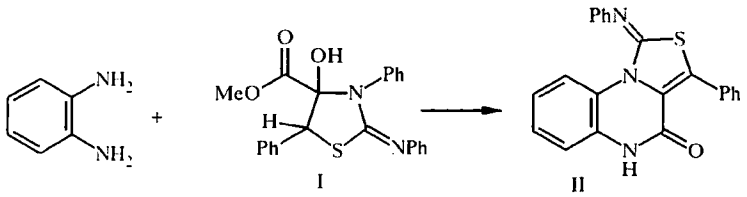
Chemistry of Heterocyclic Compounds, Vol.35, No. 12, 1999

3-ARYL-1-IMINO-4-OXO-4,5-DIHYDROTHIAZOLO-[3,4-*a*]QUINOXALINES. RETROSYNTHETIC APPROACH

V. A. Mamedov, A. A. Kalinin, A. T. Gubaidullin, I. Z. Nurkhametova, I. A. Litvinov, and Ya. A. Levin

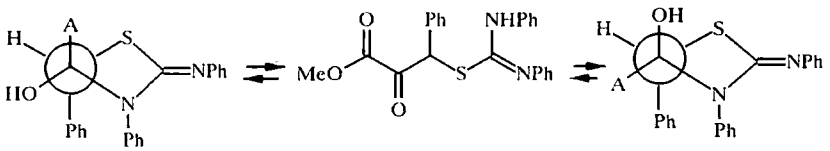
Methods of constructing condensed tricyclic 3-aryl-1-imino-4-oxo-4,5-dihydrothiazolo[3,4-a]quinoxaline systems has been effected from 3-(α-chlorobenzyl)quinoxalin-2-ones through 3-(α-isothioureidobenzyl)- and 3-(α-thiocyanatobenzyl)quinoxalin-2-ones.

On reacting *o*-phenylenediamine with 4-hydroxy-4-methoxycarbonyl-3,5-diphenyl-2-phenylimino-thiazolidine (I) in boiling acetic acid, condensation occurs with the elimination of aniline and formation of the thiazolinoquinoxaline system II [1].



I II

We were unsuccessful in directly confirming the thiazolidino-isothioureido tautomerism by means of a set of spectral methods, however hydroxythiazolidine I was established to exist in solution as a mixture of diastereomers Iα and Iβ between which equilibrium is established slowly being realized most likely *via* the open chain isothioureide structure (III) [2].

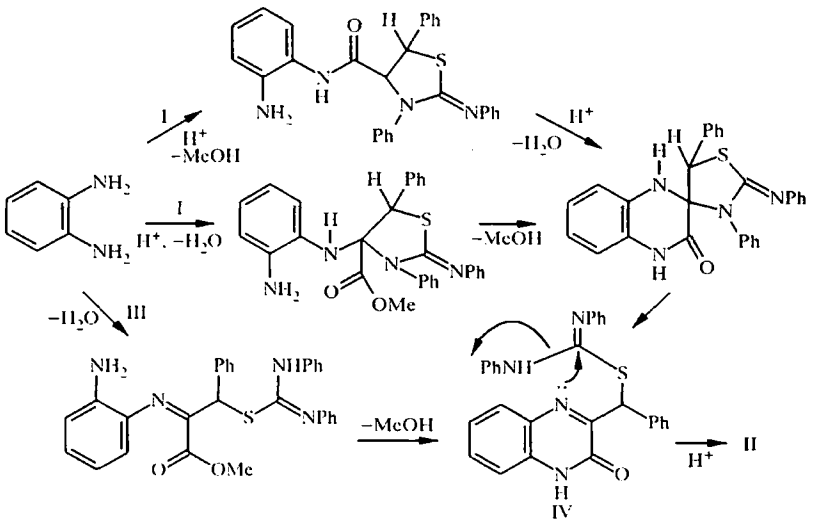


Iα III Iβ

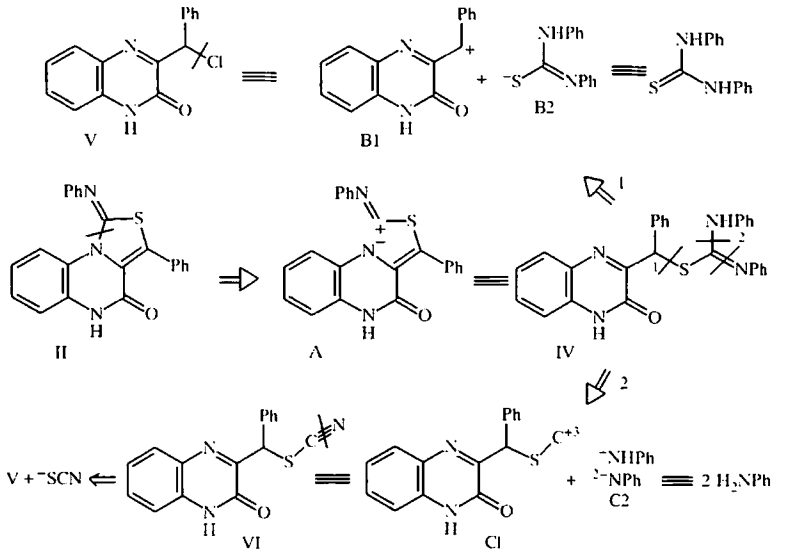
Consequently, when analyzing the possible routes of formation of thiazolinoquinoxaline II, both the thiazolidine (I) and the isothioureido (III) tautomers of the initial compound must be considered as responsible for its formation. It is easy to see that the both tautomers lead to the same intermediate IV, from which the final product II is formed. This intermediate is cyclized in acidic medium as a result of nucleophilic attack of the $N_{(4)}$ atom on the electrophilic carbon atom of the isothiourea group.

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences, Kazan 420088, Russia; e-mail: mamedov@glass.ksu.ras.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1664-1680, December, 1999. Original article submitted August 5, 1998.

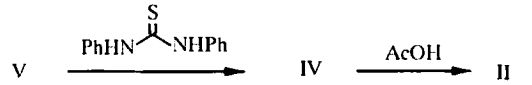
0009-3122/99/3512-1459$22.00©1999 KluwerAcademic/Plenum Publishers



Retrosynthetic analysis [3,4] shows that the structure of thiazolinoquinoxaline II is formed from a quinoxaline derivative, *viz.* 3-(α-chlorobenzyl)quinoxalin-2-one (V) through synthon A, the synthetic equivalent of which is the isothioureide derivative of quinoxaline (IV). For this, as follows from the retrosynthetic scheme, it is possible to use either synthons B1 and B2, and as their synthetic equivalents compound V and N,N'-diphenylthiourea (strategy 1), or synthons C1 and C2, the synthetic equivalents of which are thiocyanate VI and aniline (strategy 2). Compound V and potassium thiocyanate may be the precursors of thiocyanate VI.



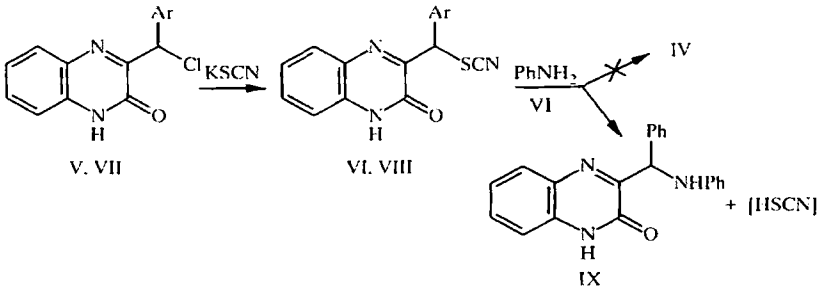
The present report is devoted to bringing about this possibility, i.e. the synthesis of tricyclic condensed heterocycles of the type II starting from quinoxaline derivatives, and to investigation of the products obtained. In reality the interaction of 3-(α-chlorobenzyl)quinoxalin-2-one (V) with N,N'-diphenylthiourea gives compound IV. The latter, as suggested, closes the thiazoline ring with elimination of aniline on boiling in acetic acid. Thiazolinoquinoxaline II is formed identical with the product obtained previously under the same conditions in the reaction of hydroxythiazolidine (I) with *o*-phenylenediamine.



Therefore strategy 1 has been put into effect.

