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Dedicated to Prof. V.M. Ismailov
on the 60th Anniversary of His Birth

Fused Polycyclic Nitrogen-Containing Heterocycles: VI.* Pyrrolo[1,2-*a*]quinoxalines

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Abstract—3-(β-Chlorobenzyl)-1,2-dihydroquinoxalin-2-one reacts with anions derived from acetylacetone, benzoylacetone, dibenzoylmethane, malononitrile, ethyl acetoacetate, and ethyl cyanoacetate to give the corresponding 3-(β-R,R'CH-benzyl)-1,2-dihydroquinoxalin-2-ones which undergo intramolecular cyclocondensation to functionally substituted pyrrolo[1,2-*a*]quinoxalines on heating in boiling acetic acid. The reaction of 3-(α-chloro-*p*-nitrobenzyl)-1,2-dihydroquinoxalin-2-one with acetylacetone anion directly leads to the corresponding pyrrolo[1,2-*a*]quinoxaline, without heating in acetic acid.

In the recent years, pyrrolo[1,2-*a*]quinoxalines have attracted persistent interest due to practically important properties of some their derivatives, specifically pronounced biological activity [2]. However, they still remain difficultly accessible compounds. Synthetic routes to pyrrolo[1,2-*a*]quinoxalines are based on reactions of quinoxaline derivatives, e.g., intramolecular cyclizations involving appropriate substituents which were preliminarily introduced into the 2-position [3–5] or condensations of methylquinoxalines with β-halocarbonyl compounds [6]. However, multistep and laborious procedures for the preparation of initial quinoxalines with required structural fragments (in the first case) and difficult quaternization of quinoxaline with β-halocarbonyl compounds [7] (in the second case) strongly restrict the scope of the above methods. Procedures for the synthesis of pyrrolo[1,2-*a*]quinoxalines from pyrrole derivatives include intramolecular cyclization of *N*-(2-substituted aryl- or cyclohexyl)pyrroles. The latter are available (not always in good yields) via multistep processes; therefore, these procedures cannot be used widely for preparation of various functionalized pyrrolo[1,2-*a*]quinoxaline derivatives [8–15]. A number of side processes and inaccessibility of initial compounds are factors that confine the application of methods based on compounds which originally possess no quinoxaline and/or pyrrole system [16–20].

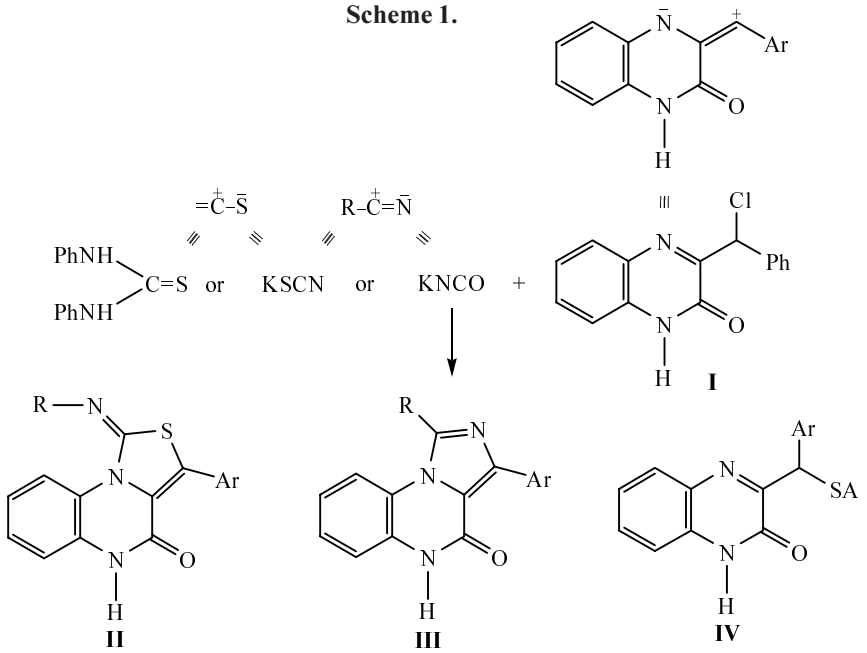
We previously showed that 3-(α-chlorobenzyl)-1,2-dihydroquinoxalin-2-one (**I**) [21], which is readily available from methyl 3-chloro-3-phenyl-2-oxopropionate and *o*-phenylenediamine, reacts with synthetic equivalents of the $S^-–C^+=$ and $N^-=C^+$ species, disubstituted thioureas and potassium thiocyanate or cyanate, to give fused tricyclic systems, thiazolo[3,4-*a*]quinoxalines **II** [22] and imidazo[1,5-*a*]quinoxalines **III** [23] or their precursors **IV** which readily undergo intramolecular cyclization (Scheme 1). Closure of one or another ring is determined by the reaction conditions and nucleophile nature. The use of C-centered nucleophiles instead of S,N-nucleophiles implies successful synthesis of pyrrolo[1,2 *a*]-quinoxalines.

In the present work we examined the behavior of 3-(α-chlorobenzyl)-1,2-dihydroquinoxalin-2-one (**I**) in reactions with C-nucleophiles which were generated by deprotonation of compounds having an activated methylene group. We have found that compound **I** smoothly reacts with acetylacetone, benzoylacetone, dibenzoylmethane, malononitrile, ethyl acetoacetate, and ethyl cyanoacetate in DMSO in the presence of KOH at room temperature, yielding products **V–X** as a result of replacement of the chlorine atom by the corresponding carbanion (Scheme 2, Table 1).

The IR spectra of compounds **V–X** contain bands typical of the quinoxaline system and also those belong-

* For communication V, see [1].

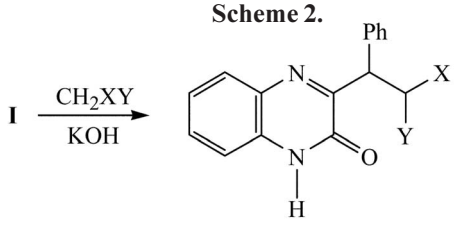
Scheme 1.



II, R = H, Ar, Cl; Ar = Ph, *m*-$O_2NC_6H_4$; **III**, R = H, OH; **IV**, A = CN, C(=NPh)NHPh.

ing to $\nu_{C=O}$ (ketone or/and ester) and/or $\nu_{C\equiv N}$ (at 2220 and 2260 cm^{-1} for compounds **VIII** and **X**, respectively; Table 2). Unlike initial в-diketones which exist mainly as enol tautomers **A**, diketones **V–VII** show in the IR spectra weak bands in the region 1570–1620 cm^{-1}, which correspond to carbonyl absorption (the frequency is reduced due to partial H-chelation with conjugation, as shown in structure **B**) and strong bands at 1725–1715 cm^{-1}, indicating that the predominant tautomer is diketone form **C**.

