STRUCTURE OF QUINOXALYFORMAZANS IN SOLUTION

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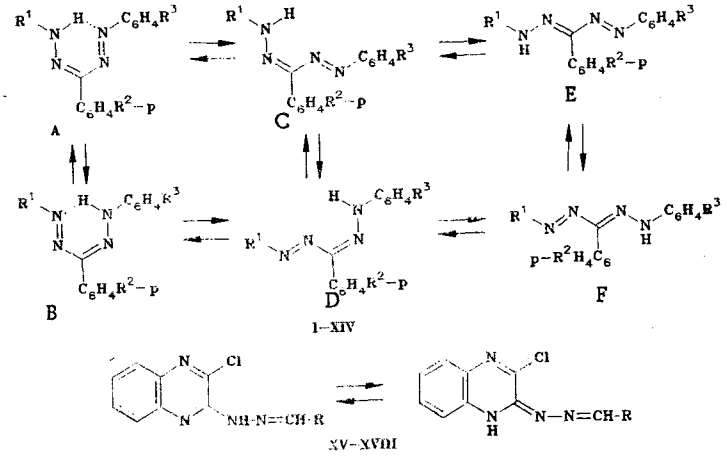
1(5),3-Diaryl-5(1)-quinoxalylformazans in the solid phase exist in the chelate syn-s-cis-trans conformation, whereas in solutions in CCl_4 and $CH(D)Cl_3$ they exist in the form of equilibrium mixtures of chelate and open forms. The percentage and conformation of the open form depend on the character of the substituents in the 1 and 3 positions of the aryl rings. It was established from the $^2J_{^{13}CNH}$ constants that the tautomeric equilibrium is shifted almost completely (no less than 90%) to favor the form with a proton attached to the nitrogen atom bonded to the heteroring.

The formation of various forms of formazans is possible both as a result of migration of a proton between different positions (azo—hydrazone [1, 2] and amino—imine [3-5] tautomerism) and as a result of a change in the geometry of the molecule (conformational isomerism [5-10]). Therefore, the determination of the structure of the formazan molecule means that one has to ascertain the conformation in which it exists and to determine the position of the prototropic equilibrium between the possible tautomeric forms.

In order to establish the structure of quinoxalylformazans I-XI we obtained their ^1H and ^{13}C NMR spectra, their IR spectra, and electronic spectra and compared them with the spectra of model compounds. As models we used 1(5)-aryl-3,5-(1)-diphenylformazans XII-XIV, (3-chloro-2-quinoxalyl)hydrazones XV-XVIII, and 1(5)-(3-chloro-2-quinoxalyl)-3-methyl-5(1)-(p-butylphenyl)- and -phenylformazans (XIX, XX).



I—XI R^1=3-chloro-2-quinoxalyl;XII—XIV $R^1=C_6H_5$; I—VI $R^2=OCH_3$; VII, VIII, XII—XIV R^2=H; IX—XI $R^2=NO_2$; I $R^3=p$-$N(CH_3)_2$; II, IX $R^3=C_3H_7$-p—i; III, VII, X $R^3=p$-C_4H_9; IV, VIII, XI, XIII R^3=H; V, XIV $R^3=p$-NO_2; VI $R^3=m$-NO_2; XII $R^3=p$-OCH_3; XV $R=p$-$C_6H_4OCH_3$; XVI $R=C_6H_5$; XVII $R=p$-$C_6H_4NO_2$; XVIII $R=CH_3$

The characteristic effects of the formation of a strong intramolecular hydrogen bond (IMHB) with a six-membered chelate ring [12, 13] are a bathochromic shift of the long-wave absorption band in the electronic spectra of formazans I-XI (Table 1) relative to the absorption band of formazans XIX and XX, which, judging from the chemical shift of the NH proton, exist in the syn-s-trans-trans conformation (Table 2, [11]), and an increase in δNH in the PMR spectra of I-XI as compared with δNH for hydrazones XV-XVII (5-6 ppm, Table 2).

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TABLE 1. Compounds I-XI and XV-XX