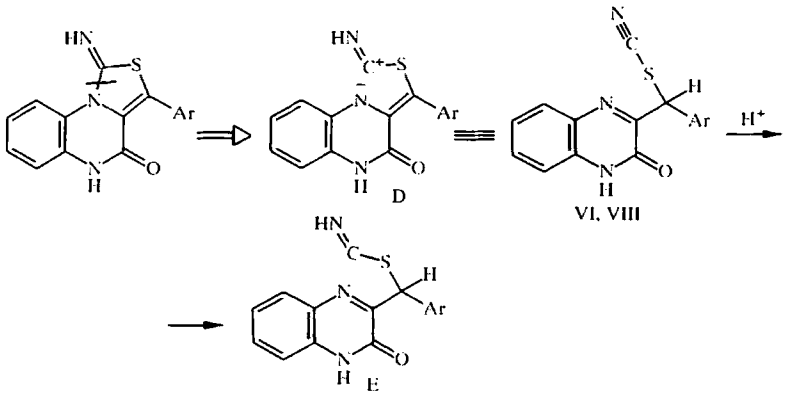
The realization of strategy 2 proved to be more complex, but also more productive. Interaction of chloro compound V with potassium thiocyanate (rhodanide) in dimethyl sulfoxide solution at room temperature led to replacement of chlorine atom by the thiocyanate group and almost quantitative preparation of thiocyanate VI, without contamination by the isomeric isothiocyanate judging from the spectral data. The nitro-substituted thiocyanate VIII was also obtained from the *m*-nitro-substituted in the benzyl group (compound VII) analog of chloro compound V. The structure of thiocyanates VI and VIII, in addition to the elemental composition (Table 1), was confirmed by the presence of intense thiocyanate absorption band ν_{SCN} 2163 cm^{-1} in their IR spectra, and by displacement of the singlet signal of the methine proton of the benzyl group in the ^1H NMR spectrum (Table 2) towards high field in comparison with the initial α-chloro derivatives. This is due to replacement of the chlorine atom by the less electron-accepting thiocyanate group (for example, 6.53 ppm for 3-(α-chlorobenzyl)quinoxalin-2-one V and 6.05 ppm for 3-(α-thiocyanatobenzyl)quinoxalin-2-one VI; an analogous picture was observed for the pair of compounds VII and VIII).

It turned out that another reaction pathway successfully competed with the addition of aniline to thiocyanate VI required to bring about synthetic strategy 2. Substitution of the pseudohalogen rhodanide group occurred in good yield and 3-(α-anilinobenzyl)-quinoxalin-2-one IX was formed. This was confirmed by the absence of sulfur in the reaction product and by spectral data (Tables 1, 2).



V, VI Ar = Ph; VII, VIII *m*-$O_2NC_6H_4$

Nonetheless we succeeded in effecting an alternative strategy for constructing the 3-aryl-1-imino-4,5-dihydrothiazolo[3,4-a]quinoxalin-2-one system from 3-(α-chlorobenzyl)quinoxalin-2-ones through the synthon C1 in accordance with the following retrosynthetic scheme:



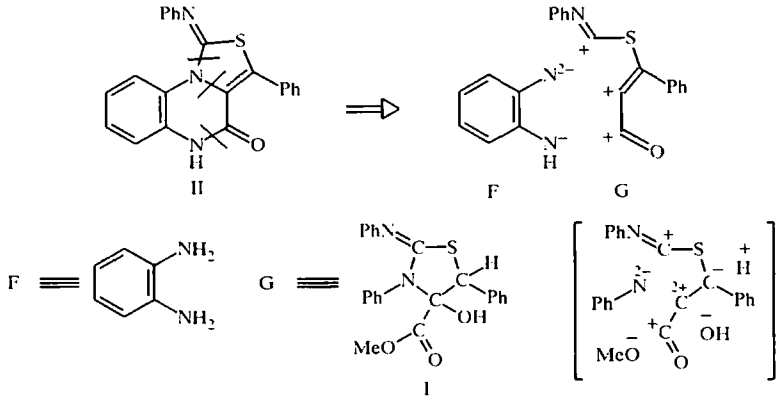
VI, X Ar = Ph; VIII, XI *m*-$O_2NC_6H_4$

This scheme reminds us that treatment of thiocyanates of type VI and VIII with strong acid may lead to their isomerization by closing the thiazoline ring *via* preliminary protonation of the nitrogen atom of the thiocyanate group and the formation of compound E, which is the synthetic equivalent of synthon D for the desired

tricyclic compounds X, XI. In reality, brief boiling of thiocyanate VI in hydrochloric acid enabled this isomerization practically quantitatively and to obtain hydrochloride XII and the tricyclic compound X itself. The nitrotricyclic compound XI and its hydrochloride XIII were obtained under the same conditions from nitrothiocyanate VIII.

Thus, if the 3-aryl-1-iminothiazoline fragment is considered to be a retron for the desired tricyclic molecules regardless of the substituent at the imine nitrogen atom, the strategy 2 of the multistrategy approach discussed above should be considered as being realized since synthon D is a variant of synthon C1. Being a supraretron, the 1-imino-4-oxo-4,5-dihydrothiazolo[3,4-*a*]pyrazine system, which includes the 1-iminothiazoline fragment as a basic (minimal) retron, provides a smooth and efficient course for cyclization in accordance with strategy 2.

Returning to the synthesis of tricyclic compound II substituted at the imine nitrogen atom from 4-hydroxy-2-phenyliminothiazolidine I and *o*-phenylenediamine [1], we note that in the language of retrosynthetic analysis [3,4] this variant of our multistrategy approach for the construction of a condensed 3-aryl-1-imino-4-oxo-4,5-dihydrothiazolo[3,4-a]quinoxaline system (synthetic strategy 3) may be represented as follows:



It is easy to see that strategy 3 for constructing the 3-aryl-1-imino-4-oxo-4,5-dihydrothiazolo[3,4-*a*]-quinoxaline system from a thiazoline fragment is related to strategy 2, being based on an initial quinoxaline fragment, but on bringing about strategy 3 the 3-aryl-1-imino-4-oxo-4,4-dihydrothiazolo[3,4-a]pyrazine system is not a supraretron but a retron. The initial 4-hydroxy-2-phenyliminothiazolidine I contains the chain -C(=NPh)-S-CPh-C-C(=O)-, which is a fragment of this retron (partial retron [3]). This partial retron enters into both the thiazole and the pyrazine components forming the tricyclic compound. The initial thiazolidine ring is broken either at the stage of the ring-chain tautomeric conversion I → III, or on effecting the alternative mechanism at the stage of rearranging the spirocyclic intermediate into compound IV. Part of the initial ring fragment -NPh- is eliminated as aniline at the acid-catalyzed recyclization stage IV → II, regenerating the thiazole structure in the composition of the tricyclic compound.

The appearance of a second low-field singlet signal from the NH group at 9.5 ppm in the ^{1}H NMR spectra of compounds X and XI, in addition to the signal of the lactam proton at about 11.2 ppm also present in the spectra of the initial thiocyanates VI and VIII (12.3-12.4 ppm), and the narrow long-wave ν_{H-N} absorption band at about 3320 cm^{-1} in the IR spectra, in addition to the broad lactam band at approximately 2500-3200 cm^{-1} present in the IR spectra of the initial compounds, indicate the presence of an unsubstituted imino group in the isomerization products.

The isomerization product of thiocyanate VI as a solvated (with DMSO) crystal was investigated by X-ray structural analysis, the data of which (Tables 5-8) confirmed that in reality the isomerization included closing of the thiazoline ring and formation of tricyclic compound X.

The four independent molecules of the tricyclic compound in the crystal unit cell (Fig. 1) have the same structure. Their geometric parameters do not vary within the limits of experimental error. The bond lengths and valence angles are normal. Regretably, the low precision of determining the geometric parameters of the molecules, caused by the small number of measurements of reflections from the weakly reflecting crystal, did not permit noting

