ether–benzene (10:1) to give 0.29 g (58%) of II, with mp 132-134° and R_f 0.27, and 0.17 g (34%) of starting I, with mp 164-165° and R_f 0.55. PMR spectrum (D_2O): singlets at 2.7, 2.9 (5- and 7-CH_3), 7.2 (6-H), and 8.8 ppm (2-H).

Hydrazinolysis of I and II. A 0.3-g (2 mmole) sample of I was dissolved in 10 g of hydrazine hydrate, and the mixture was refluxed for 6 h. The hydrazine hydrate was then vacuum evaporated to dryness, and the residue was refluxed with 20 ml of chloroform. The chloroform-insoluble 3-amino-1,2,4-triazole (VI) was separated to give 0.16 g (94%) of a product with mp 157-158° and a molecular weight (by mass spectrometry) of 84 that was chromatographically identical to a genuine sample.

Removal of the chloroform by distillation, and recrystallization of the residue from benzene gave 0.18 g (93%) of 3,5-dimethylpyrazole (V) with mp 103-104° (in agreement with the literature value) and a molecular weight (by mass spectrometry) of 96. As in the preceding experiment, 1 g of II yielded 0.54 g (95%) of VI and 0.6 g (93%) of V.

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SYNTHESIS AND SOME PROPERTIES OF QUINAZOLYLFORMAZANS

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Some previously undescribed N-quinazolylformazans were synthesized, and some of their properties were studied. The absorption spectra of the formazans and their ions are discussed. The compositions of complexes of the formazans with Ni^{2+} and their instability constants were determined.

The properties and structures of N-quinoxalylformazans were previously examined in [1]. It seemed of interest to synthesize and investigate the previously undescribed N-quinazolylformazans I, which contain an isomeric heterocyclic quinazolyl group.

Formazans Ia-e were obtained by diazo coupling of 4-quinazolylhydrazones with benzenediazonium chlorides via the scheme given below. The structure of Ia was confirmed by oxidation with Pb_3O_4 in acetic acid by the method in [2] to a tetrazolium acetate (IIa), which, as in [3], is converted to a 2,5-diphenyltetrazole (IIIa) on treatment with dilute hydrochloric acid at 20°C.

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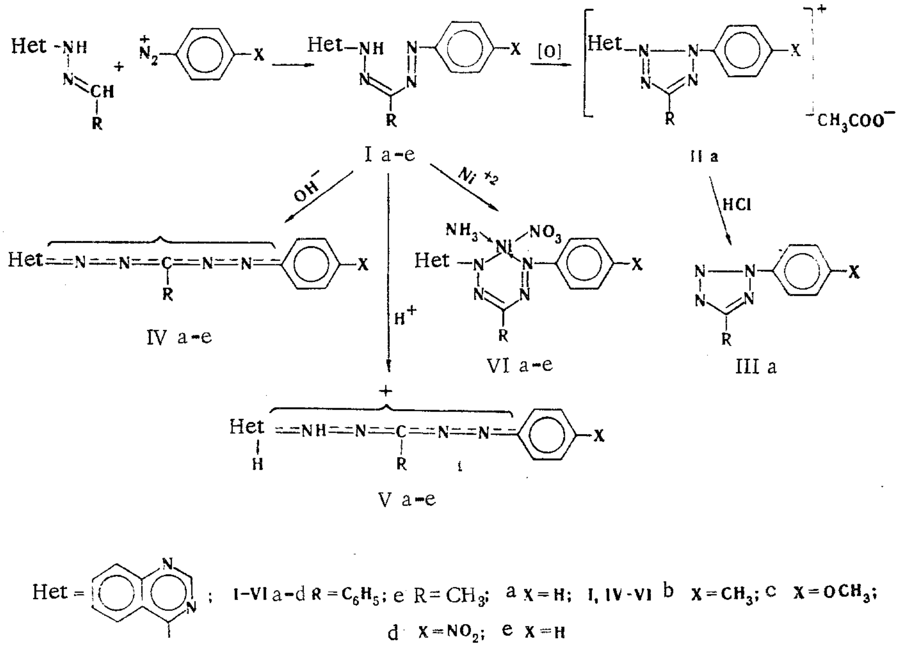

Het = ; I-VI a-d $R=C_6H_5$; e $R=CH_3$; a $X=H$; I, IV-VI b $X=CH_3$; c $X=OCH_3$; d $X=NO_2$; e $X=H$

It must be noted that acetate IIa is not reduced to the starting formazan on treatment with ascorbic acid in an alcoholic alkaline medium by the method in [4]. Salt IIa is probably decomposed in the alkaline medium of the reducing agent.

