.82–7.60 m	(6.48 s)
XIV	40 (51[c])	147–149	(1180–1290)	[1610]	3390	(6.24 s)	–	(3.68 s)	6.60–7.60 m	(6.45 s)

[a] IR spectrum of sompound **XIII** was taken from KBr pellets. [b] Compound **XII** was isolated as a mixture of diastereomers in a ratio a:b = 2.5:1, in the 1H NMR spectrum the signals of the H_A and H_B protons of the "a" isomer are shifted downfield compared to "b." [c] In parentheses are given the yields of compounds **XIII** and **XIV** obtained by one-pot technique.

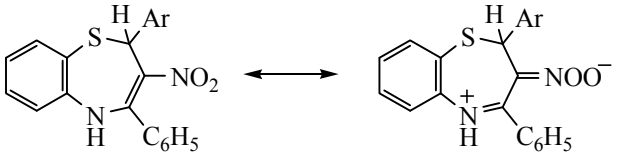
corresponding parameters of the sample described previously in the literature and obtained by another method [23].

The composition and structure of the first synthesized compounds were confirmed by elemental analysis, IR, UV, ^{1}H NMR and ^{13}C NMR spectroscopy (Tables 1 and 2). Thus, the IR spectra of 3-nitro-2,3-dihydro-1,5-benzothiazepines **VII–IX** and S-adducts **X–XII** contain strong absorption bands of stretching vibrations of nonconjugated nitro group (1560, 1355–1360 cm^{-1}). In the IR spectra of compounds with linear structure **X–XII** there are the absorption bands of the carbonyl function (1695 cm^{-1}) and of the primary amino group (3480 cm^{-1}, 3375 cm^{-1}). The stretching vibrations of C=N bond give rise to the absorption band at 1645 cm^{-1} in the spectra of 2,3-dihydro-1,5-benzothiazepine systems **VII–IX**.

Table 2. The data of ^{13}C NMR spectra of compounds **VII–XI** ($CDCl_3$, δ, ppm)

Comp. no.	CH_A	CH_B	C=O (C=N)	CH_3 (Ar)	OCH_3 [$N(CH_3)_2$]
VII	90.98	58.70	(162.76)	21.99 (120.50, 124.56, 126.39, 126.60, 129.02, 129.23,131.04, 135.28, 139.89,150.09)	–
VIII	91.30	58.43	(162.68)	22.05 (114.49, 120.59, 121.68, 124.54, 126.54, 127.69, 130.93, 132.11, 135.24, 150.00, 159.90)	55.38
IX	91.46	59.01	(162.74)	22.09 (112.41, 121.00, 124.44, 126.29, 126.41, 127.29, 130.67, 135.30, 150. 00, 150.04, 150.70)	[40.41]
X	89.34	51.09	186.31	(112.85, 115.26, 118.33, 128.20, 128.76, 129.17, 129.35, 129.73, 131.64, 135.22, 149.94)	–
XI	89.66	50.71	186.25	(113.04, 114.00, 115.22, 118.31, 128.07, 129.14, 129.33, 129.48, 129.58, 129.67, 131.58, 134.82, 135.16, 138.23, 149.96, 159.59)	55.36

The IR spectra of 3-nitro-2,5-dihydro-1,5-benzothiazepines **XIII** and **XIV** of the nitroenamine structure differ substantially from the IR spectra of 3-nitro-2,3-dihydro-1,5-benzothiazepines **VII–IX**. They do not contain the characteristic bands of a covalent nitro group, while there are strong absorption bands at 1125–1295 cm^{-1} of ionized nitro group and a set of multiple bands of C=C and $C=N^+$ bonds at 1610–1630 cm^{-1}. Such spectral pattern indicates a high polarization of the molecules due to the involvement of the nitro and amino groups and of their significant contribution into the bipolar structure of the ground state. The data of electronic spectroscopy do not contradict these findings. Thus, in the electronic spectra of 2,5-dihydro-1,5-benzothiazepines **XIII** and **XIV** dissolved in ethanol there are long-wavelength absorption band at 395 nm (ε 8700) and 394 nm (ε 6800) typical of nitroenamines [24].