TABLE 1. Characteristics of the Synthesized Compounds

Compound	Empirical formula	Found, % / Calculated, %					mp, °C (solvent)	Yield, %
		C	H	N	S	Cl		
II	$C_{22}H_{15}N_3OS$	71.33 / 71.52	4.08 / 4.09	11.27 / 11.37	8.75 / 8.68	—	301-301.5 (AcOH)	33
IV	$C_{28}H_{21}N_3OS$	72.74 / 72.86	5.12 / 4.57	11.85 / 12.14	7.13 / 6.95	—	150-155 (MeOH)	92
VI	$C_{16}H_{11}N_3OS$	66.18 / 65.51	3.53 / 3.78	14.94 / 14.32	10.64 / 10.93		205-206 (dioxane–2-PrOH, 2:1)	93
VII	$C_{15}H_{10}N_3O_3Cl$	57.57 / 57.07	2.88 / 3.19	13.11 / 13.31	—	10.75 / 11.23	224-226 (dioxane–2-PrOH, 2:1)	83
VIII	$C_{16}H_{10}N_4O_3S$	56.74 / 56.80	3.23 / 2.98	16.35 / 16.56	9.28 / 9.48	—	180-182 (MeCN)	92
IX	$C_{21}H_{17}N_3O$	76.69 / 77.04	5.24 / 5.24	12.83 / 12.84			247-249 (2-PrOH–toluene, 1:1)	79
X	$C_{16}H_{11}N_3OS \cdot 0.25\ C_2H_6OS$	63.00 / 63.34	3.86 / 4.03	12.99 / 13.43	12.01 / 12.81	—	264-266 (decomp.) (DMSO)	99
XI	$C_{16}H_{10}N_4O_3S$	56.86 / 56.80	2.89 / 2.98	16.08 / 16.56	9.08 / 9.48	—	267-270 (DMSO)	99
XII	$C_{16}H_{11}N_3OS \cdot HCl$	58.92 / 58.27	3.99 / 3.67	12.74 / 12.74	9.61 / 9.72	10.22 / 10.75	Decomp. >240 (*)	94
XIII	$C_{16}H_{10}N_4O_3S \cdot HCl$	50.96 / 51.27	3.67 / 2.96	14.62 / 14.95	8.21 / 8.55	8.91 / 9.46	Decomp. >200 (*)	72
XIV	$C_{18}H_{13}N_3O_2S$	64.39 / 64.46	3.25 / 3.91	12.26 / 12.53	8.62 / 9.46	—	344-346 (DMSO)	70
XV	$C_{18}H_{12}N_4O_4S$	56.68 / 56.80	3.44 / 3.18	14.16 / 14.72	8.48 / 8.42	—	344-346 (DMSO)	70
XVI	$C_{16}H_{10}ClN_3OS$	58.89 / 58.63	2.99 / 3.08	13.08 / 12.82	—	10.48 / 10.82	>250 (decomp.) (*)	70
XVII	$C_{16}H_9ClN_4O_3S$	51.97 / 51.55	1.92 / 2.43	15.04 / 15.03	8.59 / 8.60	9.73 / 9.51	>360 (*)	81

* Washed with 2-PrOH.

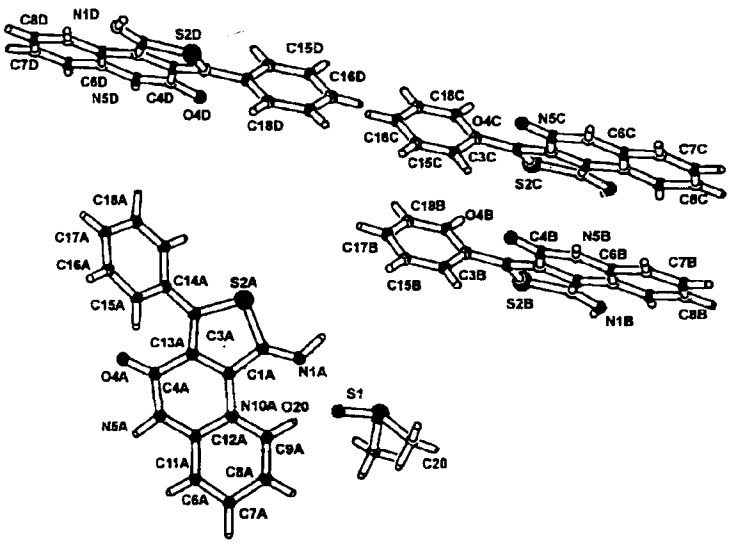
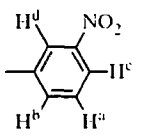


Fig. 1. Geometry of the compound X molecule.

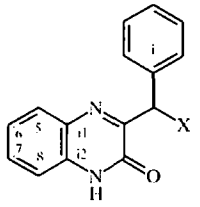
TABLE 2. IR and ^{1}H NMR Spectral Characteristics of the Synthesized Compounds

Compound	IR spectrum, ν, cm^{-1}	PMR spectrum (DMSO-d_6), δ, ppm, J, Hz
II	3200-2700 (NH); 1680 (C=O); 1620 (C=N)	7.45-7.63 (13H, m, $2C_6H_5$, 6-H–8-H); 8.36 (1H, s, 9-H); 11.23 (1H, s, NH)
IV	3280, 3270-2600 (NH); 1670 (C=O); 1625 (C=)	5.84 (1H, s, CH); 6.08-7.99 (20H, m, $3C_6H_5$, quinoxaline, amidine); 10.71 (1H, br. s, NH, lactam)
VI	3180-2500 (NH); 2163 (SCN); 1670 br. (C=O + C=N)	6.05 (1H, s, CH); 6.93-7.83 (9H, m, C_6H_5, quinoxaline); 12.41 (1H, br. s, NH)
VII	3200-2600 (NH); 1670 (C=O); 1600 (C=N); 1520, 1350 (NO_2)	6.42 (1H, s, CH); 6.84-6.93 (2H, m, CH quinoxaline); 7.24-7.33 (2H, m, CH quinoxaline); 7.15 (1H, split t, H^a, $J_{ab} = J_{ac} = J_{ad} = 0.97$); 7.65 (1H, d, H^b $^3J_{ab} = 7.79$); 7.79 (1H, split d, $J_{ac} = 8.35$, H^c $^4J_{cd} = 1.32$); 8.34 (1H, br. s, H^d); 12.55 (1H, s, NH)
VIII	3200-2500 (NH); 2163 (SCN); 1525, 1340 (NO_2), 1665 (C=O); 1615 (C=N)	6.40 (1H, s, CH); 7.20-8.50 (8H, m, C_6H_4, quinoxaline); 12.27 (1H, s, NH lactam)
IX	3415, 3175-2500 (C=N)	6.33 (1H, s, CH); 6.68-8.04 (15H, m, $2C_6H_5$, quinoxaline, H–NPh); 11.48 (1H, br. s, NH)
X	3320 (NH imine); 3180-2600 (NH lactam); 1685 (C=O); 1675 (C=N)	7.13-7.24 (3H, m, 6-H–8-H); 7.46-7.58 (5H, m, C_6H_5); 9.42 (1H, s, NH imine); 9.61 (1H, d, 9-H, $^3J = 8.00$); 11.12 (1H, s, NH lactam)
XI	3325 (NH imine); 3200-2650 (NH lactam); 1687 (C=O); 1615 (C=N); 1525, 1350 (NO_2)	7.15-7.24 (3H, m, HC quinoxaline); 7.77 (1H, t, H^a, $^3J_{ab} = {}^3Jac = 8.25$); 8.00 (1H, d, H^b, $^3J_{ab} = 7.75$); 8.31 (1H, d, H^c, $^3J_{ac} = 8.25$); 8.42 (1H, s, H^d); 9.53 (1H, s, NH imine); 9.62 (1H, d, 9-H, $^3J = 7.75$); 11.19 (1H, s, NH lactam)
XII	3250-2000 (NH, H_2'N=); 1680 (C=O); 1645 (C=N)	7.28-7.68 (8H, m, C_6H_5, 6-H–8-H); 8.22 (1H, d, 9-H, $^3J = 8.25$); 10.36 (3H, br. s, NH lactam, H_2'N=)
XIII	3250-2500 (NH, H_2'N=); 1700 (C=O); 1630 (C=N); 1535, 1360 (NO_2)	7.28-7.68 (3H, m, 6-H–8-H); 7.81 (1H, t, H^a, $^3J_{ab} = {}^3J_{ac} = 7.60$); 8.02 (1H, d, H^b, $^3J_{ab} = 7.60$); 8.12 (1H, d, H^c, $^3J_{ac} = 7.60$); 8.51 (1H, d, 9-H, $^3J = 8.05$); 8.60 (1H, s, H^d); 10.42 (3H, br. s, NH lactam, H_2'N=)
XIV	3180-2600 (NH); 1670 br. (C=O + C=O); 1620 (C=N)	2.45 (3H, s, CH_3); 7.40 (3H, m, 6-H–8-H); 7.43-7.63 (5H, m, C_6H_5); 10.01 (1H, d, 9-H, $^3J = 8.3$); 11.50 (1H, br. s, NH)
XV	3200-2600 (NH); 1700 (MeC=O); 1665 (C=O lactam); 1615 (C=N)	2.47 (3H, s, CH_3); 7.28-7.35 (2H, m, 7-H, 8-H); 7.45 (1H, d, 6-H, $^3J_{67} = 7.60$); 7.84 (1H, t, H^a, $^3J_{ab} = {}^3J_{ac} = 7.90$); 8.09 (1H, d, H^b $J_{ba} = 7.90$); 8.39 (1H, d, H^c, $^3J_{ca}$=7.90); 8.51 (1H, s, H^d); 10.03 (1H, d, 9-H, $^3J_{98} = 8.51$); 11.62 (1H, br. s, NH)
XVI	3180-2600 (NH); 1680 (C=O); 1660 (C=N)	7.21-7.30 (3H, m 6-H–8-H); 7.47-7.63 (5H, m, C_6H_5); 9.05 (1H, d, 9-H, $^3J = 8.25$); 11.28 (1H, s, NH)
XVII	3250-2400 (NH); 1680 (C=O); 1610 (C=N); 1525, 1345 (NO_2)	7.22-7.33 (3H, m, 6-H–8-H); 7.76 (1H, t, H^a, $^3J_{ab} = {}^3J_{ac} = 7.60$); 8.02 (1H, d, H^b, $J_{ba} = 7.70$); 8.31 (1H, d, H^c, $^3J_{ca} = 8.20$); 8.44 (1H, br. s, H^d); 9.04 (1H, d, 9-H, $^3J = 8.80$); 11.50 (1H, br. s, NH)

* 

any fine special features of their spatial structure leading to the crystallographic independence. Further, it is clear that this independence may be the result of differences in the participation of the tricyclic molecule in hydrogen bond formation which also determines the packing of the molecules in the crystal lattice (Fig. 2). A solvated molecule of dimethyl sulfoxide also participates in the formation of the system of hydrogen bonds.