Scheme 2.



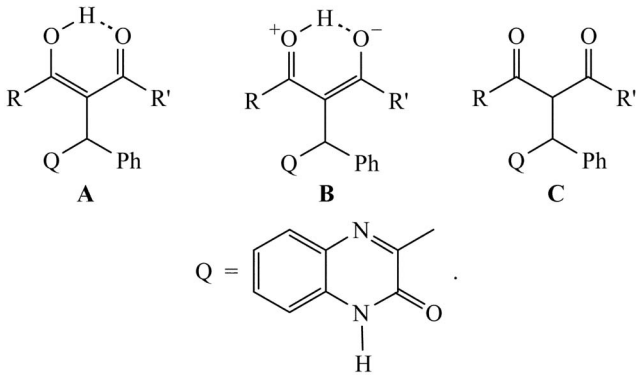
V–X

V, **VI**, **IX**, X = Ac; **VII**, **X** = Bz; **VIII**, **X**, X = CN; **V**, Y = Ac; **VI**, **VII**, Y = Bz; **VIII**, Y = CN; **IX**, **X**, Y = CO_2Et.

Table 1. Yields, melting points, and elemental analyses of 3-substituted quinoxalines **V–X** and pyrrolo[1,2-*a*]quinoxalines **XI–XVII**

Compd. no.	Yield, %	mp, °C (solvent)	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
V	73	263-265[a]	71.99	5.74	8.21	$C_{20}H_{18}N_3O_3$	71.84	5.43	8.38
VI	49	230-232"	75.75	5.16	7.02	$C_{25}H_{20}N_2O_3$	75.74	5.09	7.07
VII	38	263-265[a]	78.65	4.79	6.02	$C_{30}H_{22}N_2O_3$	78.59	4.84	6.11
VIII	77	>300 (decomp.)[3]	71.85	4.09	18.82	$C_{18}H_{12}N_4O$	71.99	4.03	18.66
IX	77	208-210 (AcOH)	69.59	5.24	7.62	$C_{21}H_{20}N_2O_4$	69.60	5.01	7.73
X	54	220-222 (AcOH)	69.00	5.03	11.91	$C_{20}H_{17}N_2O_3$	69.15	4.93	12.10
XI	92	>345 (decomp.) (AcOH)	75.85	4.99	9.02	$C_{20}H_{17}N_2O_2$	75.93	5.10	8.85
XII	65	>360 (AcOH)	79.55	4.79	7.22	$C_{25}H_{18}N_2O_2$	79.35	4.79	7.40
XIII	69	>360 (AcOH)	81.75	4.79	6.12	$C_{30}H_{20}N_2O_2$	81.80	4.58	6.36
XIV	77	>335 (decomp.) (AcOH)	71.75	4.19	18.52	$C_{18}H_{12}N_4O$	71.99	4.03	18.66
XV	89	301-303 (AcOH)	72.95	5.08	8.23	$C_{21}H_{18}N_2O_3$	72.82	5.24	8.09
XVI	87	283-287 (AcOH)	68.81	4.94	12.31	$C_{20}H_{17}N_3O_3$	69.15	4.93	12.10
XVII	60	333-335 (DMSO)	66.41	4.24	11.81	$C_{20}H_{15}N_3O_4$	66.48	4.18	11.63

[a] Washed with 2-propanol.



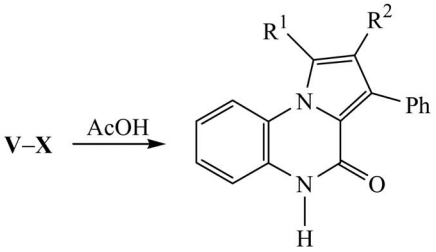
A **B** **C**

Q =

The ^{1}H NMR spectra turned out to be the most informative for determination of the structure of compounds **V**, **IX**, and **X**. We succeeded in unambiguously assigning the ^{1}H and ^{13}C signals in the NMR spectra on the basis of their position, multiplicity, and ^{1}H–^{1}H and ^{1}H–^{13}C coupling constants (Table 3). A specific emphasis should be given to the CH proton signals in the spectra of compounds **VI**–**X** and signals from the ethoxy groups in compounds **IX** and **X**, which give rise, respectively, to *AB* and ABM_3 spin systems. The CH proton signals in the spectra of **VI**, **IX**, and **X** appear as two *AB* quartets, which suggests the presence of two pairs of diastereoisomers. The corresponding protons in **V**, **VII**, and **VIII** give only one *AB* quartet. The spin–spin coupling constants range from 9.74 to 12.51 Hz (except for **VIII**), indicating *trans* orientation of the C–H bonds in the 3-substituent. The other signals in the ^{1}H NMR spectra of **VI**, **IX**, and **X** are also doubled. As follows from the signal intensities, the diastereoisomer ratio in each pair is 55:45. The presence of asymmetric carbon atoms in molecules **VI**, **IX**, and **X** makes methylene protons of the ethoxy groups therein nonequivalent; as a result, the methyl protons give rise to double doublets of doublets, and the methylene protons appear as doublets of quartets (ABM_3 system; Table 2).

By heating compounds **V**–**X** in boiling acetic acid we obtained in high yields the desired fused tricyclic products, pyrrolo[1,2-*a*]quinoxalines **XI**–**XVI** (Scheme 3). Theoretically, several ways of pyrrole ring closure are possible via nucleophilic attack by the N^4 atom on electrophilic carbon atoms of acetyl/benzoyl, acetyl/ester, and cyano/ester groups in compounds **VI**, **IX**, and **X**. For example, the cyclization of quinoxaline **IX** could lead to pyrroloquinoxalines **XV**, **XVa**, and **XVb** (Scheme 4). However, the reaction was regioselective, and only one product having a pyrrolo[1,2-*a*]quinoxaline structure was formed. Here, the attack by the ring nitrogen atom is directed at the less electrophilic ester rather than ketone

Scheme 3.



V–X AcOH **XI–XVI**

XI, **XII**, R^1 = Me; **XIII**, R^1 = Ph; **XIV**, R^1 = NH_2; **XV**, **XVI**, R^1 = OEt; **XI**, **XV**, R^2 = Ac; **XII**, **XIII**, R^2 = Bz; **XIV**, R^2 = CN; **XVI**, R^2 = $CONH_2$.

carbonyl carbon atom. This pathway is more favorable from the viewpoint of stabilization of intermediate product. Taking into account the ease of elimination of OH and OR groups from protonated species ($X–\overset{+}{O}H_2$ and $X–\overset{+}{O}HR$) [24] and greater proton affinity of alcohols as compared to ethers, stabilization of intermediate semiacetal **D** involves elimination of water (path *a*) rather than alcohol molecule (path *b*) to afford pyrrolo[1,2-*a*]quinoxaline **XV**. The IR spectrum of **XV** lacks absorption band typical of ester carbonyl, but signals from ethoxy group are present in the ^{1}H and ^{13}C NMR spectra.