XIII, XIV

The ^1H NMR spectra of linear S-adducts **X** and **XI** taken immediately after dissolving in chloroform-*d*, indicate that these substances are individual diastereomers. For example, in the ^1H NMR spectrum of compound **X** there are two distinct doublets of methine protons of H_A and H_B at 6.74 and 5.17 ppm, respectively (Δδ = 1.57 ppm) with a spin-spin coupling constant $^3J(H_AH_B)$ = 11.29 Hz; the protons of NH_2 groups give rise to a singlet at 8.4 ppm. However, after keeping the solution of compound **X** for two days, the doubling of methine proton signals occurs in the spectrum, indicating the appearance of a second diastereomer [H_A, δ = 6.73, H_B, δ = 5.12 ppm, Δδ = 1.61 ppm, $^3J(H_AH_B)$ = 11.29 Hz]. Likewise behaves compound **XI** dissolved in $CDCl_3$, which originally was diastereomerically uniform. In contrast to compounds **X** and **XI**. the S-adduct **XII** is formed, according to ^1H NMR spectra, at once as a mixture of diastereomers in a ratio of a:b = 2.5:1.

In the ^1H NMR spectra of 2,3-dihydro-1,5-benzothiazepines **VII–IX**, taken from the solutions in chloroform-d_1, same as in the spectra of linear S-adducts, there are two doublet signal of H_A and H_B protons at 5.45–5.52 and 5.23–5.27 ppm respectively (Δδ 0.20–0.25 ppm) with a spin-spin coupling constant $^3J(H_AH_B)$ = 11.90 Hz; to the protons of methyl groups (C^4–CH_3) correspond singlets at 2.43–2.44 ppm. In contrast to 2,3-dihydro-1,5-benzothiazepines **VII–IX,** in the ^1H NMR spectra of 2,5-dihydro-1,5-benzothiazepines **XIII** and **XIV** the signals of methine protons of the heterocycle appear at 6.30 and 6.24 ppm, and the signals at 6.48 and 6.45 ppm belong to the protons of NH groups in the two compounds, respectively (in the case of compounds **VII–IX** they are absent).

In the ^{13}C–{^1H} NMR spectra of linear S-adducts **X** and **XI** the signal of the carbonyl carbon atom appears at 186 ppm, whereas in the ^{13}C–{^1H} NMR spectra of 2,3-dihydro-1,5-benzothiazepines **VII–IX** the most downfield signal occurs at ~163 ppm and can be attributed to the carbon of C=N group. The signals of carbon atoms of CH_A and CH_B fragments appear at 90.98–91.46 and 58.43–59.01 ppm, respectively (compounds **VII** and **VIII**) and at 89.34–89.66 and 50.71–51.09 ppm, respectively in the case of compounds **X** and **XI**.

The final conclusion on the structure of newly synthesized 2,3-dihydro-1,5-benzothiazepines **VII–IX** containing nitro group was done on the basis of X-ray diffraction data of compound **VII** as a representative of this series (Fig. 1, Table 3). The X-ray diffraction study showed that in the molecule of compound **VII** the seven-membered heterocycle has a distorted *boat* conformation, with the deviation from the plane of the atoms C^3, C^6 and C^7 by 0.599(5), 1.214(7) and 1.226(7) Å, respectively. This conformation, in turn, leads to a lack of conjugation of the C^4–N^5 double bond with the aromatic ring, which is confirmed by the values of bond lengths [C^4–N^5 1.2742(16) Å, N^5–C^6 1.4136(15) Å], and torsion angle $C^4N^5C^6C^7$ 52.64(16)º. The seven-membered rings with similar geometry (up to similarity in bond lengths and bond angles) have been described previously in [25–27]. The location of the substituents at the C^2–C^3 corresponds to staggered conformation: the hydrogen atoms are almost anti-periplanar to each other (torsion angle $H^{2A}C^2C^3H^{3A}$ is 167º) .