Compound	mp, °C	Crystallization solvent; crystal color	λ_{max}, nm (lg ε)	Found, %				Empirical formula	Calc., %				Yield, %
				C	H	Cl	N		C	H	Cl	N	
I	170—171	Acetone; dark brown	560 (4,48)[a]; 523 (4,49); 513 (4,49)[a]; 452 (4,40)[a]; 425 (4,19)[a]; 288 (4,42)	62,4	4,7	7,9	21,1	$C_{24}H_{22}ClN_7O$	62,7	4,8	7,7	21,3	50
II	127—128	80% ethanol; brown	530 (3,95)[a]; 485 (4,13); 365 (4,14)[a]; 357 (4,12); 291 (4,38)	65,6	5,2	7,5	18,1	$C_{22}H_{23}ClN_6O$	65,4	5,1	7,7	18,3	62
III	159—160 (dec.)	Acetone; brown	526 (4,10)[a]; 490 (4,24); 363 (4,23); 291 (4,46)	65,9	5,2	7,6	17,6	$C_{26}H_{25}ClN_6O$	66,0	5,3	7,5	17,8	65
IV	178—179 (dec.)	Acetone; reddish brown	523 (4,01)[a]; 488 (4,20); 367 (4,13); 352 (4,12)[a]; 290 (4,49)	63,5	4,2	8,3	20,0	$C_{22}H_{17}ClN_6O$	63,4	4,1	8,5	20,2	79
V	186—187 (dec.)	DMF; dark violet	570 (3,90)[a]; 534 (3,98); 385 (4,08); 315 (4,22); 294 (4,36)	57,6	3,4	7,9	21,0	$C_{22}H_{16}ClN_7O_3$	57,2	3,5	7,7	21,2	78
VI	183—184 (dec.)	DMF; dark violet	570 (390)[a]; 542 (4,01)[a]; 516 (4,06); 383 (4,10); 289 (4,49)	57,5	3,5	7,8	23,4	$C_{22}H_{16}ClN_7O_3$	57,2	3,5	7,7	21,2	76
VII	163—164 (dec.)	Dioxane; reddish brown	479 (4,39); 467 (4,36)[b]; 344 (4,19); 289 (4,47)	67,9	5,3	7,9	18,9	$C_{25}H_{23}ClN_6$	67,8	5,2	8,0	19,0	67
VIII	176—177 (dec.)	Dioxane; reddish brown	510 (3,63)[a]; 475 (4,34); 460 (4,32)[a]; 435 (4,20)[a]; 320 (4,07)[a]; 286 (4,39)	65,5	3,8	9,3	21,5	$C_{21}H_{15}ClN_6$	65,2	3,9	9,2	21,7	79
IX	182—183 (dec.)	DMF; dark brown	496 (4,63)[a]; 473 (4,80); 460 (4,78)b; 348 (4,73); 258 (4,78)	60,9	4,3	7,6	20,8	$C_{24}H_{20}ClN_7O_2$	60,8	4,3	7,5	20,7	61
X	200—201 (dec.)	DMF; dark brown	500 (4,26)[a]; 474 (4,47); 458 (4,43)[a]; 363 (4,24); 256 (4,44)	61,7	4,4	7,2	20,2	$C_{25}H_{22}ClN_7O_2$	61,5	4,5	7,3	20,1	63
XI	198—199 (dec.)	DMF; dark brown	500 (4,12)[a]; 470 (4,37); 453 (4,34)[a]; 331 (4,35); 254 (4,35)	58,2	3,2	8,2	22,5	$C_{21}H_{14}ClN_7O_2$	58,4	3,3	8,2	22,7	73
XV	174—175	Ethanol; yellow	406 (4,34); 391 (4,34); 3,49 (4,09); 336 (4,05); 275 (4,23); 251 (4,22)	61,1	4,2	11,1	17,7	$C_{16}H_{13}ClN_4O$	61,4	4,2	11,3	17,9	90
XVI	193—194	Ethanol; orange	430 (3,61)[a]; 394 (3,94)[a]; 381 (3,99); 370 (3,62)[a]; 338 (3,38); 321 (4,09)[a]; 306 (4,21)	63,5	3,8	12,7	19,6	$C_{15}H_{11}ClN_4$	63,7	3,9	12,5	19,8	90
XVII	238—239	Ethanol; orange	422 (4,29); 347 (4,39); 322 (4,23); 269 (4,15)	55,2	3,1	10,9	21,0	$C_{15}H_{10}ClN_5O_2$	55,0	3,1	10,8	21,4	92
XVIII	141—142	Ethanol; orange	375 (3,99)b; 365 (4,01); 353 (3,91)[a]; 274 (4,46); 269 (4,36)b	54,7	4,2	16,0	25,4	$C_{10}H_9ClN_4$	54,4	4,1	16,1	25,4	90
XIX	136—137 (dec.)	Ethanol; red	436 (4,19)[a]; 426 (4,26); 333 (4,11)	63,1	6,5	9,3	22,2	$C_{20}H_{21}ClN_6$	63,0	5,6	9,3	22,1	83
XX	156—157 (dec.)	Ethanol; red	428 (4,26); 321 (4,26); 258 (4,33)	59,1	4,1	10,8	25,2	$C_{16}H_{13}ClN_6$	59,0	4,0	10,9	25,8	78

[a]Inflection. [b]Shoulder.