Unlike compounds **VI** and **X**, the ^{1}H NMR spectrum of **IX** contains only one set of signals. This may be regarded as a result of stereoselective alkylation of ethyl acetoacetate anion with 3-(α-chlorobenzyl)quinoxaline **I**. However, in the ^{13}C NMR spectrum of **IX** we observed 18 narrow and 10 broadened signals instead of the expected 18 signals. These data unambiguously indicate formation of two pairs of diastereoisomers. The ^{13}C–{^{1}H} NMR spectrum of **V** contained 23 signals instead of the expected 18 signals from 20 carbon atoms; in this case, only signals from the diacetylmethyl fragment were doubled, which may be due to restricted rotation about the CH–CH bond.

The reaction of 3-(α-chloro-*p*-nitrobenzyl)-1,2-dihydroquinoxalin-2-one (**Ia**) with acetylacetone directly led to formation of pyrrolo[1,2-*a*]quinoxaline **XVII** (Scheme 5).

Analysis of the ^{1}H NMR spectra of pyrrolo[1,2-*a*]-quinoxalines **XI**–**XVII**, thiazolo[3,4-*a*]quinoxalines [22, 23], and other fused azolo[*a*]quinoxalines [25, 26] and nonfused quinoxaline derivatives allowed us to reveal some specific features which can be used for identification of pyrrolo[1,2-*a*]quinoxalines. Primarily, this is a doublet signal from the 9-H proton, which is located at

Table 2. IR and ^{1}H NMR spectra of 3-substituted quinoxalines **V**–**X** and pyrrolo[1,2-*a*]quinoxalines **XI**–**XVII**