Quinazolinformazans I are less deeply colored than the corresponding quinoxalylformazans [1]; they display negative solvatochromism. Thus, for example, the longwave absorption maxima of formazans Ia,d are shifted hypsochromically as the polarity of the solvent increases solvent and λ_{max}(in nanometers): cyclohexane 450 and 470, chloroform 442 and 464, acetonitrile 422 and 442, and ethanol 370 and 355, respectively. A hypsochromic shift of the longwave absorption maximum is observed for formazans Ia-c also in dioxane as compared with the absorption spectra in cyclohexane. This may be explained by opening of the quasiaromatic ring formed by an intramolecular hydrogen bond (IHB) in the formazyl grouping in a dioxane medium. Formazans Id,e practically do not have IHB, inasmuch as the spectra of the formazans do not change substantially in dioxane solution (Table 1).

The considerable bathochromic shift of the absorption spectra of formazans I to the visible region in alcoholic alkali (62-113 nm) and concentrated sulfuric acid (164-170 nm) as compared with the spectra in cyclohexane is explained by the formation of anions IV in alkaline media and cations V in acidic media. Of the IV anions, ion IVd, which contains a nitro group, is the most deeply colored; the deepening of the color of this ion should probably be ascribed to the formation of the acid form of the nitro group in alkaline media. Ions IV and V probably have structures similar to the structure of the analogous ions of formazans of the benzazole series [5] (see the scheme above).

It was established by spectrophotometry that anions IV undergo practically no decomposition in concentrated alcoholic alkali even after 24 h. Cations V are less stable in concentrated sulfuric acid (sp. gr. 1.84) than the cations of quinoxalylformazans [1]. Thus, for example, ions Vb-d undergo complete decomposition after 5-10 min, whereas ions Va,e, although they are more stable, decompose with time: 3.8 and 4.6% decomposition, respectively, after 2 h, 5.7 and 18.5% decomposition after 3 h, and 18.9 and 35.4% decomposition after 24 h.

Formazans I form deeply colored complexes with Cu^{2+}, Ni^{2+}, Co^{3+}, etc. cations. The decompositions of the complexes (VIa-e) of the investigated formazans with Ni^{2+} (with a nickel to formazan ratio of 1:1) were determined by the isomolar-series method [6], and their instability constants were found (Table 1). The curves of the formation of the complexes have one isopiestic point, and the complexes have similar absorption spectra; this indicates the formation of complexes with identical structures.

TABLE 1. Physicochemical Properties of N-Quinazolylformazans (1)

Compound	Empirical formula	mp, °C (crystallization solvent)	Found, %	Calc., %	Yield, %[a]
Ia	$C_{21}H_{16}N_6\cdot 2H_2O$[б]	119—121 (dec., ether	21,9	21,6	38
Ib	$C_{22}H_{18}N_6\cdot 2H_2O$[б]	137—139 dec., alcohol—water	20,6	20,8	41
Ic	$C_{22}H_{18}N_6O$	125—127 (cyclohexane)	20,9	21,1	27
Id	$C_{21}H_{15}N_7O_2$	138—140 (cyclohexane	24,3	24.6	21
Ie	$C_{16}H_{14}N_6$	157—159 (benzene)	28,6	28,9	32

TABLE 1 (cont'd)