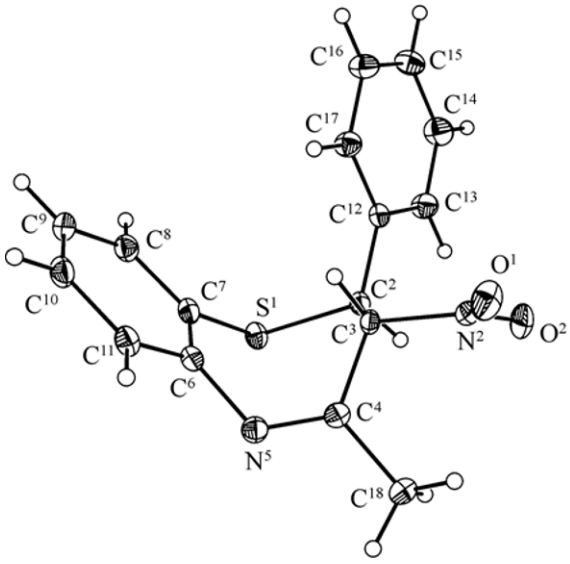


Fig. 1. General view of 4-methyl-3-nitro-2-phenyl-2,3-dihydro-1,5-benzothiazepine **VII** molecule in the representation of atomic thermal vibration ellipsoids (p = 50%).

In the crystal, the molecules are packed along b axis (Fig. 2) due to sufficiently strong CH···O interaction between C^2–H^{2A} group and the oxygen atom of the nitro group (2.36 Å), as well as due to a short contact between the electron pair of the sulfur atom and the π-density of benzothiazepine ring (the shortest S···C contact is 3.48 Å).

Summing up, it should be noted that the reaction of *gem*-acylnitroethenes with *o*-aminothiophenol should be regarded as a convenient preparative method for the synthesis of new 2,3- and 2,5-dihydro-1,5-benzothiazepine structures containing nitro group. The synthesized compounds can be recommended for further study as potential biologically active substances. Currently, in medical practice pharmaceuticals are widely used that contain the benzothiazepine heterocycle in the molecules of active substances. These are, for example, dilthiazem, showing anthianginal, antihypertensive and anthiarrhythmic action, quethiapine, belonging to neuroleptics, etc. [28, 29]. High medical significance of these drugs implies the need for comprehensive studies aimed at developing new methods of synthesis of the thiazepine structures, as well as expanding the range of their derivatives.

Table 3. Selected geometric parameters [bond lengths (d, Å) and bond angles (ω, deg)] of compound **VII**

Bond	d	Bond angle	ω	Bond angle	ω
S^1–C7	1.7692(12)	$C^7S^1C^2$	102.21(5)	$N^5C^4C^3$	121.31(10)
S^1–C^2	1.8391(12)	$C^{12}C^2C^3$	114.26(9)	$C^{18}C^4C^3$	118.37(10)
O^1–N^2	1.2276(14)	$C^{12}C^2S^1$	112.57(8)	$C^4N^5C^6$	119.69(10)
O^2–N^2	1.2176(14)	$C^3C^2S^1$	108.40(8)	$C^{11}C^6C^7$	119.64(11)
C^2–C^{12}	1.5102(15)	$O^2N^2O^1$	124.53(11)	$C^{11}C^6N^5$	118.66(10)
C^2–C^3	1.5262(16)	$O^2N^2C^3$	119.36(10)	$C^7C^6N^5$	121.58(11)
N^2–C^3	1.5141(15)	$O^1N^2C^3$	116.06(10)	$C^8C^7C^6$	119.43(11)
C^3–C^4	1.5331(15)	$N^2C^3C^2$	110.21(9)	$C^8C^7S^1$	119.66(9)
C^4–N^5	1.2742(16)	$N^2C^3C^4$	108.47(9)	$C^6C^7S^1$	120.83(9)
N^5–C^6	1.4136(15)	$C^2C^3C^4$	113.72(9)	$C^9C^8C^7$	120.49(11)
C^6–C^7	1.4080(16)	$N^5C^4C^{18}$	120.32(10)	$C^8C^9C^{10}$	119.93(11)