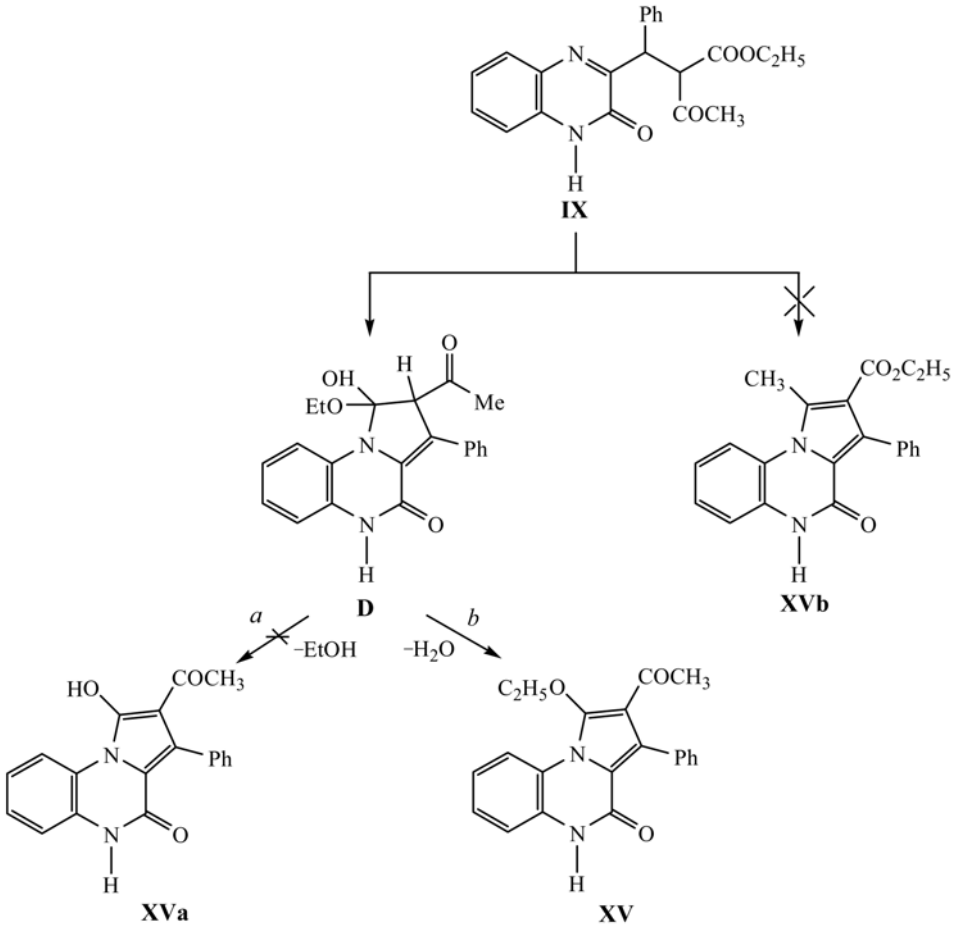
Compd. no.	IR spectrum, ν, cm^{-1}	^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz)
V	1610 (C=N), 1665 (C=O, amide), 1725 (C=O, ketone), 2400–3210 (NH)	2.00 s (3H, CH_3CO), 2.28 s (3H, CH_3CO), 5.22 d (1H, PhCH, *J* = 11.96), 5. 23 d (1H, COCHCO, *J* = 11.96), 7.20–7.36 m (7H, C_6H_5, 5-H, 8-H), 7.51 d.d.d (1H, 5-H or 7-H, *J* = 7.86, 7.54, 1.32), 7.80 d.d.d (1H, 7-H or 5-H, *J* = 7.88, 1.28), 12.23 br.s (1H, NH)
VI	1615 (C=N), 1670 (C=O, amide), 1725 (C=O, ketone), 2400–3210 (NH)	2.02 s (3H, CH_3CO), 2.24 s (3H, CH_3CO), 5.72 d (1H, PhCH, *J* = 11.67), 5.73 d (1H, PhCH, *J* = 11.58), 5.95 d (1H, COCHCO, *J* = 11.67), 6.10 d (1H, COCHCO, *J* = 11.58], 6.98–8.14 m (28H, $4C_6H_5$, $2C_6H_4$), 11.85 br.s (1H, NH), 11.90 br.s (1H, NH)
VII	1610 (C=N), 1670 (C=O, amide), 1710 (C=O, ketone), 2400–3200 (NH))	5.62 d (1H, CHPh, *J* = 12.51, 6.83 d (1H, COCHCO, *J* = 12.51), 7.01–8.03 m (19H, $3C_6H_5$, C_6H_4), 12.21 br.s (1H, NH)
VIII	1610 (C=N), 1670 (C=O, amide), 2220 (C?N), 2400–3700 (NH)	5.36 d [1H, $CH(CN)_2$, *J* = 7.93], 5.63 d (1H, PhCH, *J* = 7.93), 7.25–7.61m (9H, C_6H_5, C_6H_4), 12.69 br.s (1H, NH)
IX	1610 (C=N), 1670 (C=O, amide), 1715 (C=O, ketone), 1740 (C=O, ester), 2400–3210 (NH)	1.66 d.d (6H, $2OCH_2CH_3$, *J* = 7.17, 7.17), 2.17 s (6H, $2CH_3CO$), 3.97–4.06 m (4H, $OCH_AH_BCH_3$, *J* = 6.83), 4.97 d (2H, 2COCHCO, *J* = 11.76), 5.43 d (2H, 2PhCH, *J* = 11.76), 7.12–8.16 m (18H, $2C_6H_5$, $2C_6H_4$), 11.71 br.s (2H, 2NH)
X	1610 (C=N), 1670 (C=O, amide), 1715 (C=O, ketone), 1740 (C=O, ester), 2400–3210 (NH)	1.11 d.d (3H, CH_3CH_2O, *J* = 7.20, 6.66), 1.25 d.d (3H, CH_3CH_2O, *J* = 7.18, 6.67), 4.09 q (1H, $CH_3CH_AH_B$, *J* = 6.67), 4.10 q (1H, $CH_3CH_AH_B$, *J* = 7.18), 4.10 q (1H, $CH_3CH_AH_B$, *J* = 6.67), 4.20 q (1H, $CH_3CH_AH_B$, *J* = 7.18), 4.52 d (1H, NCCHCO, *J* = 9.74), 4.86 d (1H, NCCHCO, *J* = 10.78), 5.28 q (1H, PhCH, *J* = 10.78), 5.31 d (1H, PhCH, *J* = 9.74), 7.28–8.03 m (18H, $2C_6H_5$, $2C_6H_4$), 12.16 br.s (2H, 2NH)
XI	1610 (C=N), 1670 (C=O, amide), 1715 (C=O, ketone), 1740 (C=O, ester), 2400–3210 (NH)	1.75 s (3H, CH_3CO), 2.88 s (3H, CH_3), 7.14–7.48 m (8H, C_6H_5, 6-H, 7-H, 8-H), 8.16 d (1H, 9-H, *J* = 8.26), 11.15 br.s (1H, NH)
XII	1610 (C=C), 1650 (C=O), 2600–3230 (NH)	3.78 s (3H, CH_3), 7.05–7.61 m (13H, $2C_6H_5$, 6-H, 7-H, 8-H), 8.19 d (1H, 9-H, *J* = 9.81), 11.14 br.s (1H, NH)
XIII	1615 (C=C), 1665 (C=O), 2400–3230 (NH)	6.82–7.53 m (19H, $3C_6H_5$, 6-H, 7-H, 8-H), 7.65 d.d (1H, 9-H, *J* = 8.72, 1.60), 11.28 br.s (1H, NH)
XIV	C=C), 1680 (C=O, amide), 1750 (C=O, ester), 2220 (C?N), 2400–3330 (NH), 3350 (NH_2), 3420 (NH_2)	6.51 br.s (2H, NH_2), 7.12–7.56 m (8H, C_6H_5, 6-H, 7-H, 8-H), 8.40 d (1H, 9-H, *J* = 8.38), 10.80 br.s (1H, NH)
XV	(C=N), 1650 (C=O, amide), 1705 (C=O, ketone), 2400–3210 (NH)	0.81 t (3H, CH_3CH_2O, *J* = 7.34), 3.03 s (3H, CH_3CO), 3.93 q (2H, CH_3CH_2O, *J* = 7.34), 7.16–7.31 m (8H, C_6H_5, 6-H, 7-H, 8-H), 8.18 d (1H, 9-H, *J* = 8.27), 11.16 s (1H, NH)
XVI	(C=O), 2400–3450 (NH, NH_2)	0.79 t (3H, CH_3CH_2O, *J* = 7.32), 3.89 q (2H, CH_3CH_2O, *J* = 7.32), 6.78 br.s (2H, NH_2), 7.10–7.25 m (8H, C_6H_5, 6-H, 7-H, 8-H), 8.30 d (1H, 9-H, *J* = 8.30), 10.73 s (1H, NH)
XVII	(C=O), 2400–3220 (NH)	1.95 s (3H, CH_3), 3.06 s (3H, CH_3), 7.26 d.d.d (1H, 7-H or 8-H, *J* = 7.69, 7.69, 1.48), 7.40 d.d (1H, 8-H or 7-H, *J* = 7.45, 7.45), 7.47 d.d (1H, 6-H, *J* = 7.69, 1.48), 7.73 d (2H, 2-H, 6-H in *p*-$O_2NC_6H_4$, *J* = 8.43), 8.30 d (2H, 3-H, 5-H in *p*-$O_2NC_6H_4$, *J* = 8.43), 8.33 d (1H, 9-H, *J* = 7.95), 11.23 br.s (1H, NH)

[a] The ^{1}H NMR spectrum was recorded in $CDCl_3$.

δ 8.15–8.72 ppm ($J = 8.6 \pm 0.3$ Hz), separately from multiplet signals of the other aromatic protons. The upfield shift of the 9-H signal in the spectrum of **XIII** (δ 7.65 ppm) is likely to result from shielding of that proton be the benzene ring on C^1.

The structure of methyl 1-methyl-4-oxo-3-phenyl-4,5-dihydropyrrolo[1,2-*a*]quinoxalin-2-carboxylate (**XI**) was proved by X-ray analysis. Figure 1 shows the structure of molecule **XI** in crystal. The fused tricyclic system is planar within 0.023(2) Å. All atoms that constitute this system have a planar–trigonal configuration, i.e., they are sp^2-hybridized. The tricyclic system can be regarded as heteroaromatic: it contains 14 *p*-electrons, and the bond lengths therein are leveled (Table 4). The double $C^4{=}O^4$ bond is involved in conjugation with the ring π system: this bond is appreciably longer [$d = 1.243(2)$ Å] than the $C^{12}{=}O^{12}$ bond [$d = 1.205(2)$ Å]. The latter is unlikely to participate in conjugation with the tricyclic system, for it

Scheme 4.



Scheme 5.