TABLE 3. The ^{13}C NMR Spectral Characteristics of α-Substituted 3-Benzylquinoxalin-2-ones (solution in DMSO + DMSO-d_6, 0.9:1, δ, ppm, *J*, Hz)



X = Cl, SCN

Compound	C=O	C=N	C^{a1}, C^{a2}	C^5, C^8
V	152.64 (d, *J* = 1.4)	156.14 (d, *J* = 4.2)	130.71 (dd, *J* = 6.1; 3.9), 131.53 (dd, *J* = 7.4; 4.7)	114.97 (dd, *J* = 165.1; 8.9); 128.29 (dd, *J* = 162.9; 8.1)
VI	152.26 (br. s)	155.17 (d, *J* = 6.4)	130.37 (dd, *J* = 6.2; 1.7), 131.53 (dd, *J* = 8.2; 6.6)	115.39 (dd, *J* = 165.3; 8.6); 132.25 (dd, *J* = 164.3; 7.2)

Compound	C^6, C^7	Phenyl	Others
V	123.06 (ddd, *J* = 162.3; 11.8; 2.0), 130.42 (d, br. d, *J* = 162.2)	137.13 (split q, *J* = 12.7; 8.6; C'); 127.89 (dt, *J* = 158.2; 8.7; C''); 127.84 (dd, *J* = 159.2; 8.5; C'''); 127.91 (dt, *J* = 157.2; 8.3; C'')	57.26 (dt, *J* = 154.71; 4.24; HCX)
VI	123.40 (ddd, *J* = 164.7; 8.3; 2.7), 130.74 (d, br. d, *J* = 165.1; 8.1)	136.26 (split q, *J* = 6.5; 1.7; C'); 128.15; 128.16; 128.41	54.31 (dt, *J* = 150.43; 4.67; HCX); 112.36 (d, *J* = 3.6, SCN)

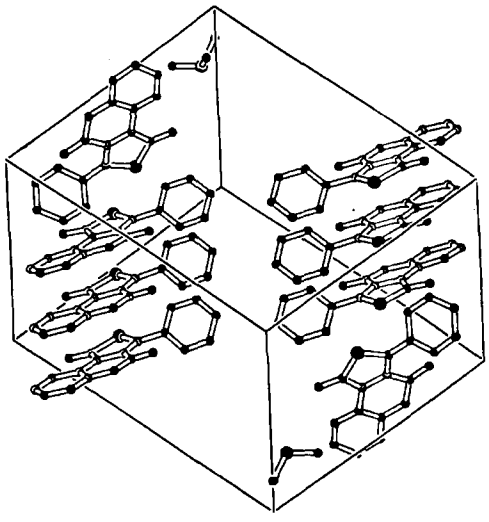
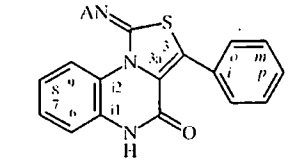
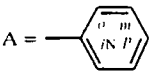


Fig. 2. Packing of the molecules of compound X in the crystal unit cell.

TABLE 4. The ^{13}C NMR Spectral Characteristics of 1-Imino-4-oxo-3-phenyl-4,5-dihydro-1H-thiazolo[3,4-*a*]quinoxalines (solution in DMSO + DMSO-d_6, 0.9:0.1, δ, ppm, *J*, Hz)



A =  (II).H (X). Cl (XVI)

Compound	C=O	C=N	C^3	C^{3a}
II	153.25 (s)	154.60 (s)	122.50 (br. s)	121.93 (t, *J* = 4.57)
X	153.63 (s)	157.56 (s)	120.73 (d, *J* = 5.2)	122.04 (t, J = 5.0)
XVI	153.40 (s)	160.01 (s)	120.73 (d, *J* = 5.2)	125.05 (t, *J* = 3.2)

Compound	C^{11}, C^{12}	C^6, C^{11}	C^7, C^8	Phenyl
II	126.21 (m), 131.42 (s)	115.61 (dd, *J* = 162.7; 8.0); 125.70 (dd, *J* = 163.2; 8.4)	118.43 (br. d, *J* = 167.6); 122.82 (br. d, *J* = 160.0)	151.25 (t, *J* = 8.4; C^N); 130.58 (dt, *J* = 161.3; 8.1; C'); 130.39 (dd, *J* = 158.75; 8.05; C''); 129.07 (dt, *J* = 160.9; 6.3; C''); 128.16 (d, br. d, *J* = 159.9; 7.3; C'''); 125.46 (br. s, C'); 124.51 (dt, *J* = 164.4; 7.1;C''); 121.17 (dt, *J* = 158.5; 7.9; C'')
X	125.24 (br. s), 130.89 (m)	114.52 (dd, *J* = 163.1; 8.1); 124.06 (dd, *J* = 162.8; 8.7)	117.39 (dt, *J* = 167.3; 5.8); 121.60 (ddd, *J* = 162.6; 6.5; 2.5)	128.02 (m, C'); 129.64 (dt, *J* = 162.4; 7.2; C''); 127.32 (dd, *J* = 162.9; 7.5; C'''); 127.31 (dt, *J* = 162.8; 7.1; C'')
XVI	128.19 (m), 129.68 (s)	115.27 (dd, *J* = 162.8; 8.0), 125.86 (dd, *J* = 163.4; 8.4)	117.54 (ddd, *J* = 166.1; 7.9; 3.0); 122.22 (dd, *J* = 163.9; 8.3)	123.71 (br. s, C'); 129.84 (dt, *J* =159.7; 6.1; C''); 127.67 (dd, *J* = 165.2; 9.2; C'''); 128.85 (dt, *J* = 158.8; 5.3; C'')

The system of hydrogen bonds is shown in Fig. 3.

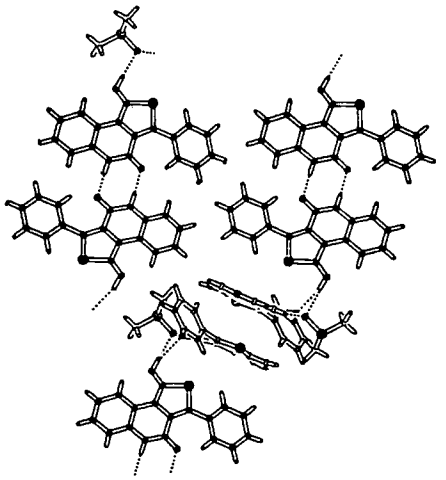


Fig. 3. System of hydrogen bonds in the crystal of compound X (hydrogen bonds are shown dotted).

TABLE 5. Coordinates* of Nonhydrogen Atoms in the Structure of Compound XI and Their Equivalent Isotropic Temperature Parameters $B = \frac{1}{3} \cdot \sum_{i=1}^{3} \sum_{j=1}^{3} (a_i \cdot a_j) \cdot B(i,j) (\text{Å}^2)$

