LITERATURE CITED

1. A. Alemany, M. Bernabe, C. Elorriaga, E. F. Alvarez, M. Lora-Tamaya, and O. Nieto, Bull. Soc. Chim. France, 8, 2486 (1966).
2. R. Elderfield (editor), Heterocyclic Compounds, Vol. 8, Wiley (1950-1967).
3. N. A. Kogan, Reakts. Sposobn. Org. Soedin., 11, No. 3, 659 (1975).
4. M. I. Vlasova and N. A. Kogan, Khim. Geterotsikl. Soedin., No. 9, 1218 (1976).
5. N. A. Kogan and M. I. Vlasova, Khim. Geterotsikl. Soedin., No. 12, 1654 (1973).
6. N. A. Kogan and M. I. Vlasova, Khim.-Farmats. Zh., No. 7, 27 (1971).

PYRIMIDINYLFORMAZANS

I. SYNTHESIS AND STUDY OF UNSYMMETRICAL 1-(4,6-DIMETHYL-2-PYRIMIDINYL)-5-ARYLFORMAZANS

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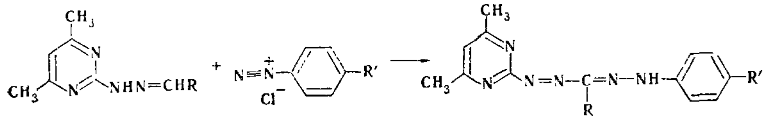
1-(4,6-Dimethyl-2-pyrimidinyl)-3-methyl(aryl)-5-arylformazans, the structures of which depend on the substituents attached to 3-C, were obtained by diazo coupling of arenediazonium salts with 4,6-dimethyl-2-pyrimidinylhydrazones.

Pyrimidinylformazans have been described only in [1]. The present research was carried out in order to ascertain the effect of the pyrimidine ring and the substituents in it on the electronic spectra of formazans.

The 1-(4,6-dimethyl-2-pyrimidinyl)-3-methyl(aryl)-5-arylformazans (III-IX) were synthesized by diazo coupling of arenediazonium salts II with 4,6-dimethyl-2-pyrimidinylhydrazones of benzaldehyde, p-chlorobenzaldehyde, and acetaldehyde (Ia-c).



I II III-IX

I—II a R=CH_3, R′=H; b R=C_6H_5, R′=CH_3; c R=p-ClC_6H_4, R′=NO_2; III R=CH_3, R′=H; IV R=CH_3, R′=CH_3; V R=CH_3, R′=NO_2; VI R=C_6H_5; R′=H; VII R=C_6H_5, R′=CH_3; VIII R=C_6H_5, R′=NO_2; IX R=p-ClC_6H_4, R′=H

Pyrimidinylformazans III-IX are orange to red-brown or greenish-black crystalline substances that can be stored for a long time without decomposition. Deeply colored solutions of the salts are formed when these compounds are dissolved in alcoholic alkali. The salts of formazans V and VIII, which contain a nitro group (Table 1), are most deeply colored (blue-violet). The color of the alcohol solutions of the formazans changes to light-yellow when they are acidified, and this color vanishes on standing.

An intense absorption band of NH stretching vibrations at 3370-3380 cm^{-1} is observed in the IR spectra of III-V with a methyl group attached to 3-C. They consequently have an open structure (probably trans-anti or trans-syn forms [2, 3]).

The spectrum of formazan IX does not contain the band of an NH bond, whereas the spectra of VI and VII have a very weak absorption band at 3360-3365 cm^{-1}. This provides a basis for the assumption that formazans with a phenyl group attached to 3-C exist in the s-cis conformation of the trans-syn form, which is stabilized by

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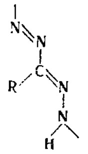
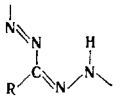
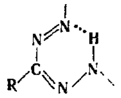
TABLE 1. Pyrimidinylformazans III-IX