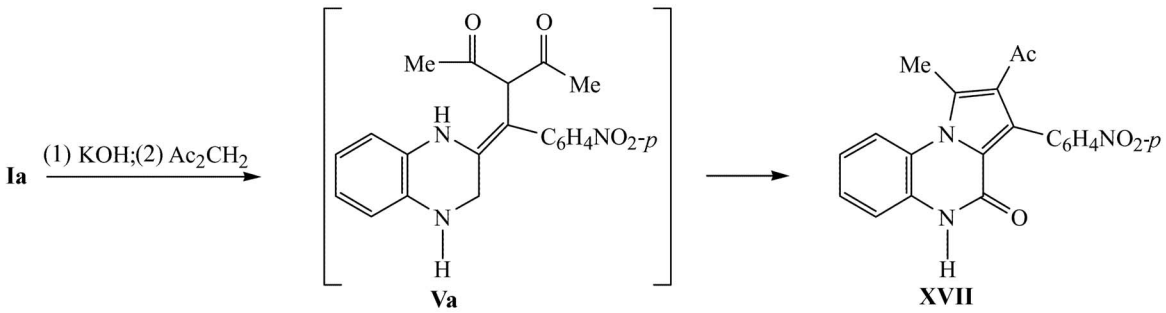
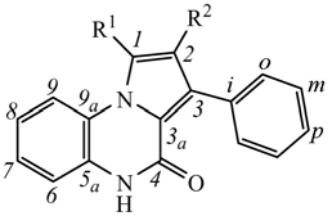


Table 3. ^{13}C NMR spectra of pyrrolo[1,2-*a*]quinoxalines **XI, XV**, and **XVI** in DMSO-d_6–acetone-d_6 (10 : 1), δ_C, ppm



Compd. no.	Alkyl carbons	C^1	C^2	C^3	C^{3a}
XI	14.08 q (CH_3, J = 129.9 Hz), 30.21 q ($CO\mathbf{C}H_3$, J = 127.6 Hz)	131.61 q (J = 6.9 Hz)	126.52 m	118.10 s	127.13 s
XV	13.32 q.t ($\mathbf{C}H_3CH_2$, J = 126.8, 2.6 Hz), 15.07 q ($\mathbf{C}H_3CO$, J = 130.0 Hz), 59.63 t.q (CH_3CH_2, J = 147.6, 4.4 Hz)	134.74 m	133.98 m	118.06 m	119.37 s
XVI	12.10 q.t ($\mathbf{C}H_3CH_2$, J = 128.7, 2.4 Hz), 58.10 t.q ($CH_3\mathbf{C}H_2$, J = 146.4, 4.6 Hz)	96.25 s	112.07 s	128.15 br.s	144.9 s

Compd. no.	C^6, C^9	C^7, C^8	C^{5a}, C^{9a}	C_{arom}	C=O, C^4
XI	125.24 d.d (J = 63.6, 8.2 Hz), 115.62 d.d (J = 63.0, 8.2 Hz)	121.12 d.d (J = 65.0, 7.4 Hz), 116.79 d.d (J = 62.9, 6.5 Hz)	122.79 m, 129.09 m	126.25 d.d.d (C^p, J = 160.4, 6.6, 6.6 Hz), 129.48 d.d.d (C^o, J = 160.4, 6.7, 6.5 Hz), 126.47 d.d (C^m, J = 159.7, 6.6 Hz), 133.79 d.d (C^i, J = 7.8, 7.8 Hz)	196.97 q (J = 6.3 Hz), 153.92 s
XV	122.08 d.d.d (J = 65.0, 6.3, 3.0 Hz), 126.16 d.d (J = 63.7, 8.3 Hz)	116.58 d.br.d (J = 163.1, 7.6 Hz), 117.62 d.m ($J \approx$ 162.0 Hz)	129.90 m, 123.75 m	126.38 d.d.d (C^p, J = 159.7, 7.1, 7.1 Hz), 130.25 d.d.d (C^o, J = 159.4, 7.0, 6.9 Hz), 126.66 d.d (C^m, J = 163.60, 6.9 Hz), 128.94 m (C^i)	164.66 m, 154.71 s
XVI	124.92 d.d (J = 63.4, 8.1 Hz), 120.92 d.d (J = 64.3, 8.0 Hz)	116.03 d.m (J ≈ 162.9 Hz), 115.21 (J = 162.6, 8.2, 1.2 Hz)	128.99 m, 122.32 m	129.89 d.m (C^o, $J \approx$ 161.0 Hz), 125.64 d.m (C^m, $J \approx$ 161.0 Hz), 125.58 d.m (C^p, $J \approx$ 160.0 Hz), 134.15 m (C^i)	164.92 m, 154.40 s

deviates from the heteroring plane: the torsion angle $C^1C^2C^{12}O^{12}$ is 44.1(3)°. There exists almost no conjugation between the tricyclic system and the phenyl substituent on C^3: the dihedral angle between the corresponding planes is 58.62(9)°, and the torsion angle $C^2C^3C^{31}C^{36}$ is 54.6(3)°. Presumably, the substituents on C^2 and C^3 in molecule **XI** are turned apart for steric reasons: fairly bulky groups are attached to contiguous carbon atoms of the five-membered ring. The substituents in **XI** are characterized by standard geometric parameters.

Molecules **XI** in crystal are linked by the hydrogen bonds N^5–H^5…$O^{4'}$ (2 – x, –y, 2 – z) with the following parameters N^5–H^5 0.92(2) E, H^5…$O^{4'}$ 1.86(2) Å, N^5…$O^{4'}$ 2.772(2) Å, ∠$N^5H^5O^{4'}$ 172(2)°. As a result, centrosymmetrical dimers are formed (Fig. 1). Probably, the C^4=O^4 bond is appreciably extended due to its participation in the above H-bonding. The O^{12} atom is involved in a bifurcate bond like C–H…O: intramolecular with the H^{111} methyl proton [H^{111}…O^{12} 2.51(4) Å, ∠$C^{11}H^{111}O^{12}$ 129(3)°] and intermolecular with the $H^{33'}$ proton (1 + x, y, 1 + z) of the phenyl substituent of the neighboring molecule [$H^{33'}$…O^{12} 2.52(3) Å, ∠$C^{33'}H^{33'}O^{12}$ 168(3)°.