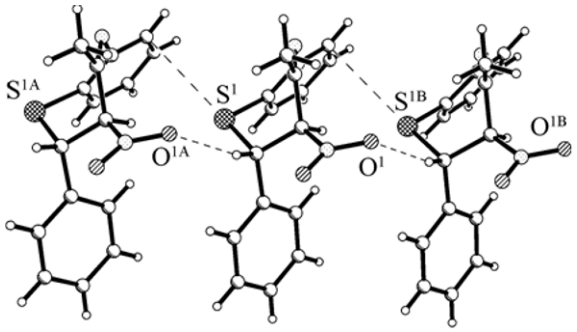


Fig. 2. Fragment of crystal packing of compound **VII**, illustrating the C–H···O bonding and S···π interaction.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Jeol JNM-ECX400A spectrometer with operating frequencies 100.53 (^{13}C) and 399.78 (^{1}H) MHz from the samples in chloroform-d_1 using the residual signal of undeuterated solvent as an internal reference. The IR spectra were obtained on a Shimadzu IR Prestige-21 Fourier spectrometer (from solutions in chloroform, *c* 0.1–0.001 M, and pellets with KBr). The electron absorption spectra were recorded on a SHIMADZU UV-2401 PC spectrophotometer, ethanol was used as the solvent. The elemental analysis was performed on the analyzer EuroVector (EA 3022 CHN Dual).

X-ray diffraction analysis of compound VII. Crystals of **VII** for X-ray analysis were grown from a solution in diethyl ether, $C_{16}H_{14}N_2O_2S$ (M = 298.35), at 100 K monoclinic, space group $P2_1/c$; a = 14.2490(12) Å, b = 5.5159(5) Å, c = 18.3825(15) Å, β = 96.9715(17)°, V = 1434.1(2) Å^3, Z = 4 (Z' = 1), d_{calc} = 1.382 g cm^{-3}, μ(MoK_α) = 1.70 cm^{-1}, F(000) = 624. The intensities of 10859 reflections were measured on a Bruker Smart Apex II CCD diffractometer [μ(MoK_α) = 0.71072 Å, ω-scanning, 2θ < 58°], 3809 independent reflections (R_{int} = 0.0305) were used in further refinement. The structure was solved by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation on F^2_{hkl}. The positions of the hydrogen atoms were calculated from the geometric considerations and refined with fixed thermal parameters U_{iso} equal to 1.2C_{iso} in the isotropic approximation. The final value of the factors of uncertainty: R_1 = 0.0345 [calculated from F_{hkl} for 3313 reflections with $I > 2\sigma(I)$], wR_2 = 0.0998 (calculated on F^2_{hkl} for all 3809 independent reflections), GOF = 1.005. The calculations were performed using the program package SHELXTL 5.10 [30]. Atomic coordinates, bond lengths and angles, and anisotropic displacement parameters are deposited in the Cambridge structural data base, no. 805415.

Synthesis of the initial *gem*-acylnitrostyrenes **I–VI** was carried out using the methods described in [11, 31]. *o*-Aminothiophenol was obtained by the procedure in [32].

4-Methyl-3-nitro-2-phenyl-2,3-dihydro-1,5-benzothiazepine (VII). To 0.38 g of 3-nitro-4-phenyl-3-butene-2-one **I** was added 0.25 g of *o*-aminothiophenol dissolved in 10 ml of methanol. After 10 min 0.39 g of colorless crystals of compound **VII** was filtered off. From the mother liquor additionally 0.09 g of substance **VII** was isolated. The total yield of compound **VII** 0.48 g (81%), mp 136–137ºC (from petroleum ether). Found, %: C 64.61, H 4.91, N 9.15. $C_{16}H_{14}N_2O_2S$. Calculated, %: C 64.41, H 4.73, N 9.39.

4-Methyl-2-(4-methoxyphenyl)-3-nitro-2,3-dihydro-1,5-benzothiazepine (VIII). To 0.44 g of 4-(4-methoxyphenyl)-3-nitro-3-buten-2-one **II** was added 0.25 g of *o*-aminothiophenol dissolved in 10 ml of methanol. After 10 min 0.60 g of pale yellow crystals of substance **VIII** was filtered off. From the mother liquor additionally 0.04 g of substance **VIII** was isolated. The total yield of compound **VIII** 0.64 g (98%), mp 132–134ºC (from ethanol). Found, %: N 8.80. $C_{17}H_{16}N_2O_3S$. Calculated, %: N 8.53.