Compound	mp, °C (solvent)	Empirical formula	Found, %			Calculated, %			IR spectrum, cm^{-1}	λ_{max}, nm (lg ε)				Yield, %
			C	H	N	C	H	N		benzene	dioxane	ethanol	ethanol+ NaOH	
III	177—178 (methanol)	$C_{14}H_{16}N_6$	62,7	6,0	31,3	62,7	6,0	31,3	3370	390	376	376 (4,22)	490	93
IV	197—197,5 (methanol)	$C_{15}H_{18}N_6$	63,6	6,3	30,1	63,8	6,4	29,8	3380	392	380	382 (4,32)	490	97
V	225 (dec., acetonitrile)	$C_{14}H_{15}N_7O_2$	53,7	4,8	31,0	53,6	4,9	31,3	3373	407	405	406 (4,36)	578	80
VI	148—149 (methanol)	$C_{19}H_{18}N_6$	69,3	5,7	25,3	69,1	5,5	25,4	3365 w	457	448	440 (4,01)	492	91
VII	147,5—148 (acetonitrile)	$C_{20}H_{20}N_6$	69,8	5,8	24,5	69,7	5,8	24,4	3360 w	457	448	439 (4,13)	473	53
VIII	173 (dec., benzene)	$C_{19}H_{17}N_7O_2$	61,1	4,6	25,8	60,8	4,6	26,1	3340 m	490	425 482	413 (4,02) 471 (4,05)	584	75
IX	157 (methanol)	$C_{19}H_{17}ClN_6$	62 6	4,7	22,8	62,6	4,7	23,0	None	458	449	440 (4,16)	496	96

an intramolecular hydrogen bond [2-5]. This is also confirmed by the sharp shift in the absorption band to the long-wave region with a simultaneous decrease in the extinction (Table 1). Opening of the chelate structure is observed only in alcoholic alkali, as attested to by the close location of the absorption maxima of alkaline solutions of formazans III, IV and VI, IX.


trans-anti


trans-syn


trans-syn-s-cis

The appearance in the spectrum of VIII of a low-intensity band at 3340 cm^{-1} is explained by weakening of the hydrogen bond as a result of the effect of the nitro group. In contrast to the remaining formazans, the electronic spectrum of VIII has two absorption maxima in the visible region, one of which can evidently be assigned to the open structure of the molecule (413 nm), the other of which can be assigned to a structure with a hydrogen bond (471 nm).

A hypsochromic shift of the absorption band in ethanol by, respectively, 36 and 48 nm, is observed in the spectra of formazans III and VI as compared with their phenyl analogs (λ_{max} 412 and 488 nm [6, 7]); this shift is due to the effect of the pyrimidine ring.

EXPERIMENTAL

The IR spectra of 0.03-0.05 M solutions of the compounds in CCl_4 were recorded with a UR-20 spectrometer. The electronic spectra of $5 \cdot 10^{-5}$ M solutions of the compounds were recorded with a Specord UV-vis spectrophotometer. Hydrazone Ib (mp 160°) was obtained by the method in [8].

Acetaldehyde 4,6-Dimethyl-2-pyrimidinylhydrazone (Ia). A solution of 0.69 g (5 mmole) of 2-hydrazino-4,6-dimethylpyrimidine [9] in 20 ml of water and a solution of 0.5 g (10 mmole) of acetaldehyde in 2 ml of ethanol were mixed, and the mixture was allowed to stand overnight, after which it was vacuum evaporated, and the residue was refluxed with two 40-ml portions of hexane. A total of 0.67 g (82%) of hydrazone Ia, with mp 122-123° (hexane), crystallized from the solution. The product was quite soluble in water and alcohol and sublimed in vacuo. Found: C 58.6; H 7.3; N 34.1%. $C_8H_{12}N_4$. Calculated: C 58.5; H 7.4; N 34.1%.

p-Chlorobenzaldehyde 4,6-Dimethyl-2-pyrimidinylhydrazone (Ic). A solution of 1.38 g (10 mmole) of 2-hydrazino-4,6-dimethylpyrimidine and a solution of 1.5 g (11 mmole) of p-chlorobenzaldehyde in 45 ml of methanol were mixed, and the mixture was heated for 1 h, after which it was allowed to stand overnight. It was then evaporated to one-third of its original volume, and the resulting precipitate was separated. The filtrate was vacuum evaporated, and the residue was stirred with 5 ml of water and worked up to give 1.94 g (75%) of Ic with mp 151-152° (benzene, acetonitrile). Found: Cl 13.9; N 21.5%. $C_{13}H_{13}ClN_4$. Calculated: Cl 13.6; N 21.5%.

The product had photochromic properties — the crystals, which were colorless in light, took on a yellow color in the dark.