The crystal packing is determined mainly by numerous π–π and π–H interactions between the aromatic electron systems (Fig. 2). Each molecule in the dimer participates in π–π interactions with two neighboring molecules, which are related to each other through the inversion and translation operations by +1 and –1 along the 0x crystallographic axis. The minimal distance between the ring planes is 3.36 Å, and the dihedral angle is 0.75°. As a result, stacks are formed along the 0x axis. The stacks are linked together through the existing hydrogen bonds N–H…O and C–H…O so that two-dimensional (layered) supramolecular structures parallel to the x0z plane are obtained. The phenyl substituents in molecules **XI** are

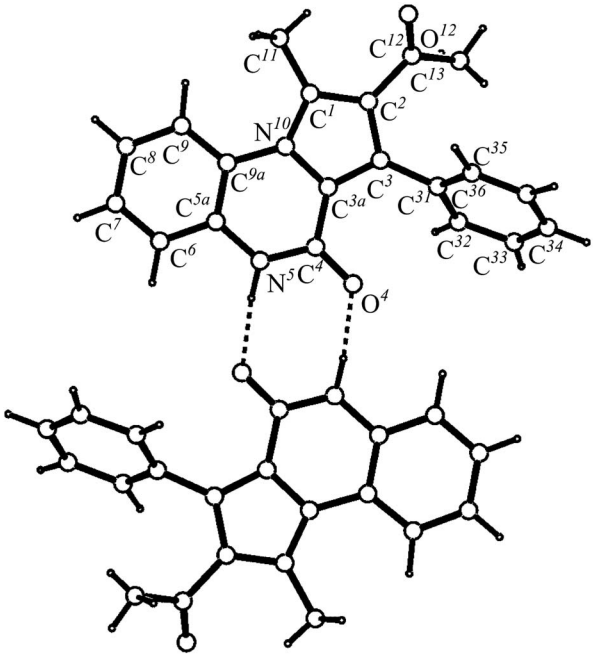


Fig. 1. Structure of the molecule of methyl 1-methyl-4-oxo-3-phenyl-4,5-dihydropyrrolo[1,2-*a*]quinoxalin-2-carboxylate (**XI**) in crystal (H-bonded dimer); hydrogen bonds are shown as dashed lines.

arranged at the outer sides of the layers (Fig. 3), giving rise to π–π contacts with the phenyl fragments of molecules located in the opposite layer. However, these contacts are weak: the distance between the benzene ring centers is 5.46 E, and the dihedral angle between their planes is 33.1°. Thus, crystals of **XI** include areas possessing different lipophilicities: layers containing mainly tricyclic fragments alternate with those containing phenyl, methyl, and acetyl substituents. Stacking effect makes crystal packing of the tricyclic fragments fairly tight, but mutual orientation of the substituents hampers such a tight packing (Fig. 3) The calculated crystal packing coefficient is equal to 0.67, which is closer to the lower limit of that parameter for organic crystals (0.65–0.77) [28].

EXPERIMENTAL

The melting points were determined on a Boetius device. The IR spectra were recorded on a UR–20 spectrometer in mineral oil. The ^{1}H NMR spectra of compounds **V**, **VI**, and **IX** were measured on a Bruker MSL–400 instrument at 400.13 MHz, and of the others, on a Bruker 250 spectrometer at 250.13 MHz. The ^{13}C NMR spectra were obtained on a Bruker MSL 400 instrument at 100.6 MHz. X–Ray diffraction data for compound **XI** were acquired on an Enraf–Nonius CAD–4 automatic four–circle diffractometer (λCuK_α irradiation, graphite monochromator, $\omega/2\theta$ scanning to $\theta \le 76°$) at the X–Ray Laboratory, Spectral Analytical Center of the Russian Foundation for Basic Research at the Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences. Total of 3648 reflections were measured, 2595 of which with $I >$

Table 4. Bond lengths *d*, bond angles ω, and torsion angles φ in the structure of methyl 1-methyl-4-oxo-3-phenyl-4,5-dihydropyrrolo[1,2-*a*]quinoxalin-2-carboxylate (**XI**)

Bond	*d*, Å	Bond	*d*, Å
O^4–C^4	1.243(2)	C^8–H^8	0.97(2)
O^{12}–C^{12}	1.205(2)	C^{9a}–C^9	1.389(3)
N^5–C^4	1.350(2)	C^9–H^9	1.02(3)
N^5–C^{5a}	1.395(2)	C^{12}–C^{13}	1.497(3)
N^5–H^5	0.92(2)	C^{5a}–C^6	1.401(3)
N^{10}–C^1	1.378(2)	C^{5a}–C^{9a}	1.406(3)
N^{10}–C^{9a}	1.394(2)	C^6–C^7	1.373(3)
N^{9a}–C^{9a}	1.428(2)	C^6–H^6	0.99(2)
C^1–C^2	1.387(3)	C^7–C^8	1.376(3)
C1–C^{11}	1.494(3)	C^7–H^7	0.96(3)
C^2–C^3	1.412(2)	C^8–C^9	1.389(3)
C^2–C^{12}	1.496(3)	C^{3a}–C^{34}	1.447(2)
C^{3a}–C^3	1.384(2)	C^3–C^{31}	1.486(3)
Angle	ω, deg	Angle	ω, deg
$C^4N^5C^{5a}$	124.1(2)	$N^5C^{5a}C^6$	118.7(2)
$C^1N^{10}C^{3a}$	108.4(1)	$N^5C^{5a}C^{9a}$	121.0(2)
$C^1N^{10}C^9$	131.2(1)	$N^{10}C^{9a}C^{5a}$	116.8(2)
$C^{3a}N^{10}C^{9a}$	120.4(1)	$N^{10}C^{9a}C^9$	124.7(2)
$N^{10}C^{3a}C^3$	109.2(1)	$O^{12}O^{12}C^2$	121.6(2)
$N^{10}C^{3a}C^4$	121.7(2)	$0^{12}C^{12}C^{13}$	120.3(2)
$C^3C^{3a}C^4$	129.1(2)	$C^2C^{12}C^{13}$	118.1(2)
$C^2C^3C^{3a}$	105.7(1)	$C^{3a}C^3C^{31}$	128.0(2)
$C^2C^3C^{31}$	125.9(2)	$O^4C^4N^5$	121.2(2)
$N^5C^4C^{3a}$	115.9(2)	$O^4C^4C^{3a}$	122.8(2)
Angle	φ, deg	Angle	φ, deg
$C^{5a}N^5C^4C^{3a}$	0.0(3)	$C^1C^2C^3C^{31}$	−173.9(1)
$C^4N^5C^{5a}C^{9a}$	−1.1(2)	$C^{12}C^2C^3C^{3a}$	−177.7(1)
$C^{3a}N^{10}C^1C^2$	0.8(2)	$C^1C^2C^{12}O^{12}$	44.1(3)
$C^{9a}N^{10}C^1C^2$	−178.7(1)	$C^3C^2C^{12}C^{13}$	43.1(3)
$C^1N^{10}C^{3a}C^3$	−0.9(2)	$N^{10}C^{3a}C^3C^2$	0.6(2)
$C^{9a}N^{10}C^{3a}C^3$	178.7(1)	$C^4C^{3a}C^3C^2$	−179.5(1)
$C^1N^{10}C^{9a}C^9$	−0.1(2)	$N^{10}C^{3a}C^4N^5$	1.1(2)
$C^{3a}N^{10}C^{9a}C^{5a}$	−0.1(2)	$C^3C^{3a}C^4O^4$	0.4(3)
$N^{10}C^1C^2C^3$	−0.5(2)	$C^2C^3C^{31}C^{32}$	−123.1(2)
$C^{11}C^1C^2C^{12}$	−0.8(3)	$C^{3a}C^3C^{31}C^{32}$	64.3(2)