TABLE 2. Characteristics of the N–H Bond in the IR and PMR Spectra of Solutions of I, III-VIII, X, and XV-XX[a]

Compound	νNH, cm^{-1}		A_{NH}, liters · mole^{-1} · cm^{-2}		δNH, ppm		Estimate of the amt. of the open form, %		
							IR	PMR	
	CCl_4	$CDCl_3$	CCl_4	$CDCl_3$	CCl_4	$CDCl_3$		b	c
I	3336	3336	1800	3000	14,54	14,32	30	28	17
III	3340	3339	700	1700	14,70	14,45	17	17	10
IV		3337		1700		14,49	17	17	10
V	3326 sh, 3334	3333	1400	2300	14,90	14,72	23	10	7
VI	3324, 3343 sh	3323	1100	2200	14,63	14,46	22	10	7
VII	3336	3338	900	1300	14,90	14,70	13	14	8
VIII		3337		1400		14,74	14	14	8
X	3341	3342	250	400	15,20	15,18	5	5	3
XV[d]	3355	3355	8300	9800	8,70	8,96			
XVI[d]	3352	3353	9500	10200	8,83	8,96			
XVII[d]	3348	3348		8400	8,96	9,08			
XVIII	3360	3359	8600	7800	8,49	8,67			
XVIII[e]	3385	3388	8700	8100	8,55	8,72			
XIX						11,50			
XX	3350	3349	8800	8600	11,38	11,49			

[a]The spectral characteristics of II, IX, and XI are not presented, since they differ little from the characteristics of III and X, respectively. [b]Note that δ_O = δNH for XIX-XX. [c]Note that δ_O = δNH for XV-XVII. [d]The characteristics of the N–H bond of the amino tautomers based on 100% content are presented; for the imino tautomers νNH 3433, 3434, and 3430 cm^{-1}, respectively, for XV, XVI, and XVII. [e]For the anti isomer.

The absorption band of the stretching vibrations of the N–H bond at 3100-3500 cm^{-1} is absent in the IR spectra of formazans I-XI in the solid phase; this indicates the presence of an intramolecular hydrogen bond (IMHB) [14]). Absorption bands of medium intensity of free NH groups at 3340-3360 cm^{-1} (see [4]) are observed in the IR spectra of hydrazones XV-XVII both in the solid phase and in solutions (Table 2). It is apparent from the data in Table 2 that an absorption band at 3320-3360 cm^{-1} is also observed in the IR spectra of formazans I-XI in solutions in CCl_4 and $CH(D)C_{l_3}$. In analogy with the data in [3, 4], this band undoubtedly is due to the νNH band of the free NH group of the amino tautomers (C-F). However, the intensities* of the νNH bands of the formazans are much lower than in the case of the hydrazones (Table 2). In addition, the intensities of the νNH bands of the formazans change by almost an order of magnitude, depending on the R^2 and R^3 substituents (Table 2). Such marked variations in the intensities cannot be due to the direct effect of substitution in the benzylidine fragment (see Table 2, XV-XX) but are evidently associated with the change in the ratio between the open and chelate conformations, as in [16]. The increase in the intensity of this band on passing from CCl_4 to the polar $CH(D)Cl_3$, its reversible changes in a mixed solvent (CCl_4 _ $CDCl_3$), and the absence of a change with time constitute evidence in favor of the existence of an equilibrium between the open and chelate conformations of the formazan (see [17]).

It is known that the NH proton is primarily attached to the nitrogen atom bonded to the more electron-acceptor substituent [18]. Proceeding from the acceptor properties of quinoxaline and, therefore, assuming the A, C, and [illegible] forms to be preponderant, we estimated the amounts of the open conformations of formazans I-XI in $CDCl_3$ with respect to the intensities of the νNH absorption bands of the formazans and hydrazones with identical R^2 substituents (Table 2).

In the NMR spectra of formazans I-IV and VII-XI (in contrast to V and VI; see Table 3) the number of observed signals of multiplets corresponds to the number of groups of rings, i.e., one observes an averaged (over all possible forms) spectrum owing to the rapid (on the NMR time scale; greater than 10^3 Hz) interconversions between the conformations. The estimation of the fraction of each of the conformations under such conditions is possible from a comparison of the observed δNH values with their values for each form within the approximation of fast exchange [20]:

$$P_o = (\delta_x - \delta_{obs})/(\delta_x - \delta_o) \cdot 100, \quad (1)$$

*The intensity of the νNH (A) band was determined by the Ramsay method [15].

TABLE 3. Chemical Shifts of the Signals of the Protons in the PMR Spectra of I-XI and XV-XIX in $CDCl_3$