2-(4-*N,N*-Dimethylaminophenyl)-4-methyl-3-nitro-2,3-dihydro-1,5-benzothiazepine (IX). To 0.47 g of (4-*N,N*-dimethylaminophenyl)-3-nitro-3-buten-2-one **III** was added 0.25 g of *o*-aminothiophenol dissolved in 10 ml of methanol. After 15 minutes 0.65 g of pale orange crystals of substance **IX** was filtered off. From the mother liquor 0.02 g of compound **IX** was additionally isolated. The total yield of compound **IX** 0.67 g (98%), mp 144–146ºC (from ethanol). Found, %: N 12.01. $C_{18}H_{19}N_3O_2S$. Calculated, %: N 12.31.

3-(2-Aminophenylsulfanyl)-1,3-diphenyl-2-nitropropan-1-one (X). To 0.51 g of 1,3-diphenyl-2-nitro-2-propen-1-one **IV** was added 0.25 g of *o*-aminothiophenol dissolved in 10 ml of methanol. After 10 min 0.69 g of light yellow crystals of substance **X** was filtered off. From the mother liquor an additional 0.05 g portion of compound **X** was isolated. The total yield of substance **X** 0.74 g (98%), individual diastereomer, mp 124–126ºC (from ethanol). Found, %: C 67.07, H 4.86, N 7.15. $C_{21}H_{18}N_2O_3S$. Calculated, %: C 66.65, H 4.79, N 7.40.

3-(2-Aminophenylsulfanyl)-3-(4-methoxyphenyl)-2-nitro-1-phenylpropan-1-one (XI). To 0.57 g of 3-(4-methoxyphenyl)-2-nitro-1-phenyl-2-propen-1-one **V** was added 0.25 g of *o*-aminothiophenol dissolved in 10 ml of methanol. After 20 min 0.61 g of light yellow crystals of substance **XI** was filtered off. From the mother liquor an additional 0.04 g portion of substance **XI** was isolated. The total yield of compound **XI** 0.65 g (80%), individual diastereomer, mp 104–106ºC (from ethanol). Found, %: C 64.96, H 5.04, N 6.66. $C_{22}H_{20}N_2O_4S$. Calculated, %: C 64.69, H 4.94, N 6.86.

3-(2-Aminophenylsulfanyl)-3-(4-*N,N*-dimethylaminophenyl)-2-nitro-1-phenylpropan-1-one (XII). To 0.59 g of 3-(4-N,N-dimethylaminophenyl)-2-nitro-1-phenyl-2-propen-1-one **VI** was added 0.25 g of *o*-aminothiophenol dissolved in 10 ml of methanol. After 10 min 0.63 g of light orange crystals of substance **XII** was filtered off. From the mother liquor an additional 0.04 g portion of compound **XII** was isolated. The total yield of substance **XII** 0.67 g (80%), a mixture of diastereomers at a ratio of a:b = 2.5:1, mp 102–104ºC (from ethanol).

2,4-Diphenyl-3-nitro-2,5-dihydro-1,5-benzothiazepine (XIII). *a*. To a suspension of 0.13 g of 3-(2-aminophenylsulfanyl)-1,3-diphenyl-2-nitropropan-1-one **X** in 5 ml of methanol was added 10 drops of concentrated hydrochloric acid, the reaction solution was heated for 3 h and then poured into a Petri dish. After evaporation of the solvent, the residue was treated with ethanol. 0.07 g (57%) of yellow fine-grained compound **XIII** was obtained, mp 161–163ºC (from ethanol). Found, %: N 7.42. $C_{21}H_{18}N_2O_2S$. Calculated, %: N 7.77.

b. To a mixture of 0.51 g of 1,3-diphenyl-2-nitro-2-propen-1-one **IV**, 0.25 g of *o*-aminothiophenol, and 10 ml of methanol was added 10 drops of concentrated hydrochloric acid, the reaction solution was heated for 3 h and then poured into a Petri dish. The residue after solvent evaporation was treated with ethanol. 0.23 g (32%) of yellow fine-grained substance **XIII** was isolated, mp. 161–163ºC (from ethanol). The mixed sample with the compound synthesized by the method *a* showed no melting point depression.