Atom	x	y	z	$B_{(A2)}$
1	2	3	4	5
$S_{(1)}$	0.2153(3)	0.8949(3)	0.9705(2)	3.93(8)
$S_{(2d)}$	0.9478(3)	0.2166(2)	0.7760(2)	2.55(6)
$S_{(2b)}$	0.6178(3)	0.2171(2)	0.7806(2)	2.74(7)
$S_{(2a)}$	1.3799(3)	0.4940(3)	0.9177(2)	4.96(9)
$S_{(2c)}$	0.2783(3)	0.2185(2)	0.7794(2)	2.76(7)
$O_{(1c)}$	0.0708(7)	0.1149(5)	0.5514(4)	3.2(2)
$O_{(4d)}$	0.7310(7)	0.1106(5)	0.5516(4)	3.3(2)
$O_{(4b)}$	0.4027(7)	0.1186(5)	0.5533(4)	2.9(2)
$O_{(4a)}$	1.1108(7)	0.2143(6)	0.9583(5)	3.9(2)
$O_{(2f)}$	0.2097(7)	0.8250(6)	1.0306(4)	3.5(2)
$N_{(1a)}$	1.248(1)	0.6176(8)	0.8656(7)	6.5(4)
$N_{(1d)}$	0.9746(9)	0.0469(7)	0.8324(5)	3.5(2)
$N_{(1b)}$	0.6388(9)	0.0454(7)	0.8320(5)	3.7(2)
$N_{(1c)}$	0.298(1)	0.0484(7)	0.8351(5)	4.6(3)
$N_{(5a)}$	0.9808(8)	0.3162(7)	0.9450(5)	3.1(2)
$N_{(5d)}$	0.7331(8)	-0.0421(6)	0.5835(5)	2.5(2)
$N_{(5c)}$	0.0647(8)	-0.0383(6)	0.5853(5)	2.4(2)
$N_{(5b)}$	0.4031(8)	-0.0332(6)	0.5833(5)	2.5(2)
$N_{(10a)}$	1.1519(8)	0.4642(6)	0.9040(5)	2.9(2)
$N_{(10b)}$	0.5337(7)	0.0387(6)	0.7154(4)	2.0(2)
$N_{(10d)}$	0.8656(7)	0.0364(6)	0.7146(4)	1.9(2)
$N_{(10c)}$	0.2003(8)	0.0398(6)	0.7154(5)	2.5(2)
$C_{(1a)}$	1.250(1)	0.5367(9)	0.8893(7)	4.2(3)
$C_{(1d)}$	0.932(1)	0.0860(7)	0.7797(6)	2.2(2)
$C_{(1b)}$	0.5981(9)	0.0891(8)	0.7810(6)	2.5(3)
$C_{(1c)}$	0.260(1)	0.0910(9)	0.7819(6)	3.2(3)
$C_{(3a)}$	1.305(1)	0.3860(8)	0.9452(6)	2.8(3)
$C_{(3c)}$	0.2115(9)	0.2029(8)	0.6897(5)	2.1(2)
$C_{(3b)}$	0.5455(9)	0.2044(8)	0.6928(5)	2.0(2)
$C_{(3d)}$	0.8758(9)	0.1998(7)	0.6873(5)	2.0(2)
$C_{(4b)}$	0.4343(9)	0.0660(7)	0.5973(6)	2.2(3)
$C_{(4c)}$	0.0988(9)	0.0609(7)	0.5951(6)	2.1(2)
$C_{(4d)}$	0.7638(9)	0.0569(8)	0.5956(6)	2.4(3)
$C_{(4a)}$	1.096(1)	0.2975(7)	0.9484(6)	3.0(3)
$C_{(6a)}$	0.831(1)	0.4063(9)	0.9183(6)	3.5(3)
$C_{(6d)}$	0.720(1)	-0.2102(8)	0.6140(6)	2.7(3)
$C_{(6c)}$	0.052(1)	-0.2043(8)	0.6146(6)	2.8(3)
$C_{(6b)}$	0.388(1)	-0.2010(8)	0.6095(6)	3.0(3)
$C_{(7a)}$	0.789(1)	0.4858(9)	0.8928(7)	5.6(4)
$C_{(7d)}$	0.745(1)	-0.2728(8)	0.6620(6)	3.6(3)
$C_{(7b)}$	0.408(1)	-0.2701(8)	0.6546(7)	3.6(3)
$C_{(7c)}$	0.080(1)	-0.2697(8)	0.6596(7)	3.5(3)
$C_{(8a)}$	0.877(1)	0.5579(9)	0.8667(7)	5.5(3)
$C_{(8b)}$	0.472(1)	-0.2340(8)	0.7224(7)	3.4(3)
$C_{(8d)}$	0.808(1)	-0.2359(8)	0.7274(6)	3.8(3)
$C_{(8c)}$	0.151(1)	-0.2349(8)	0.7241(7)	3.5(3)
$C_{(9a)}$	0.995(1)	0.5527(8)	0.8686(6)	4.3(3)
$C_{(9c)}$	0.194(1)	-0.1337(8)	0.7427(6)	3.2(3)
$C_{(9d)}$	0.849(1)	-0.1353(8)	0.7472(6)	2.9(3)
$C_{(9b)}$	0.516(1)	-0.1332(8)	0.7450(6)	2.7(3)
$C_{(11a)}$	0.951(1)	0.4015(8)	0.9217(6)	3.0(3)

TABLE 5 (continued)

1	2	3	4	5
$C_{(11b)}$	0.4291(9)	-0.0995(7)	0.6301(6)	2.2(2)
$C_{(11d)}$	0.7597(9)	-0.1092(7)	0.6313(5)	2.1(2)
$C_{(11c)}$	0.092(1)	-0.1033(7)	0.6332(6)	2.4(3)
$C_{(12d)}$	0.8260(9)	-0.0691(7)	0.6996(6)	2.3(3)
$C_{(12c)}$	0.1639(9)	-0.0656(7)	0.6984(6)	2.2(2)
$C_{(12b)}$	0.4936(9)	-0.0647(7)	0.6982(5)	2.0(2)
$C_{(12a)}$	1.0332(9)	0.4791(7)	0.9004(6)	2.2(2)
$C_{(13c)}$	0.1737(9)	0.1045(7)	0.6653(6)	2.2(2)
$C_{(13d)}$	0.8373(9)	0.1027(7)	0.6640(5)	1.8(2)
$C_{(13b)}$	0.5066(9)	0.1075(8)	0.6680(5)	2.3(2)
$C_{(13a)}$	1.184(1)	0.3827(7)	0.9337(6)	2.5(3)
$C_{(14b)}$	0.541(1)	0.2978(8)	0.6615(6)	2.8(3)
$C_{(14d)}$	0.8743(9)	0.2907(7)	0.6533(6)	2.2(3)
$C_{(14c)}$	0.2080(9)	0.2946(7)	0.6569(6)	2.2(2)
$C_{(14a)}$	1.366(1)	0.3225(8)	0.9811(6)	3.1(3)
$C_{(15a)}$	1.337(1)	0.2897(9)	1.0482(7)	4.1(3)
$C_{(15c)}$	0.237(1)	0.3037(8)	0.5851(6)	2.8(3)
$C_{(15d)}$	0.901(1)	0.2977(8)	0.5802(6)	2.7(3)
$C_{(15b)}$	0.571(1)	0.3060(8)	0.5883(6)	3.0(3)
$C_{(16d)}$	0.903(1)	0.3856(8)	0.5521(6)	3.1(3)
$C_{(16a)}$	1.402(1)	0.229(1)	1.0833(7)	5.0(4)
$C_{(16b)}$	0.571(1)	0.3944(9)	0.5600(7)	4.0(3)
$C_{(16c)}$	0.237(1)	0.3898(8)	0.5562(6)	3.4(3)
$C_{(17d)}$	0.878(1)	0.4686(8)	0.5937(7)	3.6(3)
$C_{(17a)}$	1.487(1)	0.191(1)	1.0496(9)	8.9(5)
$C_{(17c)}$	0.211(1)	0.4714(8)	0.5980(7)	4.1(3)
$C_{(17b)}$	0.542(1)	0.4744(9)	0.6026(7)	4.2(3)
$C_{(18c)}$	0.185(1)	0.4633(8)	0.6692(7)	3.7(3)
$C_{(18a)}$	1.520(1)	0.230(1)	0.9844(9)	6.1(4)
$C_{(18b)}$	0.517(1)	0.4666(9)	0.6736(7)	4.2(3)
$C_{(18d)}$	0.856(1)	0.4634(8)	0.6659(6)	3.1(3)
$C_{(19a)}$	1.460(1)	0.292(1)	0.9497(7)	5.9(4)
$C_{(19b)}$	0.516(1)	0.3793(8)	0.7039(7)	3.2(3)
$C_{(19c)}$	0.185(1)	0.3765(7)	0.6989(6)	2.5(3)
$C_{(19d)}$	0.852(1)	0.3746(8)	0.6949(6)	2.6(3)
$C_{(20)}$	0.193(2)	1.011(1)	1.0109(9)	7.4(5)
$C_{(21)}$	0.079(1)	0.852(1)	0.9144(7)	6.4(5)

* Standard deviations are given in parentheses.