Compound	1-Aryl			3-Aryl			5-Quinoxalyl				Remaining protons
	2,6-H	3,5-H	4-R[3]	2,6-H	3,5-H	4-R[2]	5-H	6-H	7-H	8-H	
I	7,98	6,78	3,14	8,12	6,98	3,89	7,87	7,50	7,67	8,02	
II	8,00	7,45	3,06	8,15	7,01	3,90	7,90	7,54	7,70	8,04	$(CH_3)_2$ 1,37; NH 14,48
III	7,99	7,39	2,74	8,16	7,00	3,90	7,90	7,53	7,69	8,06	$(CH_2)_2$ 1,20—1,80; CH_3 0,97
IV	8,07	7,49—7,56		8,18	7,02	3,89	7,92	7,56	7,72	8,07	
V[a]	8,15	8,45	—	8,14	7,02	3,90	7,93	7,60	7,75	8,08	
VI[b]				8,11	7,00	3,88	7,90	7,57	7,71	8,04	2-H 8,78; 4-H 8,41; 5-H 7,79; 6-H 8,31
VII	8,02	7,42	2,76	8,23	7,44—7,56		7,94	7,56	7,72	8,09	$(CH_2)_2$ 1,20—1,80; CH_3 0,98
VIII	8,08	7,55—7,66		8,22	7,44—7,54		7,92	7,55	7,72	8,08	
IX	7,98	7,46	3,02	8,42	8,29	—	7,91	7,59	7,75	8,06	$(CH_3)_2$ 1,34; NH 15,23
X	7,96	7,40	2,71	8,41	8,28	—	7,91	7,59	7,73	8,05	$(CH_2)_2$ 1,20—1,80; CH_3 0,94
XI	8,10	7,60—7,70		8,46	8,33	—	7,96	7,62	7,79	8,10	NH 15,29
XV[c]	—			7,75	6,91	3,83	7,84	7,46	7,64	7,94	CH=N 8,16
XVI[c]				7,82	7,39—7,51		7,89	7,49	7,67	7,99	CH=N 8,22
XVII[c]				7,96	8,28	—	7,91	7,54	7,70	7,97	CH=N 8,40
XVIII[d]							7,87	7,53	7,67	8,00	CH=N 7,62; CH_2 2,23
XIX	7,84	7,39	2,75	—	—	—	7,89	7,50	7,67	8,05	3-CH_3 2,44; $(CH_2)_2$ 1,20—1,80; CH_3 0,97

[a]Conformation E: δOCH_3 3.93 ppm, δNH 9.66 ppm. [b]Conformation E: δOCH_3 3.93, NH 9.48, and δ_{2-H} 8.73 ppm. [c]The δH values for the amino tautomers, the amounts of which are 72% for XV, 74% for XVI, and 81% for XVII. [d]The δH values for the amino tautomers in the syn conformation (∿65%) to which the greatest δ(CH=N) value [19] correspond; δ(CH=N) of the anti conformer is 7.21 ppm.

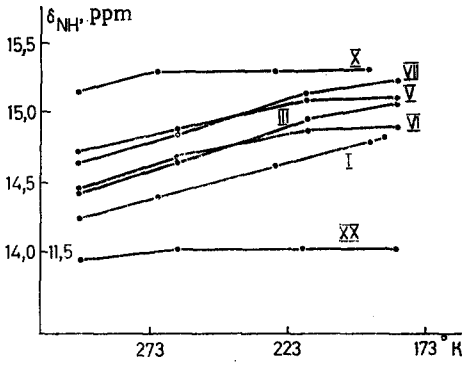

Fig. 1. Dependence of δ_{NH} on the temperature for formazans I, III, V-VII, X, and XX in CH_2Cl_2.

where P_o is the fraction of the open form, δ_{obs} is the δNH value observed in the spectrum, δ_o is the δNH value of the open form, and δ_x is the δNH value of the chelate form.

An increase in the amount of the chelate conformation leads to an increase in the δNH value (Table 2), and the magnitude of the δNH chemical shift of the chelate form was therefore assumed to be equal to its limiting value, which is reached as the temperature is decreased, for each formazan (Fig. 1).

The following two variants of the estimates were examined for the δ_o value: a) δ_o = δNH of hydrazones XV-XVII (8.9-9.1 ppm), which corresponds, as one might assume, to the δNH value in the E conformation; b) δ_o = δNH of formazans XIX and XX (11.5 ppm), which corresponds to the δNH value in the C conformation, according to the data in [11].

A comparison of the estimates obtained from the data from the IR and PMR spectra (Table 1) showed better agreement when δ_o = δNH of formazans was used, and this constitutes evidence in favor of the preferableness of syn-s-trans-trans conformation C for the open form of formazans I-XI.

The low-frequency shift of νNH and the increase in δNH in the spectra of formazans XIX and XX relative to hydrazone XVIII (Table 2) are apparently due to the formation of a weak intramolecular hydrogen bond (IMHB) [21].

TABLE 4. Changes in the Chemical Shifts (ppm) of the Signals of the Carbon Atoms of the Aryl Substituents in the ^{13}C NMR Spectra of I-V, VII, IX, X, and XII-XIV Induced by the Introduction of a Formazyl Grouping

Compound[a]	Carbon atom			
	ipso	ortho	meta	para
	1-Aryl			
I	24,3	−1,6	−1,4	2,8
II	25,1	−5,0	1,4	6,4
III	25,0	−5,2	1,0	6,3
IV	23,9	−5,3	1,2	4,7
V	20,4	−6,2	1,1	1,1
VII	24,2	−5,6	0,8	5,0
IX	24,7	−5,0	2,0	7,0
X	24,6	−5,4	1,1	7,0
XII	25,4	−6,0	0,6	2,0
XIV	24,6	−6,0	1,1	3,8
XIX	25,4	−4,3	1,2	6,6
b	24,0	−5,8	0,3	2,2
	5-Aryl			
XII	15,8	−12,9	0,9	−4,6
XIV	14,5	−14,8	2,2	−7,9
c	16,2	−15,8	0,8	−8,4
XIII	19,4	−9,7	0,9	−1,0
XIII[d]	20,6	−9,5	0,8	−1,3
XIII[e]	19,5	−10,4	1,6	−2,0
XIII[f]	20,1	−10,8	0,6	−3,2