2-(4-Methoxyphenyl)-3-nitro-4-phenyl-2,5-dihydro-1,5-benzothiazepine (XIV). *a*. To a suspension of 0.29 g of 3-(2-aminophenylsulfanyl)-3-(4-methoxyphenyl)-2-nitro-1-phenylpropan-1-one **XI** in 15 ml of methanol was added 15 drops of concentrated hydrochloric acid, the reaction solution was refluxed for 50 min and then poured into a Petri dish. After evaporation of the solvent the residue was treated with ethanol. 0.11 g (40%) of yellow fine-grained material **XIV** was obtained, mp 147–149ºC (from ethanol). Found, %: C 67.44, H 4.74, N 6.92. $C_{21}H_{18}N_2O_3S$. Calculated, %: C 67.67, H 4.65, N 7.17.

b. To a mixture of 0.57 g of 3-(4-methoxyphenyl)-2-nitro-1-phenyl-2-propen-1-one **V**, 0.25 g of *o*-aminothiophenol, and 10 ml of methanol was added 10 drops of concentrated hydrochloric acid, and the reaction solution was refluxed for 50 min and then poured into a Petri dish. The residue after solvent evaporation was treated with ethanol. 0.40 g (51%) of yellow fine-grained material **XIV** was isolated, mp 147–149ºC (from ethanol). The mixed sample with the substance synthesized by the method *a* showed no melting point depression.

2-(4-*N,N*-dimethylaminophenyl)benzothiazole (XV). Solid 3-(2-aminophenylsulfanyl)-3-(4-*N,N*-dimethylaminophenyl)-2-nitro-1-phenylpropan-1-one **XII** when stored for ~2 weeks at room temperature, slowly became a semi-solid mass with colorless needles of nitroacetophenone, mp 98–100ºC, mixing the sample with an authentic sample showed no melting point depression. After treating the mass with acetone pale orange crystals of substance **XV** were isolated, mp 176–178ºC (from ethanol), published data: mp 174–175ºC [23]. Found, %: C 70.49, H 5.64, N 10.71. $C_{15}H_{14}N_2S$. Calculated, %: C 70.83, H 5.55, N 11.01.

REFERENCES

1. Orlov, V.D, Kolosov, M.A., Kotlyar, V.N. Marrugo Gonzalez, A.Kh., Sidorenko, D.Yu., Pushkarev, A.P., and Baraban, A.Yu., in *Korshunovskie chteniya* (Korshunov Readings), All-Russian Scientific and Practical Conf., Tol'yatti, 2008, p. 11.
2. Shikhaliev Kh.E., Falaleev, A.V., and Kryl'skii, D.V., *Izbrannye metody sinteza i modifikatsii geterocyclov* (Selected Methods of Synthesis and Modification of Heterocycles), Kartsev, V.G., Ed., Moscow: IBS Press, 2003, vol. 1, p. 450.
3. Desenko, S.M., Chebanov, V.A., Kolos, N.N., and Orlov, V.D., *Izbrannye metody sinteza i modifikatsii geterocyclov* (Selected Methods of Synthesis and Modification of Heterocycles), Kartsev, V.G., Ed., Moscow: IBS Press, 2003, vol. 1, p. 140.
4. Desenko, S.M. and Orlov, V.D., *Azageterotsikly na osnove aromaticheskikh nepredel'nykh ketonov* (Aza-Heterocycles Based on Aromatic Unsaturated Ketones), Khar'kov: Folio, 1998.