Table 5. Coordinates of atoms in the structure of methyl 1-methyl-4-oxo-3-phenyl-4,5-dihydropyrrolo[1,2-*a*]quinoxalin-2-carboxylate (**XI**) and their equivalent isotropic temperature factors $B = 4/3 \sum_{i=1}^{3} \sum_{j=1}^{3} (a_i a_j) B(i, j)$ (Å^2) and isotropic temperature parameters of hydrogen atoms (Å^2)

Atom	*x*	*y*	*z*	*B*
O^4	0.9101(2)	0.05389(5)	0.9624(2)	5.15(3)
O^{12}	0.5079(3)	0.19084(6)	0.3355(2)	7.09(4)
N^5	0.8590(2)	–0.00172(5)	0.7710(2)	4.00(3)
N^{10}	0.7253(2)	0.05847(5)	0.5078(2)	3.42(3)
C^1	0.6667(3)	0.09532(6)	0.4050(2)	3.78(3)
C^2	0.6949(3)	0.13265(6)	0.5081(2)	3.77(3)
C^{3a}	0.7869(2)	0.07292(6)	0.6742(2)	3.45(3)
C^3	0.7706(3)	0.11906(6)	0.6778(2)	3.48(3)
C^4	0.8552(3)	0.04180(6)	0.8130(2)	3.79(4)
C^{5a}	0.8019(2)	–0.01745(6)	0.6060(2)	3.76(3)
C^6	0.8154(3)	–0.06344(7)	0.5788(3)	4.51(4)
C^7	0.7576(3)	–0.07999(7)	0.4179(3)	5.23(5)
C^8	0.6874(3)	–0.05128(8)	0.2836(3)	5.46(5)
C^{9a}	0.7315(2)	0.01205(6)	0.4692(2)	3.58(3)
C^9	0.6742(3)	–0.00554(8)	0.3078(3)	4.71(4)
C^{11}	0.5936(4)	0.09473(8)	0.2173(3)	5.26(5)
C^{12}	0.6593(3)	0.18008(7)	0.4490(2)	4.63(4)
C^{13}	0.8207(5)	0.21414(8)	0.5320(4)	7.06(7)
C^{31}	0.8023(3)	0.14848(6)	0.8268(2)	3.99(4)
C^{32}	0.9906(4)	0.15267(8)	0.9499(3)	6.01(6)
C^{33}	1.0101(5)	0.1832(1)	1.0813(4)	7.80(7)
C^{34}	0.8465(6)	0.20838(9)	1.0886(3)	7.93(8)
C^{35}	0.6625(5)	0.20348(9)	0.9711(3)	7.23(6)
C^{36}	0.6363(4)	0.17377(8)	0.8384(3)	5.15(5)
H^5	0.927(3)	–0.0211(8)	0.856(3)	4.7(5)
H^6	0.866(3)	–0.0841(8)	0.676(3)	5.1(5)
H^7	0.779(3)	–0.1112(9)	0.402(3)	6.0(5)
H^8	0.642(4)	–0.063(1)	0.170(3)	6.8(6)
H^9	0.608(4)	0.0127(9)	0.202(3)	6.7(6)
H^{32}	1.108(4)	0.135(1)	0.945(3)	8.7(8)
H^{33}	1.136(5)	0.181(1)	1.155(4)	9.5(8)
H^{34}	0.849(5)	0.229(1)	1.182(4)	9.9(9)
H^{35}	0.542(6)	0.223(2)	0.988(4)	11(1)
H^{36}	0.490(4)	0.1690(9)	0.747(3)	6.5(6)
H^{111}	0.595(6)	0.124(2)	0.191(5)	11(1)
H^{112}	0.459(4)	0.079(1)	0.177(3)	6.9(6)
H^{113}	0.702(4)	0.080(1)	0.177(3)	7.6(7)
H^{131}	0.805(4)	0.243(1)	0.480(4)	8.0(7)
H^{132}	0.947(8)	0.207(2)	0.488(5)	15(1)
H^{133}	0.801(8)	0.221(2)	0.625(6)	15(1)

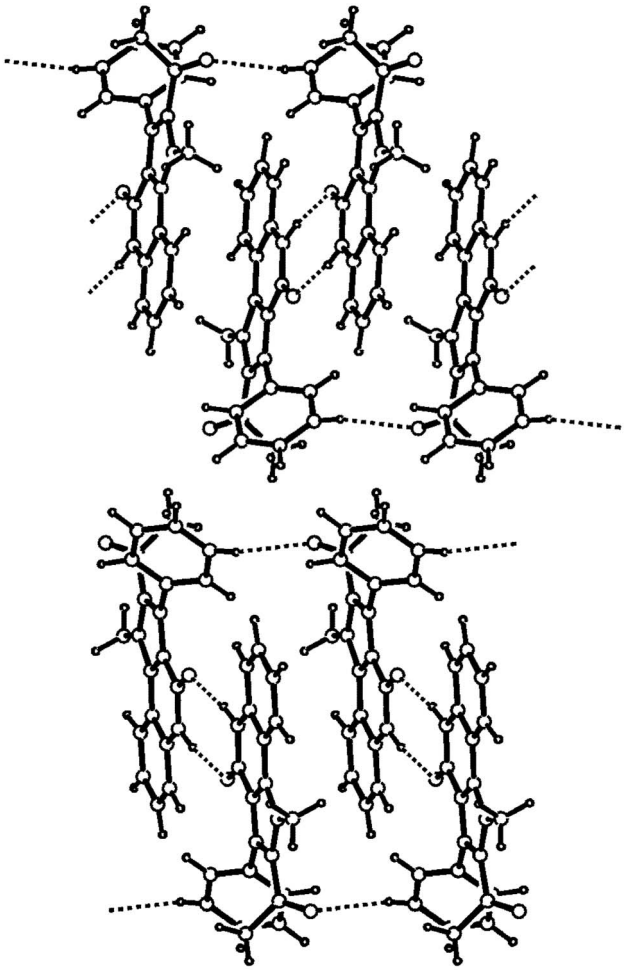


Fig. 2. Layered supramoleculyar structure of compound **XI** in crystal (view along the 0*b* edge of the unit cell); hydrogen bonds N–H…O and C–H…O are shown by dashed lines.