[a]1-Formazyl for a 1-aryl substituent in the case of I-V, VII, IX, X, XII, XIV, and XIX; 5-formazyl for a 5-aryl substituent in the case of XII and XIV, and 1(5)-formazyl in the case of XIII. [b]For azobenzene [23]. [c]For benzaldehyde phenylhydrazone [24]. [d-f]Calculation from the averaging of the CCS values of the 1- and 5-formazyl groups of XII and XIV and the azo and hydrazono groups, respectively.

The data in Table 2 showed that the amount of the formazan in the C conformation increases as the electron-donor capacities of the R^2 and R^3 substituents increase. The introduction of a nitro group into the para or meta position of the 1-phenyl ring (formazans V and VI) leads to the appearance in the PMR spectra of additional signals of the methoxy and 1(5)-aryl groups and the NH proton (Table 3). The δNH value is close to the δNH value of hydrazone XV and evidently corresponds to anti-s-trans-conformation E.

The contradiction between the estimates of the percentage of the open form from the δNH value, on the one hand, and from the intensity of the νNH band, on the other (Table 2), and the appearance in the IR spectra of formazans V and VI of an additional νNH band (Table 2) are explained by the existence of this conformation (∿13% at 30°C). This is evidently due to the fact that in $CH(D)Cl_3$ the frequencies of the νNH bands of the C and E conformations coincide, whereas they differ in CCl_4.

For the determination of the position of the tautomeric equilibrium in solutions of formazans I-XI, XIX, and XX we used NMR spectroscopy, which makes it possible to make this estimate within the approximation of rapid exchange.

In contrast to [5], for the estimation of the fractions of the possible tautomers we used ^{13}C NMR spectroscopy, since the changes in the ^{13}C shifts correlate with the changes in the electron densities on the carbon atoms [22]. In addition, we expected that spin–spin coupling between the carbon-13 atoms in the ipso positions and the NH proton may be observed in the ^{13}C NMR spectra.

As the indicator parameters for the estimation of the amounts of tautomers we used the changes in the $\delta^{13}C$ chemical shifts (CCS) of the carbon atoms of the 1(5)-aryl group of the formazan relative to a model R^3-benzene. We determined the limiting ^{13}C CCS values for the aryl groups in the 1 and 5 positions in the case of formazans XII and XIV, the proton in which is localized virtually at one of the nitrogen atoms [2]. We noted better agreement between the experimental and calculated CCS values of the 1(5)-phenyl ring of formazan XIII (Table 4) when we used the CCS values of formazan for the calculation. The CCS value of the formazyl substituent was calculated via an additive scheme with allowance for the contributions of other substituents to the CCS [23].

A comparison of the calculated CCS values of formazans II-IV, VII, IX, and X with model compounds demonstrated the closeness of the former to the CCS values of the 1-formazyl and azo groups (Table 4). Thus these formazans exist primarily in the form of tautomer A. Transition to the syn-s-trans-trans conformation of the molecule does not have a substantial effect on the position of the NH proton (Table 4, formula XIX). Formazans I and V with strong donor and acceptor substituents in the phenyl ring constitute an exception. The amounts of tautomer B in them may increase somewhat.

The existence of a $^2J_{^{13}CNH}$ constant at the carbon atoms in the ipso position relative to the formazyl group of formazans XII-XIV also makes it possible to use its value to estimate the amounts of tautomers. The signals of the ipso-carbon-13 atoms in the monoresonance spectra have a more complex structure, since coupling with the meta protons of the phenyl ring also occurs. We therefore used the method of selective double heteronuclear $^{13}C-\{H_{meta}\}$ resonance; the power of the irradiation in this case was selected in such a way that the magnitude of the distortions by the field of the irradiation of the splittings in the spectrum did not exceed the other errors in the determination of $^2J_{^{13}CNH}$. The ratio of tautomers A and B was determined within the approximation of rapid exchange [20]; since $^2J_{^{13}CNH} = 0$ for the 1-formazyl group, the computational equation is simplified to the expression [25]:

$$P_B = J_{obs} / J_B, \quad (2)$$

where P_B is the fraction of tautomer B, J_{obs} is the observed spin–spin coupling constant (SSCC), and J_B is the SSCC of tautomer B, which was assumed to be twice the $^2J_{^{13}CNH}$ value of formazan XIII (7.2 Hz).

The amount of tautomer B in formazans XII-XIV determined from Eq. (2) corresponds [within the limits of the accuracy of the determination (±5%)] to the previously established value [2]. Spin–spin coupling of the ipso-carbon-13 atom of the 5(1)-quinoxalyl group with the NH proton is observed in the ^{13}C NMR monoresonance spectra of formazans I-III, IX, and X (Table 5). It is not seen at the ipso-carbon atom of the 1(5)-aryl group, i.e., $^2J_{^{13}CNH} \leqslant$ 0.6 Hz (the minimal determinable value predetermined by the spectral recording conditions). Consequently, the amount of tautomer B $\leqslant$ 9% for formazans I-III, IX, and X.