5. Baichurin, R.I., Aboskalova, N.I., Berkova, G.A., and Berestovitskaya, V.M., *Zh. Org. Khim*., 2009, vol. 45, no. 8, p. 1196.
6. Remennikov, G.A., *Khim. Geterotsikl. Soedinin*., 1997, no. 12, p. 1587.
7. Bakhareva, S.V., Aboskalova, N.I., and Berestovitskaya, V.M., *Zh. Obshch. Khim.,* 2001, vol. 71, no. 9, p. 1577.
8. Aboskalova, N.I., Berestovitskaya, V.M., Bakhareva, S.V., and Fel'gendler, A.V., *Khim. Geterotsikl. Soedin*., 2002, no. 10, p. 1462.
9. Berestovitskaya, V.M., Aboskalova, N.I., Ishmaeva, E.A., Bakhareva, S.V., Berkova, G.A., Vereshchagina Ya.A., Fel'gendler, A.V., and Fattakhova, G.R., *Zh. Obsch. Khim*., 2001, vol. 71, p. 2049.
10. Aboskalova, N.I., Smirnova, N.N., Kataeva, O.N., Baichurin, R.I., Fel'gendler, A.V., Berkova, G.A., and Berestovitskaya, V.M., *Zh. Obsch. Khim*., 2008, vol. 78, no. 9, p. 1478.
11. Fel'gendler, A.V., Aboskalova, N.I., and Berestovitskaya, V.M., *Zh. Obsch. Khim*., 2000, vol. 70, no. 7, p. 1158.
12. Cram, D.J. and Hammond, G.S., *Organicheskaya khimiya* (Organic Chemistry), Moscow: Mir, 1964, p. 288.
13. Morrison, R.T. and Boyd, R.N., *Organicheskaya khimiya* (Organic Chemistry), Moscow: Mir, 1974, p. 600.
14. Saikes, P., *Reaction Mechanism in Organic Chemistry*, Moscow: Khimiya, 2000, p. 107.
15. Khanna, M.S., Kumar, D., Garg, C.P., and Kapoor, R.P., *Indian. J. Chem., Sect., B*., 1995, vol. 34, no. 4, p. 333.
16. Orlov, V.D., Kolos, N.N., and Ruzhitskaya, N.N., *Khim. Geterotsikl. Soedin*., 1983, no. 12, p. 1638.
17. Gupta, A.K., Singh, V.K., and Pant, U.C., *Indian. J. Chem., Sect., B*., 1983, vol. 22, no. 10, p. 1057.
18. Stephens, W. and Field, L., *J. Org. Chem*., 1959, vol. 24, no. 10, p. 1576.
19. Khatik, G.L., Sharma, G., Kumar, R., and Chakraborty, A.K., *Tetrahedron*, 2007, vol. 63, no. 5, p. 1200.
20. Sharma, G., Kumar, R., and Chakraborty, A.K., *Tetrahedron Lett*., 2008, vol. 49, no. 27, p. 4272.
21. Wang, L., Zhang, P., Zhang, X., Zhang, Y., Li, Y., and Wang, Y., *Eur. J. Med. Chem*., 2009, vol. 44, no. 7, p. 2815.
22. Li, W., Lan, J., Li, C., Cao, Y., Wang, H., Wang, L., Zhang, P., Wang, Y., and Li, Y., *Acta Chimica Sinica (Huaxue Xuebao),* 2009, vol. 67, no. 23, p. 2732.
23. Shirinyan, V.Z., Melkova, S.Yu., Belen'kii, L.I., Krayuskhin, M.M., *Izv. Akad. Nauk, Ser. Khim*., 2000, no. 11, p. 1887.
24. Rajappa, S., *Tetrahedron*, 1999, vol. 55, no. 23, p. 7065.
25. Kumar, R.R. and Perumal, S., *Tetrahedron*, 2007, vol. 63, no. 33, p. 7850.
26. Parvez, M., Umbreen, S., Ansari, F.L., *Acta Cryst., Sect., C.,* 2003, vol. 59, no. 6, p. o298.
27. Sathunuru, R., Koh, B., Zhang, H., and Biehl, E., *Heterocycles*, 2005, vol. 65, no. 10, p. 2493.
28. Mashkovskii, M.D., *Lekarstvennye sredstva* (Drugs), Moscow: RIA "Novaya Volna," 2007, pp. 72, 433.
29. *Registr lekarstvennykh sredstv Rossii. Encyclopediya lekarstv* (Register of Drugs of Russa. Encyclopedia of Drugs), "RLS-2002," 2002, vol. 9, pp. 298, 411.
30. Sheldrick, G.M., *Acta Cryst., Sect. A,* 2008, vol. 64, no. 1, p. 112.
31. Sokolov, N.A., Tishchenko, I.G., Karpitskaya, N.V., and Grinkevich, V.G., *Vestn. Bel. Gos. Univ*., 1978, no. 3, p. 29.
32. *Metody polucheniya khimicheskikh reagentov i preparatov* (Methods of Obtaining Chemical Reagents and Preparations), Moscow: IREA, 1964, vol. 9, p. 26.