1-(4,6-Dimethyl-2-pyrimidinyl)-3-methyl(aryl)-5-arylformazans (III-IX). A solution of diazonium salt II [from 11 mmole of arylamine, 7 ml of HCl (1 : 1), and 0.8 g (11 mmole) of sodium nitrite in 5 ml of water] was added slowly to a cooled (to −5°) solution of 10 mmole of I in 50 ml of methanol, and the mixture was stirred at 0° for 30 min, after which 2 M NaOH solution was added gradually until the mixture had pH 8, whereupon the colored reaction product precipitated (Table 1). In the preparation of formazans III-V the reaction was carried out in methanol—water (1 : 4). Compounds III-IX were readily soluble in ordinary organic solvents but less soluble in CCl_4 and petroleum ether.

Depending on the solvent, formazan VIII crystallized in two different forms: needles (mp 157-158°) from polar solvents (acetonitrile, methanol) and plates (mp 173°) from nonpolar solvents (benzene, hexane).

LITERATURE CITED

1. E. S. Karavaeva, N. P. Bednyagina, T. A. Sharkova, and I. I. Mudretsova, Khim. Geterotsikl. Soedin., No. 10, 1420 (1975).
2. A. P. Zeif, G. N. Lipunova, N. P. Bednyagina, L. N. Shchegoleva, and L. I. Chernyavskii, Zh. Org. Khim., 6, 2590 (1970).

3. G. McConnachie and F. A. Neugebauer, Tetrahedron, 31, 555 (1975).
4. A. P. Novikova, M. P. Kozina, D. N. Shigorin, and I. Ya. Postovskii, Zh. Obshch. Khim., 38, 934 (1968).
5. G. N. Lipunova, N. N. Gulemina, A. P. Zeif, and N. P. Bednyagina, Khim. Geterotsikl. Soedin., No. 4, 493 (1974).
6. N. P. Bednyagina, A. P. Novikova, N. V. Serebryakova, I. I. Mudretsova, and I. Ya. Postovskii, Zh. Org. Khim., 4, 1613 (1968).
7. I. Hausser, D. Terchel, and R. Kuhn, Ber., 82, 515 (1949).
8. J. D. Bower and F. P. Doyle, J. Chem. Soc., 727 (1957).
9. M. P. V. Boarland, J. F. W. McOmie, and R. N. Timms, J. Chem. Soc., 4691 (1952).

MASS SPECTRA OF 1H-2,3-DIHYDRO-1,4-BENZODIAZEPINE-2-THIONES

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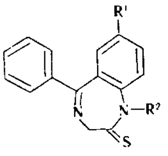
The mass-spectrometric fragmentation of 1H-2,3-dihydro-1,4-benzodiazepine-2-thiones differs substantially from the fragmentation of the corresponding oxo derivatives with respect to the presence of $[M - HCN]^+$ and $[M - SH]^+$ ions. This is due to the tautomeric transformation of the molecular ions of the thiones to enethiol and eniminothiol tautomeric forms. The approximate percentages of each of the tautomeric forms were estimated.

In order to compare the mass-spectrometric behavior of 1,4-benzodiazepin-2-ones [1, 2] with their thio analogs, we studied the mass spectra of the following 1,4-benzodiazepine-2-thiones:



I-VII

I R^1=H, R^2=H; II R^1=H, R^2=D; III R^1=CH_3, R^2=H; IV R^1=Cl, R^2=H; V R^1=Br, R^2=H; VI R^1=NO_2, R^2=H; VII R^1=Cl, R^2=CH_3

The investigated compounds were synthesized as previously described in [3, 4]. The m/e values and the relative intensities of the peaks of the principal ions in the mass spectra of I-VII are presented in Table 1. The W_M values (the fraction of the molecular ions in the total ion current, which characterizes the stability of the molecule with respect to electron impact [5]) for the corresponding oxo and thio derivatives are compared in Table 2, and the ratios of the intensities of the peaks of some of the characteristic fragment ions to the intensity of the molecular ion for the investigated thiones are also presented.

It follows from a comparison of the W_M values that the thiones have considerably higher stability with respect to electron impact than the corresponding oxo compounds. The W_M values for the thiones exceed the corresponding values for the benzodiazepinones by a factor of 2-2.5.

The free p and d orbitals of the sulfur atom evidently participate to a great extent in stabilization of the positive charge in the molecular ions of the thiones.

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