In contrast to the method in [2], the proposed method for the determination of the amounts of tautomers does not require isotropic enrichment. The accuracy in the determination of the SSCC is limited only by the resolving power of the spectrometer. The indicated approach can be used to estimate the position of prototropic equilibria and in other tautomeric systems.

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EXPERIMENTAL

The IR spectra of I-XX in CCl_4 and $CH(D)Cl_3$ and in KBr pellets were obtained with a UR-20 spectrometer (the concentration of the solutions ranged from 10^{-3} to 10^{-1} mole/liter). The absorption spectra of solutions in $CHCl_3$ ($5\cdot10^{-4}$ to $5\cdot10^{-3}$ mole/liter) were obtained with Shimadzu MPS-50L and Specord UV-vis spectrophotometers. The PMR spectra (100 MHz) were obtained for solutions in CCl_4, $CDCl_3$, and CH_2Cl_2 ($5\cdot10^{-3}$ to 10^{-1} mole/liter) with a Varian XL-100-12 spectrometer with tetramethylsilane as the internal standard. The assignment of

TABLE 5. Chemical Shifts (δ, ppm) in the ^{13}C NMR Spectra of I-VII, IX, and X and XII-XIV, and XIX in $CDCl_3$[a]

Compound	1-Aryl				3-Aryl						5-Quinoxalyl								$^2J_{^{13}CNH}$, Hz
	$C_{(1)}$	$C_{(2,6)}$	$C_{(3,5)}$	$C_{(4)}$	$C_{(1)}$	$C_{(2,6)}$	$C_{(3,5)}$	$C_{(4)}$	R^2	$C_{(3)}$	$C_{(2)}$	$C_{(3)}$	$C_{(5)}$[k]	$C_{(6)}$	$C_{(7)}$	$C_{(8)}$	$C_{(9)}$	$C_{(10)}$	
I[b]	143,25	127,77	111,73	153,82	128,82	129,47	113,56	160,37	55,30	147,56	145,14	137,40	127,50	126,53	130,36	125,89	141,42	138,07	9,5
II[c]	150,77	123,32	127,72	155,09	128,26	129,28	113,86	160,69	55,33	146,73	145,03	137,18	127,99	127,29	130,58	127,72	141,20	138,59	9,0
III[d]	150,68	123,16	129,62	149,25	128,35	129,25	113,86	160,68	55,31	146,57	145,03	137,20	127,89	127,21	130,52	127,76	141,24	138,59	9,0
IV	152,42	123,16	129,66	133,15	128,34	129,30	113,97	160,80	55,37	146,66	145,06	137,21	127,98	127,45	130,67	127,80	141,24	138,73	—
V[e]	155,04	123,21	125,05	149,46	127,65	128,91	113,99	160,81	55,28	144,55	144,55	137,23	128,17	127,87	130,83	127,87	141,13	139,06	—
VI[f]	152,68	116,29	149,34	126,43	127,62	129,07	114,09	160,89	55,38	146,20	144,34	137,05	128,02	127,85	130,87	128,02	141,02	138,99	—
VII[g]	150,75	123,23	129,69	149,40	135,76	127,76	128,45	129,25	—	146,58	145,01	137,24	127,95	127,51	130,68	127,76	141,18	138,78	—
IX[h]	150,36	123,24	127,94	155,73	142,12	127,70	123,62	147,82	—	143,35	144,51	137,05	127,95	128,25	130,94	127,91	140,87	139,08	9,8
X[h]	150,26	123,10	129,74	150,01	142,11	127,64	123,62	147,83	—	143,21	144,49	137,04	127,99	128,19	130,87	127,89	140,87	139,08	9,4
XIX[i]	151,06	124,05	129,64	149,61	—	—	—	—	—	154,17	143,30	136,61	127,98	126,79	130,68	127,41	141,01	138,04	—
											$C_{(1)}$	$C_{(2,6)}$	$C_{(3,5)}$	$C_{(4)}$					
XII[j]	144,26	123,45	114,70	161,94	137,66	126,02	128,34	127,55	—	141,05	146,20	115,64	129,42	123,91					7,1
XIII	147,93	118,77	129,39	127,45	137,42	125,87	128,35	127,61	—	141,22	147,93	118,77	129,39	127,45					3,6
XIV	152,06	122,51	129,60	132,29	136,07	126,68	128,56	128,76	—	143,02	149,13	114,56	125,79	143,12					6,8