3σ(*I*). No decrease in the intensity of three control reflections was observed during the data acquisition. The absorption was not taken into account, for it was negligible (μCu 6.47 cm^{-1}). Monoclinic crystals, $C_{20}H_{16}N_2O_2$, with the following unit cell parameters (20°C): a = 6.784(3), b = 29.88(2), c = 8.379(4) E; β = 108.21(4)°; V = 1613(2) E^3; Z = 4; d_{calc} = 1.30 g/cm^3; space group $P2_1/a$. The structure was solved by the direct method using SIR program [28] and was refined first in isotropic and then in anisotropic approximation. The positions of hydrogen atoms were determined from the difference electron density series and were refined in isotropic approximation. The final divergence factors were R = 0.051, R_W = 0.064 (from 1925 independent reflections with $F^2 \geq 3\sigma$. All calculations were performed on an Alpha Station 200 PC using MolEN software package [29]. Intermolecular interactions were analyzed, and the structures were plotted, using PLATON software [30]. The principal geometric parameters are given in Table 4, and the coordi-

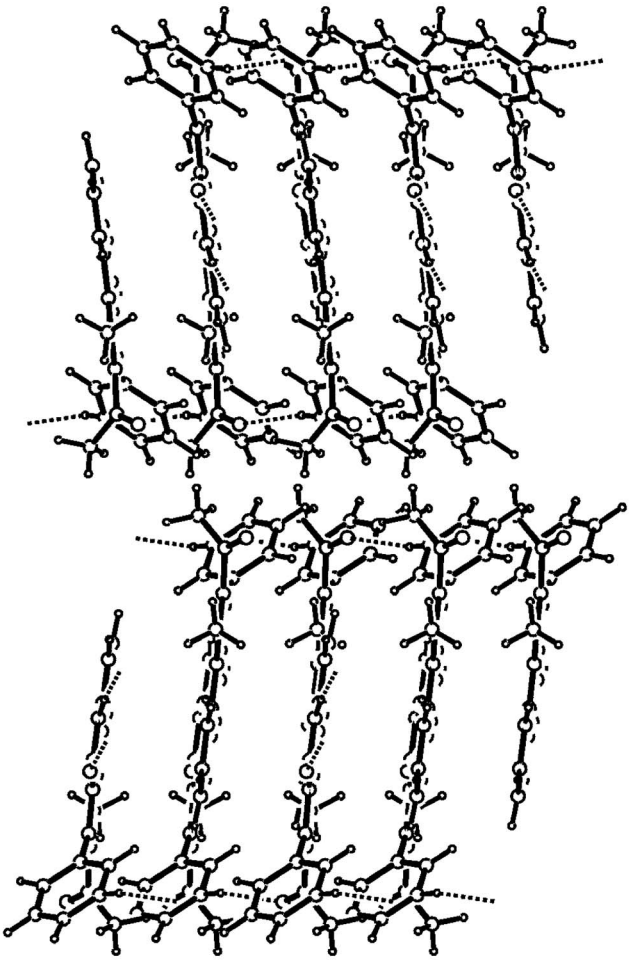


Fig. 3. Packing of molecules **XI** in crystal (view along the 0*z* axis

nates of atoms are listed in Table 5. The structure of molecule **XI** in crystal and hydrogen bond system therein are shon in Figs. 1–3.

3-(α-X-Benzyl)-1,2-dihydroquinoxalin-2-ones V–X (*general procedure*). A solution of 1.00 g of quinoxaline **I** in 10 ml of DMSO was added with stirring to a suspension of 0.31 g of KOH and 1 ml of the corresponding CH acid in 5 ml of DMSO, and the mixture was left to stand overnight. The product, quinoxaline **V**–**VII** was filtered off and washed with isopropyl alcohol and water. An additional amount of compound **V**–**VII** was isolated from the filtrate by precipitation with isopropyl alcohol. In the synthesis of compounds **VIII**–**X**, the reaction mixture was poured into water, and the precipitate was filtered off and washed with water. ^{13}C NMR spectrum of compound **V** (DMSO-d_6–acetone–d_6, 9:1), δ_C, ppm: 202.76 m, 202.79 m, 201.77 m, and 201.76 m (**C**OCH$_3$); 160.20 d (C^3, J = 6.6 Hz); 153.62 d (C^2); 137.23 m (C^i); 131.70 m and 131.07 m (C^{4a}, C^{8a}); 129.98 d.d (C^6 or C^7); 128.91 d.t.d (C^o, J = 158.2, 6.4, 5.8 Hz), 128.46 d.d (C^m, J = 160.5, 7.2 Hz); 128.26 d.d (C^5 or C^8, J = 157.0, 5.5 Hz); 127.25 d.d (C^p, J = 160.0, 6.5 Hz); 123.34 d.d (C^8 or C^5, J = 164.6, 6.6 Hz); 115.31 d.m (C^7 or C^6, J = 163.2 Hz); 70.95 d.m (Ph**C**H, J = 136.6 Hz); 46.58 d.d and 46.55 d.d (CO**C**HCO, J = 124.2, 3.8 Hz); 30.94 q, 30.91 q, 30.48 q, and 30.45 q (CH$_3$, J = 128.0 Hz). ^{13}C–{^1H} NMR spectrum of **IX** (DMSO-d_6–acetone–d_6, 9:1), δ_C, ppm: 158.06 br.s, 157.69 br.s, 136.16 s, 136.13 s, 135.98 s, 135.97 s, 131.01 br.s, 130.60 s, 130.44 s, 128.94 br.s, 128.72 br.s, 128.63 s, 128.59 s, 128.52 s, 128.45 br.s, 128.01 br.s, 127.87 s, 123.62 s, 123.55 s, 116.32 s, 116.17 s, 115.55 s, 115.47 s, 62.50 br.s, 62.12 br.s, 25.24 br.s, 13.59 s, 13.54 s.

1,2-Substituted 4-oxo-3-phenyl-4,5-dihydropyrrolo[1,2-*a*]quinoxalines XI–XVI (*general procedure*). A solution of 0.50 g of quinoxaline **V**–**X** in 10 ml of acetic acid was heated for 4 h under reflux and was left overnight. The crystals were filtered off and washed with isopropyl alcohol.

2-Acetyl-1-methyl-3-*p*-nitrophenyl-4,5-dihydropyrrolo[1,2-*a*]quinoxalin-4-one (XVIII). A solution of 0.60 g of quinoxaline **I** in 10 ml of DMSO was added with stirring to a suspension of 0.20 g of KOH and 0.5 ml of acetylacetone in 5 ml of DMSO, and the mixture was left overnight. It was then poured into water, and the precipitate was filtered off and washed with 5% aqueous acetic acid and isopropyl alcohol.

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