The imine $N_{(1)}$ atom of molecule A does not form short contacts which might be interpreted as hydrogen bonds. Atom $N_{(5a)}$ forms hydrogen bond with molecule of dimethyl sulfoxide, $N_{(5a)}$–H···$O_{(20')}$ (1-x, 1-y, 1-z) with parameters $N_{(5a)}$···$O_{(20')}$ 2.73(1) Å; $N_{(5a)}$–H 0.98 Å; H···$O_{(20')}$ 1.77 Å; angle $N_{(5a)}$–H···$O_{(20')}$ 169°. The imino group of molecule B forms hydrogen bond with the same molecule of dimethyl sulfoxide. Bond parameters were $N_{(1b)}$···$O_{(20')}$ 3.13(1) Å; $N_{(1b)}$–H 0.95 Å; H···$O_{(20')}$ 2.18 Å; angle $N_{(1b)}$–H···$O_{(20')}$ 176°. Atom $N_{(5b)}$ forms hydrogen bond with the $O_{(4)}$ atom of the symmetrically dependent molecule D. The parameters of the bond are $N_{(5b)}$···$O_{(4d'')}$ (1-x, -y, 1-z) (centrosymmetrical dimer) 2.82(1) Å; $N_{(5b)}$–H 0.96 Å; H···$O_{(4d)}$ 1.85 Å; angle $N_{(5b)}$–H···$O_{(4d'')}$ 176°. The imino group of molecule C does not form hydrogen bonds. The $N_{(5c)}$ amino atom forms a hydrogen-bonded dimer through atom $O_{(4c'')}$ (-x, -y, 1-z) with the neighboring molecule C. The distance $N_{(5c)}$···$O_{(4c'')}$ is 2.84(1) Å; N(5c)–H 0.96 Å; H···$O_{(4c'')}$ 1.88 Å; angle $N_{(5c)}$–H···$O_{(4c'')}$ 174°. The imino group of molecule D forms hydrogen bond with the $O_{(4)}$ atom of molecule A, distance $N_{(1d)}$···$O_{(4a)}$ 3.16(1) Å; $N_{(1d)}$–H 0.95 Å; H···$O_{(4a)}$ 2.23 Å; angle $N_{(1d)}$–H···$O_{(4a)}$ 167°. The amino group $N_{(5d)}$ atom forms hydrogen bond with the atom $O_{(4b'')}$ (1-x, -y, 1-z) (centrosymmetrical dimer) with parameters $N_{(5d)}$···$O_{(4b'')}$ 2.85 Å; $N_{(5d)}$–H 0.96 Å; H···$O_{(4b'')}$ 1.89 Å; angle $N_{(5d)}$–H···$O_{(4b'')}$ 176°.

TABLE 6. Valence Angles (ω*) in Compound XI

Angle	ω*, deg.			
	molecule A	molecule B	molecule C	molecule D
$O_{(20)}$–$S_{(1)}$–$C_{(20)}$	108.1(6)			
$O_{(20)}$–$S_{(1)}$–$C_{(21)}$	104.8(6)			
$C_{(20)}$–$S_{(1)}$–$C_{(21)}$	99.7(8)			
$C_{(1)}$–$S_{(2)}$–$C_{(3)}$	94.9(6)	93.3(5)	93.2(5)	93.7(5)
$C_{(4)}$–$N_{(5)}$–$C_{(11)}$	124.4(9)	125.4(8)	126.6(8)	126.6(8)
$C_{(1)}$–$N_{(10)}$–$C_{(12)}$	124(1)	126.3(9)	125.7(9)	124.1(9)
$C_{(1)}$–$N_{(10)}$–$C_{(13)}$	113(1)	111.1(8)	113.0(8)	113.8(7)
$C_{(12)}$–$N_{(10)}$–$C_{(13)}$	122.6(9)	122.5(8)	121.3(8)	122.1(7)
$S_{(2)}$–$C_{(1)}$–$N_{(1)}$	125(1)	125.9(7)	126.2(8)	125.3(7)
$S_{(2)}$–$C_{(1)}$–$N_{(10)}$	106.8(9)	109.8(8)	109.3(8)	107.1(7)
$N_{(1)}$–$C_{(1)}$–$N_{(10)}$	128(1)	124(1)	124(1)	127.6(9)
$S_{(2)}$–$C_{(3)}$–$C_{(13)}$	108.6(9)	109.4(8)	109.9(8)	110.1(8)
$S_{(2)}$–$C_{(3)}$–$C_{(14)}$	120.6(8)	116.5(7)	116.4(7)	116.3(7)
$C_{(13)}$–$C_{(3)}$–$C_{(14)}$	130(1)	134.0(9)	133.8(9)	133.6(9)
$O_{(4)}$–$C_{(4)}$–$N_{(5)}$	119.9(9)	120.3(9)	123.8(9)	122.1(9)
$O_{(4)}$–$C_{(4)}$–$C_{(13)}$	127(1)	123.3(8)	120.9(9)	120.3(9)
$N_{(5)}$–$C_{(4)}$–$C_{(13)}$	113(1)	116.4(9)	115.3(9)	118(1)
$C_{(7)}$–$C_{(6)}$–$C_{(11)}$	123(1)	122(1)	121(1)	120(1)
$C_{(6)}$–$C_{(7)}$–$C_{(8)}$	114(1)	117(1)	120(1)	121(1)
$C_{(7)}$–$C_{(8)}$–$C_{(9)}$	123(1)	123(1)	120(1)	121(1)
$C_{(8)}$–$C_{(9)}$–$C_{(12)}$	120(1)	118(1)	121(1)	120(1)
$N_{(5)}$–$C_{(11)}$–$C_{(6)}$	117(1)	119.3(9)	119.8(9)	121.4(9)
$N_{(5)}$–$C_{(11)}$–$C_{(12)}$	123(1)	120.7(9)	119.8(8)	118.2(8)
$C_{(6)}$–$C_{(11)}$–$C_{(12)}$	120(1)	120(1)	120(1)	120(1)
$N_{(10)}$–$C_{(12)}$–$C_{(9)}$	125(1)	123.3(8)	124.3(9)	124.1(9)
$N_{(10)}$–$C_{(12)}$–$C_{(11)}$	114.4(9)	117.1(9)	117.7(9)	118.0(9)
$C_{(9)}$–$C_{(12)}$–$C_{(11)}$	119(1)	119.5(9)	117.9(9)	117.8(9)
$N_{(10)}$–$C_{(13)}$–$C_{(3)}$	116.5(9)	116.4(8)	114.7(9)	115.2(8)
$N_{(10)}$–$C_{(13)}$–$C_{(4)}$	121(1)	117.8(8)	119.1(8)	117.3(8)
$C_{(3)}$–$C_{(13)}$–$C_{(4)}$	122(1)	126(1)	126(1)	127(1)
$C_{(3)}$–$C_{(14)}$–$C_{(15)}$	123(1)	119(1)	121(1)	121.9(9)
$C_{(3)}$–$C_{(14)}$–$C_{(19)}$	120(1)	121(1)	120(1)	119.8(9)
$C_{(15)}$–$C_{(14)}$–$C_{(19)}$	117(1)	120(1)	118(1)	118(1)
$C_{(14)}$–$C_{(15)}$–$C_{(16)}$	121(1)	119(1)	121(1)	119(1)
$C_{(15)}$–$C_{(16)}$–$C_{(17)}$	122(1)	120(1)	121(1)	122(1)
$C_{(16)}$–$C_{(17)}$–$C_{(18)}$	115(2)	120(1)	119(1)	119(1)
$C_{(17)}$–$C_{(18)}$–$C_{(19)}$	124(1)	122(1)	121(1)	120(1)
$C_{(14)}$–$C_{(19)}$–$C_{(18)}$	120(1)	119(1)	120(1)	122(1)

* Standard deviations are given in parentheses.

Probably the packing of the four independent molecules of compound X is determined by the cocrystallization of one DMSO solvate molecule, forming hydrogen bonds with two of them.

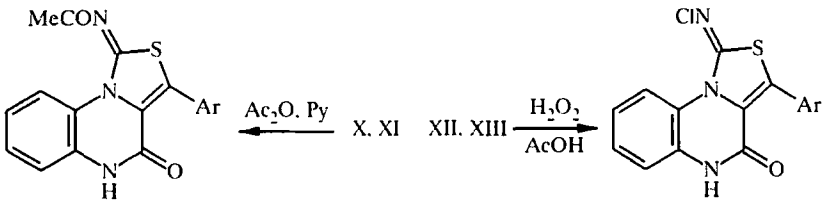
While attempts to acetylate 3-α-chlorobenzylquinoxalin-2-one V at the endocyclic amino group were unsuccessful, acetylation of iminotricyclic compounds X and XI was effected without difficulty. This probably means that acetylation occurs at the imino nitrogen atom with the formation of tricyclic acetylimines XIV and XV. The ^{1}H NMR spectra of the acetylation products (Table 2) also indicate this. In comparison with the initial compounds the proton singlets near 9.5 disappear. These are absent from the spectra of all compounds having no unsubstituted imino group. On the other hand the singlets at about 11.5 ppm remain. These are present in the spectra of all the quinoxalinones in Table 2 (11-12.5 ppm) and undoubtedly belong to the lactam protons.