Compound	Absorption spectra, λ_{max}, nm ($\varepsilon\cdot 10^4$)					Complexes VI	
	alcohol	dioxane	cyclohexane	KOH + alcohol (pH > [4]	H_2SO_4 (d 1,84)	alcohol + buffer (pH 7.0)	K_{inst} 10^{-6}, g-mole/liter
Ia	290 (1,96), 360 (2,1), 370 (2,0)[c]	290 (0,77), 380 (0,82), 420 (0,62)[c]	290 (2,50), 450 (1,46)	515 (1,01)	620 (0.44)	613 (0,89)	2,3
Ib	285 (1,92), 370 (2,2)	290 (0,96), 405 (1,4), 435 (1,32)	385 (1,78), 455 (1,46)	517 (0,45)	—	612 (1,1)	0,8
Ic	285 (1,62), 360 (3,0), 400 (2,16)[c]	335 (1,05), 350 (1,05), 400 (1,06), 425 (1,7), 440 (1,6)	335 (1,66), 450 (1,84)	518 (1,38)	—	618 (1,32)	0,2
Ie	290 (1,6), 355 (1,5)	365 (1,0), 393 (0,92), 465 (0,66)	290 (1,4), 355 (1,62), 385 (0,8), 470 (0,36)	583 (0,67)	—	652 (0,97)	3,6
Id	310 (0,84), 410 (2,4)	293 (0,92), 420 (1,76)	305 (0,8), 405 (1,6), 420 (1,46)[в]	507 (1,72)	584 (0,52)	592 (1,08)	0,2

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[a] This is the yield after chromatographic purification.

[b] Crystallization water is lost on vacuum drying and is accompanied by decomposition of the formazan.

[c] Shoulder.

EXPERIMENTAL

The absorption spectra of alcohol, dioxane, and cyclohexane solutions of formazans I ($5\cdot 10^{-5}$ M) were recorded with an SF-4a spectrophotometer (spacing 5 nm); the absorption spectra of alcoholic alkali and concentrated sulfuric acid solutions of the compounds ($1\cdot 10^{-4}$ M) were recorded with an SF-10 spectrophotometer.

The spectra of complexes VI were recorded with an SF-10 spectrophotometer. Alcohol solutions of the formazans and $Ni(NO_3)_2\cdot 6H_2O$ in a concentration of $1\cdot 10^{-4}$ M were used. An ammonium acetate solution with pH 7.0 was used as the buffer solution.

1-(4'-Quinazolyl)-3,5-diphenylformazan (Ia). A solution of diazotized aniline, obtained from 1.12 g (12 mmole) of aniline and 0.8 g (12 mmole) of sodium nitrite in 20 ml of water and 20 ml of hydrochloric acid (sp. gr. 1.19), was added to a cooled (to 0°) solution of 3 g (12 mmole) of benzaldehyde 4-quinazolylhydrazone in 70 ml of dimethylformamide (DMF), after which 2 N NaOH solution was added dropwise with cooling and stirring. The pH of the solution was brought up to 9.0, and the mixture was allowed to stand at 0° for 1 h. It was then neutralized to pH 6.0 with 18% hydrochloric acid, and the resulting red precipitate was removed by filtration and washed with water to give 2.6 g (60%) of crude formazan. The crude formazan was purified by chromatography with aluminum oxide (elution with benzene) and subsequent crystallization from ether. The product was quite soluble in alcohol, benzene, and chloroform but only slightly soluble in cyclohexane.

Compounds Ib-e were obtained by the method used to prepare formazan Ia (the formazan and the solvent used for chromatography are given): 1-(4'-quinazolyl)-3-phenyl-5-(p-tolyl)formazan (Id), benzene; 1-(4'-quinazolyl)-3-phenyl-5-(p-methoxyphenyl)formazan (Ic), benzene-alcohol; 1-(4'-quinazolyl)-3-phenyl-5-(p-nitrophenyl)formazan (Id), chloroform; 1-(4'-quinazolyl)-3-methyl-5-phenylformazan (Ie), benzene.

Oxidative Cleavage of N-Quinazolylformazan (Ia). A 1.2-g (2 mmole) sample of Pb_3O_4 was added to a solution of 0.7 g (2 mmole) of the formazan in 15 ml of glacial acetic acid, and the mixture was shaken until the solution became colorless. The acetic acid was then removed by vacuum distillation at 40°, the residue was drenched with 30 ml of 18% HCl, and the mixture was stirred at 20° for 20 min. The resulting precipitate was removed by filtration, dried, and extracted with hot alcohol. The alcohol was evaporated, and the 2,5-diphenyltetrazole (IIIa) was crystallized from ethanol to give 0.32 g (79%) of a product with mp 101-102° (mp 101.5-102° [7]). The structure of tetrazole IIIa was confirmed by comparison with an authentic sample obtained by the method in [7].

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