[a]The spectra of VIII and XI were not obtained because of their low solubilities. [b]For $N(CH_3)_2$: 40.17 ppm. [c]For CH: 34.35 ppm; for $(CH_3)_2$: 23.70 ppm. [d]For 1-CH_2: 35.74 ppm; for 2-CH_2: 33.20 ppm; for 3-CH_2: 23.33 ppm; for CH_3: 13.88 ppm. [e]For $C_{(5)}$: 130.56 ppm; for $C_{(6)}$: 123.54 ppm. [f]For 1-CH_2: 35.80 ppm; for 2-CH_2: 22.37 ppm; for CH_3: 13.89 ppm. [g]For CH: 33.40 ppm; for $(CH_3)_2$: 23.66 ppm. [h]For 1-CH_2: 35.78 ppm; for 2-CH_2: 33.15 ppm; for 3-CH_2: 22.37 ppm; for CH_3: 13.84 ppm. [i]For 1-CH_2: 35.80 ppm; for 2-CH_2: 33.22 ppm; for 3-CH_2: 22.33 ppm; for CH_3: 13.92 ppm; for 3-CH_3: 15.76 ppm. [j]For OCH_3: 55.66 ppm. [k]Except for I and XIX, the assignment of the signals may be reversed.

the signals in the PMR spectra was made with the aid of homonuclear INDOR [20]. It was assumed that the 6-H proton of the quinoxaline fragment is located at strongest field, as has been established for the amino forms of quinoxalylhydrazones with an intramolecular hydrogen bond [26]. The chemical shifts of the signals of the protons were determined with respect to the centers of the multiplets. The accuracy in the determination for the most strongly coupled 6- and 7-H protons of the quinoxalyl group, according to a calculation by the method in [20], was ±0.03 ppm.

The ^{13}C NMR spectra (25.16 MHz) were recorded under pulse conditions with Fourier transformation with the same spectrometer. The assignment of the signals was made on the basis of an analysis of the spectra obtained for both complete and selective decoupling from the spin–spin coupling with the protons and also by a comparison of them with the spectra of quinoxaline derivatives [27] and with the results of calculations of the $\delta^{13}C$ values from additive parameters [23]. In addition, for the assignment we used the spectra without decoupling from the spin–spin coupling with the protons.

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The accuracy in the determination of the chemical shifts in the PMR spectra was ±0.01 ppm, as compared with ±0.05 ppm in the ^{13}C NMR spectra. The chemical shifts are given on the δ scale with respect to TMS.

Formazans I-XI, XIX, and XX (Table 1) were obtained by coupling hydrazones XV-XVIII with the corresponding diazonium salts in an alkaline medium [28]. Formazans XII-XIV were synthesized by the method in [29]. The purity of the compounds obtained was monitored by thin-layer chromatography (TLC) on Silufol UV-254 plates.

4-Methoxybenzaldehyde (3-Chloro-2-quinoxalyl)hydrazone (XV). A suspension of 1.94 g (0.01 mole) of 2-hydrazino-3-chloroquinoxaline and 1.36 g (0.01 mole) of 4-methoxybenzaldehyde in 50 ml of acetic acid was stirred at room temperature for 15–20 min, during which the suspension became a solution, after which the yellow precipitate that formed was removed by filtration and dried.

Hydrazones XVI-XVIII. These compounds were similarly obtained (Table 1).

1,3-Diphenyl-5-(3-chloro-2-quinoxalyl)formazan (VIII). A 0.93-g (0.01 mole) sample of aniline in 10 ml of dilute (2:1) hydrochloric acid was diazotized at 0°C with 0.7 g (0.01 mole) of sodium nitrite, and the resulting solution was added dropwise with stirring to a cooled (to 0–2°C) solution of 2.82 g (0.01 mole) of hydrazone XVI in 100 ml of dimethylformamide (DMF); a 40% aqueous solution of sodium hydroxide was added simultaneously, thereby maintaining pH 8.5–9.0. The mixture was maintained at 0–4°C for 1.5 h, after which it was diluted to 400 ml with water. The aqueous solution was neutralized with cooling with dilute (1:1) hydrochloric acid to pH 6–7. The precipitate was removed by filtration, washed with water, and dried.

Formazans I-VII, IX-XI, XIX, and XX. These compounds were similarly obtained (Table 1).

LITERATURE CITED

1. G. V. D. Tiers and S. Plovan, J. Org. Chem., 25, 285 (1960).
2. P. B. Fischer, B. L. Kaul, and H. Zollinger, Helv. Chim. Acta, 51, 1449 (1968).
3. E. S. Karavaeva, N. P. Bednyagina, T. A. Sharkova, and I. I. Mudretsova, Khim. Geterotsikl. Soedin., No. 10, 1420 (1975).
4. I. I. Mudretsova and S. L. Mertslov, Khim. Geterotsikl. Soedin., No. 12, 1666 (1975).
5. B. I. Buzykin and N. N. Bystrykh. Zh. Org. Khim., 19, 1069 (1983).
6. G. N. Kipunova, N. N. Gulemina, A. P. Zeif, and N. P. Bednyagina, Khim. Geterotsikl. Soedin., No. 4, 493 (1974).
7. I. A. Nasyr and V. M. Cherkasov, Khim. Geterotsikl. Soedin., No. 10, 1409 (1976).
8. G. V. Avramenko, G. A. Maksakova, V. A. Maksakov, and B. I. Stepanov, Zh. Obshch. Khim., 51, 2521 (1981).
9. J. W. Lewis and C. Sandorfy, Can. J. Chem., 61, 809 (1983).
10. A. V. El'tsov, A. I. Yalandina, A. I. Ponyaev, G. N. Lipunova, and N. P. Bednyagina, Zh. Obshch. Khim., 53, 2587 (1983).
11. A. T. Hutton and M. N. H. Irving, Chem. Commun., No. 16, 763 (1980).
12. A. P. Zeif, G. N. Lipunova, N. P. Bednyagina, L. N. Shchegoleva, and L. I. Chernyavskii, Zh. Org. Khim., 6, 2590 (1970).