TABLE 7. Bond Lengths (d*) in Compound XI

Bond	d, Å			
	molecule A	molecule B	molecule C	molecule D
$S_{(1)}$–$O_{(20)}$	1.541(9)			
$S_{(1)}$–$C_{(20)}$	1.75(1)			
$S_{(1)}$–$C_{(21)}$	1.79(1)			
$S_{(2)}$–$C_{(1)}$	1.80(1)	1.73(1)	1.73(1)	1.78(1)
$S_{(2)}$–$C_{(3d)}$	1.71(1)	1.74(1)	1.74(1)	1.75(1)
$O_{(4e)}$–$C_{(4e)}$	1.23(1)	1.23(1)	1.23(1)	1.25(1)
$N_{(1)}$–$C_{(1)}$	1.24(2)	1.28(2)	1.29(2)	1.28(1)
$N_{(5)}$–$C_{(4)}$	1.41 (2)	1.33(1)	1.33(1)	1.33(1)
$N_{(5)}$–$C_{(11)}$	1.39(2)	1.39(1)	1.39(1)	1.41(1)
$N_{(10)}$–$C_{(1)}$	1.42(1)	1.40(1)	1.40(1)	1.40(1)
$N_{(10)}$–$C_{(12)}$	1.44(1)	1.40(1)	1.42(1)	1.42(1)
$N_{(10)}$–$C_{(13)}$	1.41(1)	1.42(1)	1.41(1)	1.44(1)
$C_{(3)}$–$C_{(15)}$	1.39(2)	1.34(1)	1.35(1)	1.33(1)
$C_{(3)}$–$C_{(14)}$	1.43(2)	1.48(2)	1.47(2)	1.47(2)
$C_{(4)}$–$C_{(13)}$	1.46(1)	1.49(1)	1.50(1)	1.47(1)
$C_{(6)}$–$C_{(7)}$	1.40(2)	1.38(2)	1.36(2)	1.36(2)
$C_{(6)}$–$C_{(11)}$	1.41 (2)	1.38(1)	1.37(1)	1.37(1)
$C_{(7)}$–$C_{(8)}$	1.42(2)	1.39(2)	1.38(2)	1.35(2)
$C_{(8)}$–$C_{(9)}$	1.39(2)	1.38(1)	1.38(1)	1.37(1)
$C_{(9)}$–$C_{(12)}$	1.36(2)	1.40(2)	1.39(2)	1.38(2)
$C_{(11)}$–$C_{(12)}$	1.39(1)	1.40(1)	1.40(1)	1.42(1)
$C_{(14)}$–$C_{(15)}$	1.40(2)	1.41(2)	1.39(2)	1.40(2)
$C_{(14)}$–$C_{(19)}$	1.38(2)	1.38(2)	1.37(1)	1.39(2)
$C_{(15)}$–$C_{(16)}$	1.42(2)	1.38(2)	1.35(2)	1.37(2)
$C_{(16)}$–$C_{(17)}$	1.36(2)	1.39(2)	1.38(2)	1.39(2)
$C_{(17a)}$–$C_{(18a)}$	1.41(2)	1.36(2)	1.37(2)	1.37(2)
$C_{(18a)}$–$C_{(19a)}$	1.39(2)	1.38(2)	1.37(2)	1.38(2)

* Standard deviations are given in parentheses.

One further not altogether usual type of N-imino substitution in tricyclic compounds X and XI was successfully effected during unsuccessful attempts to oxidize them with hydrogen peroxide in acetic acid at the sulfur or nitrogen atoms with the aim of obtaining the corresponding sulfoxide, sulfone, or N-oxide. However, on reacting this agent not with the bases X and XI but with their hydrochlorides XII and XIII under mild conditions N-chlorination occurred. This was confirmed by an additional test with sodium iodide (formation of iodine) on the products formed. The absence of features of the imino group from their IR and ^{1}H NMR spectra indicates that chlorination had occurred at the imino group with the formation of compounds XVI and XVII.



XIV Ar = Ph; XV m-$O_2NC_6H_4$

XVI Ar = Ph; XVII m-$O_2NC_6H_4$

The formation of N-chloroimine is probably explained by the reaction of tricyclic imine X with hypochlorous acid, acetyl hypochlorite, or chlorine formed as a result of the oxidation of chloride anion present in the system.

TABLE 8. Torsion Angles (τ*) in Compound XI

Angle	τ, deg.	Angle	τ, deg.
$C_{(11a)}$-$N_{(5a)}$-$C_{(4a)}$-$O_{(4a)}$	-168.47(1.00)	$C_{(12a)}$-$N_{(10a)}$-$C_{(1a)}$-$S_{(2a)}$	169.30(0.78)
$C_{(11a)}$-$N_{(5a)}$-$C_{(4a)}$-$C_{(13a)}$	7.35(1.42)	$C_{(12a)}$-$N_{(10a)}$-$C_{(1a)}$-$N_{(1a)}$	-6.62(1.91)
$C_{(14c)}$-$C_{(3c)}$-$C_{(13c)}$-$C_{(4c)}$	-8.70(1.97)	$C_{(1a)}$-$N_{(10a)}$-$C_{(12a)}$-$C_{(9a)}$	14.25(1.63)
$S_{(2c)}$-$C_{(3c)}$-$C_{(14c)}$-$C_{(15c)}$	134.73(0.95)	$C_{(1a)}$-$N_{(10b)}$-$C_{(12a)}$-$C_{(11a)}$	-175.88(0.99)
$S_{(2c)}$-$C_{(3c)}$-$C_{(14c)}$-$C_{(19c)}$	-40.17(1.34)	$C_{(13a)}$-$N_{(10a)}$-$C_{(12a)}$-$C_{(9a)}$	-175.97(1.03)
$C_{(13c)}$-$C_{(3c)}$-$C_{(14c)}$-$C_{(15c)}$	-44.88(1.82)	$C_{(13a)}$-$N_{(10a)}$-$C_{(12a)}$-$C_{(11a)}$	-6.10(1.38)
$C_{(13c)}$-$C_{(3c)}$-$C_{(14c)}$-$C_{(19c)}$	140.22(1.28)	$C_{(1a)}$-$N_{(10b)}$-$C_{(13a)}$-$C_{(3a)}$	1.09(1.33)
$C_{(14b)}$-$C_{(3b)}$-$C_{(13b)}$-$C_{(4b)}$	-5.33(1.99)	$C_{(1a)}$-$N_{(10b)}$-$C_{(13a)}$-$C_{(4a)}$	-176.28(0.97)
$S_{(2b)}$-$C_{(3b)}$-$C_{(14b)}$-$C_{(15b)}$	132.32(0.96)	$C_{(12a)}$-$N_{(10a)}$-$C_{(13a)}$-$C_{(3a)}$	-169.64(0.93)
$S_{(2b)}$-$C_{(3b)}$-$C_{(14b)}$-$C_{(19b)}$	-43.62(1.39)	$C_{(12a)}$-$N_{(10a)}$-$C_{(13a)}$-$C_{(4a)}$	12.98(1.45)
$C_{(13b)}$-$C_{(3b)}$-$C_{(14b)}$-$C_{(15b)}$	-46.26(1.83)	$C_{(12b)}$-$N_{(10b)}$-$C_{(1b)}$-$S_{(2b)}$	-175.20(0.81)
$C_{(13b)}$-$C_{(3b)}$-$C_{(14b)}$-$C_{(19b)}$	137.79(1.33)	$C_{(12b)}$-$N_{(10b)}$-$C_{(1b)}$-$N_{(1b)}$	6.93(1.68)
$C_{(14d)}$-$C_{(3d)}$-$C_{(13d)}$-$C_{(4d)}$	-9.12(2.00)	$C_{(12d)}$-$N_{(10d)}$-$C_{(1d)}$-$N_{(1d)}$	5.66(1.73)
$S_{(2d)}$-$C_{(3d)}$-$C_{(14d)}$-$C_{(15d)}$	133.65(0.97)	$C_{(13d)}$-$N_{(10d)}$-$C_{(1d)}$-$S_{(2d)}$	3.51(1.03)
$S_{(2d)}$-$C_{(3d)}$-$C_{(14d)}$-$C_{(19d)}$	-42.70(1.34)	$C_{(14a)}$-$C_{(3a)}$-$C_{(13a)}$-$C_{(4a)}$	-10.27 (1.82)
$C_{(13d)}$-$C_{(3d)}$-$C_{(14d)}$-$C_{(15d)}$	-42.85(1.87)	$S_{(2a)}$-$C_{(3a)}$-$C_{(14a)}$-$C_{(15a)}$	127.80(1.11)
$C_{(13d)}$-$C_{(3d)}$-$C_{(14d)}$-$C_{(19d)}$	140.80(1.27)	$S_{(2a)}$-$C_{(3a)}$-$C_{(14a)}$-$C_{(19a)}$	-51.32(1.49)
$O_{(4c)}$-$C_{(4c)}$-$C_{(13c)}$-$C_{(3c)}$	4.03(1.71)	$C_{(13a)}$-$C_{(3a)}$-$C_{(14a)}$-$C_{(15a)}$	-44.06(1.84)
$O_{(4a)}$-$C_{(4a)}$-$C_{(13a)}$-$N_{(10a)}$	162.68 (1.04)	$C_{(13a)}$-$C_{(3a)}$-$C_{(14a)}$-$C_{(19a)}$	136.82(1.34)
$O_{(4a)}$-$C_{(4a)}$-$C_{(13a)}$-$C_{(3a)}$	-14.55(1.73)	$C_{(8a)}$-$C_{(9a)}$-$C_{(12a)}$-$C_{(11a)}$	8.81(1.67)
$N_{(5a)}$-$C_{(4a)}$-$C_{(13a)}$-$N_{(10a)}$	-12.77(1.38)		

* Standard deviations are given in parentheses.

The IR and ^{1}H NMR spectra given in Table 2 for the obtained compounds correspond to the structures proposed for them. Apart from the features indicated it may be mentioned that, in difference to the phenyl substituent, the four protons in *m*-nitrophenyl group were displayed separately and it was possible to assign signals to each of them in accordance with their multiplicity for all the investigated compounds. In thiazoloquinoxalines, unlike quinoxalines, one of the quinoxaline protons was deshielded significantly more strongly than the others and appeared separately in the spectrum, resonating at lower field. Its chemical shift reacts significantly more strongly than those of the other quinoxaline protons to a change in the nature of the substituent at the imino nitrogen atom (H, Ph, Ac, Cl). This suggests that this proton $H_{(9)}$ is spatially adjacent to the imino group.

The number of signals, their chemical shifts, multiplicity, and values of the coupling constants in the ^{13}C NMR spectra (Tables 3, 4) also corresponded to the structures proposed for the compounds synthesized.

EXPERIMENTAL

Melting points were determined on a Boetius stage. The IR spectra were taken on a UR 20 spectrometer (Nujol mull). The ^{1}H NMR spectra were recorded on a Bruker MCL 250 spectrometer with an operating frequency of 250.13 MHz. Chemical shifts are given in the δ scale [measured experimentally relative to $(CD_3)_2SO$].

3-(α-Chlorobenzyl)quinoxalin-2-one V was obtained [5] by the interaction of phenylchloropyruvic acid methyl ester [6] with *o*-phenylenediamine. 3-(α-Chloro-*m*-nitrobenzyl)quinoxalin-2-one VII was synthesized analogously.

X-ray Structural Investigation. Crystals of composition 4(X)·DMSO of mp 264-266°C (decomp.) were triclinic. At 20°C a = 11.641(1), b = 13.778(6), c = 18.303(7) Å; α = 96.69(3), β = 93.53(2), γ = 101.61(2)°; V = 2845(2) Å^3; d_{calc} = 1.46 g/cm^3; Z = 2; space group P-1 (four independent molecules A, B, C, D and molecule of DMSO). The parameters of the unit cell and the intensities of 8391 reflections, 3836 of which with $I \geq 3\sigma$, were measured on an Enraf-Nonius CAD-4 automatic four-circle diffractometer (λCuKα, graphite monochromator,

$\omega/2\theta$ scanning, $\theta \leq 57°$). No fall was observed in the intensity of three control reflections in 57 h of plotting the experiment. An empirical registration was made of the absorption (μCu 23.68 cm^{-1}). The structure was solved by the direct method using the SIR program [7] and was refined in an isotropic, then in an anisotropic approach. All hydrogen atoms were revealed from electron density difference series, their contributions to the structural amplitudes were calculated with fixed positions and with isotropic temperature parameters at the final stage of refinement. The final values of the divergence factors were $R = 0.066$, $R_w = 0.075$ at 3365 independent reflections with $F^2 \geq 3\sigma$. All calculations were carried with the MolEN program set [8]. The coordinates of non-hydrogen atoms are given in Table 5, the geometry of the molecules is shown in Fig. 1 and their packing in Fig. 2. Bond lengths, valence, and torsion angles are given in Tables 6-8.

2-Oxo-3-(α-N,N'-diphenylisothioureidobenzyl)-1,2-dihydroquinoxaline (IV). Suspension of compound V (2.00 g, 7.4 mmol) and N,N'-diphenylthiourea (1.69 g, 7.4 mmol) in DMSO (80 ml) was stirred for 6 h and left overnight. The resulting solution was poured into water (150 ml), and solution of Na_2CO_3 was added to alkaline reaction. The solid was filtered off, and washed with water (2 × 30 ml).

4-Oxo-3-phenyl-1-phenylimino-4,5-dihydrothiazolo[3,4-*a*]quinoxaline (II). Compound IV (0.40 g, 0.86 mmol) in AcOH (15 ml) was boiled for 2 h. After cooling the solution, the crystals were filtered off, and washed with 2-PrOH (2 × 10 ml).

2-Oxo-3-(α-thiocyanobenzyl)-1,2-dihydroquinoxaline (VI). Solution of chloro compound V (10.70 g, 40 mmol) and KSCN (4.30 g, 44 mmol) in DMSO (120 ml) was stirred for 6 h and then left overnight. The precipitated crystals were filtered off, and washed with 2-PrOH (2 × 10 ml).

2-Oxo-3-(α-thiocyano-3'-nitrobenzyl)-1,2-dihydroquinoxaline (VIII). Solution of chloro compound VIII (2.20 g, 7 mmol) and KSCN (0.68 g, 7.3 mmol) in DMSO (50 ml) was stirred for 6 h then left overnight. The solution was poured into water (150 ml), the resulting crystals were filtered off, and washed with water (2 × 30 ml).

3-(α-Anilinobenzyl)-2-oxo-1,2-dihydroquinoxaline (IX). Solution of thiocyano derivative VI (2.00 g, 6.1 mmol) and aniline (0.60 g, 6.6 mmol) was boiled for 3 h. The crystals which separated on cooling were filtered off.

1-Imino-2-oxo-3-phenyl-4,5-dihydrothiazolo[3,4-a]quinoxaline (X). Thiocyano derivative VI (4.00 g, 14 mmol) was boiled with 6 N hydrochloric acid (15 ml) for 30 min. The reaction mixture was cooled, the solid was filtered off, washed with water (2 × 20 ml), then with dilute alkali solution (2 × 20 ml), and once again with water (2 × 20 ml).

1-Imino-3-(4'-nitrophenyl)-4-oxo-4,5-dihydrothiazolo[3,4-*a*]quinoxaline (XI) was obtained analogously.

1-Imino-4-oxo-3-phenyl-4,5-dihydrothiazolo[3,4-*a*]quinoxaline Hydrochloride (XII) was obtained analogously to the corresponding base, but without washing the product with alkali solution.

1-Imino-3-(4'-nitrophenyl)-4-oxo-4,5-dihydrothiazolo[3,4-*a*]quinoxaline Hydrochloride (XIII) was obtained analogously to compound XII.

1-Acetylimino-4-oxo-3-phenyl-4,5-dihydrothiazolo[3,4-*a*]quinoxaline (XIV). Iminotricyclic compound X (0.30 g, 1.02 mmol) was boiled for 1 h in mixture of Ac_2O (20 ml) and pyridine (5 ml). The reaction mixture was cooled, the precipitate filtered off, and washed with 2-propanol (2 × 20 ml).

1-Acetylimino-3-(4'-nitrophenyl)-4-oxo-4,5-dihydrothiazolo[3,4-*a*]quinoxaline (XV) was obtained analogously from the iminotricyclic compound XI.

1-Chloroimino-4-oxo-3-phenyl-4,5-dihydrothiazolo[3,4-*a*]quinoxaline (XVI). Hydrochloride XII (1.48 g, 4.5 mmol) was dissolved with heating to 70°C in mixture of AcOH (20 ml) and 30% H_2O_2 (10 ml) and maintained at this temperature for 10 min. The reaction mixture was cooled, the precipitated crystals were filtered off, and washed with 2-PrOH (2 × 20 ml).

1-Chloroimino-3-(4'-nitrophenyl)-4-oxo-4,5-dihydrothiazolo[3,4-*a*]quinoxaline (XVII) was obtained analogously from the hydrochloride XIII.

REFERENCES

1. V. A. Mamedov and Ya. A. Levin, *Khim. Geterotsikl. Soedin.*, No. 7, 1005 (1996).
2. V. A. Mamedov, I. Z. Nurkhametova, R. R. Shagidullin, A. V. Chernova, and Ya. A. Levin, *Khim. Geterotsikl. Soedin.*, No. 7, 975 (1999).
3. E. J. Corey and Xue-Min Chang, *The Logic of Chemical Synthesis*, Wiley, New York (1989).
4. C. L. Willis and M. Wills, *Organic Synthesis*, Oxford University Press, (1995).
5. V. A. Mamedov, I. A. Nuretdinov, and F. G. Sibgatullina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 6, 1412 (1989).
6. V. A. Mamedov, I. A. Nuretdinov, and F. G. Sibgatullina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 3, 2172 (1988).
7. A. Altomare, G. Cascarano, C. Giacovazzo, and D. Viterbo, *Acta Crystallogr. A*, **47**, 744 (1991).
8. L. H. Straver and A. J. Schirbeek, *MolEN. Structure Determination System. Vol. 1. Program Description*, Nonius B.V., Delft (1994).