13. L. W. Reeves, F. A. Allan, and K. O. Strömme, Can. J. Chem., 38, 1249 (1960).
14. N. A. Klyuev, V. G. Zhil'nikov, G. G. Aleksandrov, I. I. Grandberg, and G. N. Lipunova, Zh. Org. Khim., 19, 2615 (1983).
15. D. A. Ramsay, J. Am. Chem. Soc., 74, 72 (1952).
16. B. E. Zaitsev, G. V. Sheban, G. V. Shandurenko, G. V. Avramenko, and B. I. Stepanov, Zh. Obshch. Khim., 52, 49 (1982).
17. M. Kh. Karapet'yants, Introduction to the Theory of Chemical Processes [in Russian], 3rd Edition, Vyssh. Shkola, Moscow (1981), p. 34.
18. B. I. Buzykin, in: The Chemistry of Hydrazones [in Russian], Nauka, Moscow (1977), p. 196.
19. Yu. P. Kitaev and B. I. Buzykin, Hydrazones [in Russian], Nauka, Moscow (1974), p. 53.
20. N. M. Sergeev, NMR Spectroscopy [in Russian], Izd. Mosk. Gos. Univ., Moscow (1981), p. 280.
21. G. Pimentel and O. MacClellan, The Hydrogen Bond, W. H. Freeman, San Francisco (1964).
22. G. C. Levy and G. L. Nelson, Carbon-13 Nuclear Magnetic Resonance for Organic Chemists, New York (1975).
23. D. F. Ewing, Org. Magn. Reson., 12, 499 (1979).
24. S. Balt, J. Meuldijk, and W. E. Renkema, Trans. Met. Chem., 5, 357 (1980).
25. V. Bekarek, K. Rothschein, P. Vetesnik, and M. Vecera, Tetrahedron Lett., No. 34, 3711 (1968).
26. V. M. Dziomko, M. N. Stopnikova, L. V. Shmelev, Yu. S. Ryabokobylko, G. M. Adamova, and R. V. Poponova, Khim. Geterotsikl. Soedin, No. 10, 1408 (1980).
27. H. Mchab, J. Chem. Soc., Perkin Trans. I, No. 2, 357 (1982).
28. W. Ried, Angew. Chem., 64, 391 (1952).
29. H. Pechmann, Ber., 27, 1678 (1894).

INVESTIGATION OF THE DECOMPOSITION OF 1,3-DIARYL-5-(3-CHLORO-2-QUINOXALYL)-FORMAZANS BY PMR AND MASS SPECTROMETRY

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In contrast to triarylformazans, 1,3-diaryl-5-(3-chloro-2-quinoxalyl)formazans are unstable in ordinary organic solvents. When they are heated in chloroform, they undergo acidic cleavage, which leads to the formation of 3-chloro-2-quinoxalylhydrazones of p-substituted benzaldehydes and arenediazonium cations. These compounds, as a result of a redox reaction with the participation of the solvent, are converted to 4-chloro-1-(4-Y-phenyl)-1,2,4-triazolo[4,3-a]quinoxalines, substituted benzenes, nitrogen, and hydrogen chloride. The formation of the latter transforms the entire decomposition process into an autocatalytic process. Effects of chemical polarization of the nuclei (CPN), which unambiguously indicate the intermediate formation of diazoaryl radicals during the process, are observed in the PMR spectra of the final products. Such CPN effects, which were also observed in dimethyl sulfoxide (DMSO) and glacial acetic acid, indicate a process involving the oxidative formation of annelated triazoles from α-azahetarylhydrazones via a radical pathway within a solvent "cage."

We have previously shown [1] that when 1,3-diaryl-5-(3-chloro-2-quinoxalyl)formazans I-XII are heated in chloroform, they undergo cleavage, as a result of which, three ring 4-chloro-1-(4-Y-phenyl)-1,2,4-triazolo[4,3-a]quinoxalines (XVI-XVIII), substituted benzenes (XIX-XXIII), nitrogen, and hydrogen chloride are formed (see Scheme 1).

Sedov and co-workers [2] have demonstrated the instability of quinoxalylformazans in acidic media; this is, on the whole, also characteristic for other unsymmetrical hetaryl-

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