STRUCTURE OF 1-PHENYL-3-[o-HYDROXY(METHOXY)PHENYL]-5-BENZAZOLYLFORMAZANS

G. N. Lipunova, L. V. Rodnenko,
N. P. Bednyagina, I. I. Mudretsova,
and N. V. Marina

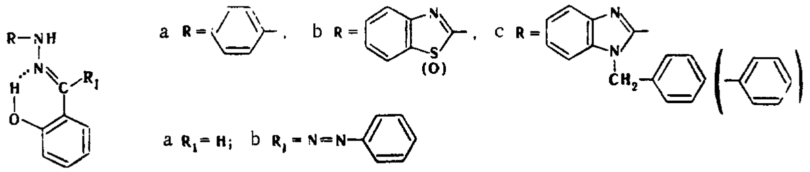
UDC 785'789 : 543.422.4.6 : 541.651

A number of benzazolylhydrazones and benzazolylformazans containing an o-hydroxy or o-methoxy group in the phenyl ring attached to the meso-carbon atom were synthesized. The structure of the compounds in various solvents was studied by means of IR and UV spectroscopy and by determination of the ionization constants. The participation of the o-hydroxy group in the formation of an intramolecular hydrogen bond was demonstrated. The interrelationship between the structure and color of the formazans was investigated.

The presence or absence of an intramolecular hydrogen bond (IHB) in aryl- and hetarylformazans, the configuration of the chain, and amine—imine tautomerism are determined by the character of the substituents attached to the N_5 atom and the methylidyne carbon atom [1-4].

In the present research we investigated the structure of newly synthesized 1-phenyl-3-[o-hydroxy(methoxy)phenyl]-5-benzazolylformazans and their corresponding hydrazones.

A study of the IR spectra of compounds with an o-hydroxyl group (Figs. 1 and 2) showed that narrow intense absorption bands at 3430-3490 cm^{-1} (ν_{NH} of the imine tautomeric form) and 3330-3370 cm^{-1} (ν_{NH} of the amine tautomeric form) and a broad band at 3200-3280 cm^{-1}, which can be assigned to the absorption of a hydroxy group tied up by hydrogen bonds, are observed in the spectra of both the hydrazones and the formazans. The position and intensity of this band are independent of the concentration of the solutions, and this indicates intramolecular character of the hydrogen bonds. On the basis of the IR spectral data it might be concluded that a six-membered ring with an IHB with participation of the azomethine nitrogen atom is present in the hydrazones and formazans.



The IR spectra of o-methoxybenzaldehyde hydrazones (II, IV, VI, and VIII, Table 1) and 3-(o-methoxyphenyl)formazans (XI, XIII, XVI, and XVIII) do not contain a band at 3200-3280 cm^{-1}, whereas the bands at 3430-3490 cm^{-1} and 3330-3370 cm^{-1} are retained; this confirms the correctness of the assignment of the absorption at 3200-3280 cm^{-1} to the OH group tied up by hydrogen bonds.

As previously indicated [5, 6], from the ratio of the ν_{NH} bands at 3300-3500 cm^{-1} one may form a judgment regarding the presence and shift of an amine—imine equilibrium and regarding the presence or absence of N—H... N hydrogen bonds of the formazan chain.

S. M. Kirov Ural Polytechnic Institute, Sverdlovsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1498-1504, November, 1976. Original article submitted December 30, 1975.

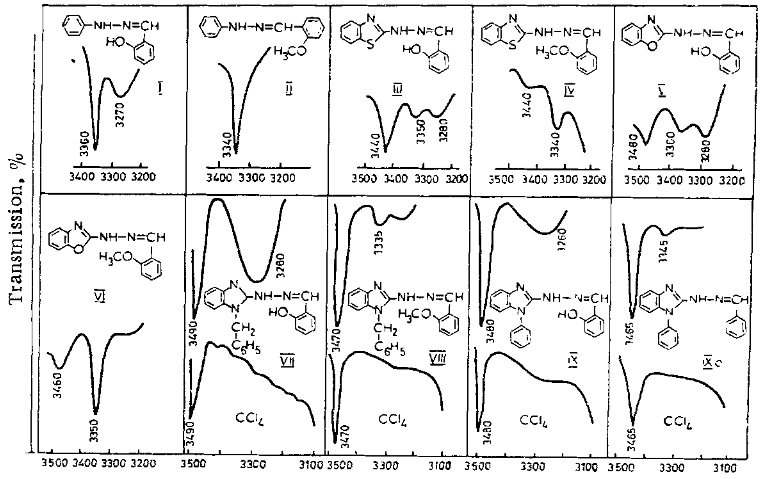


Fig. 1. IR spectra of hydrazones I-IXa in chloroform.

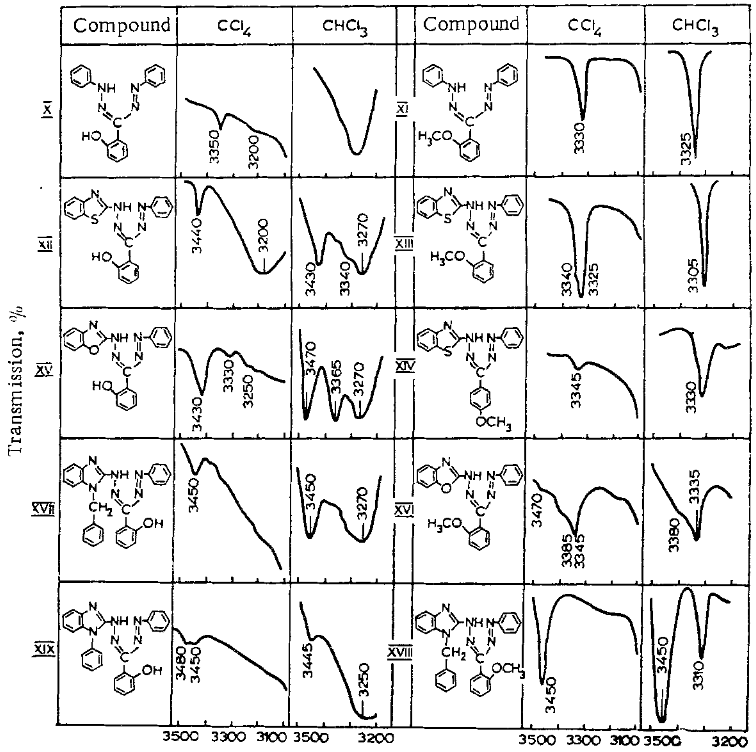


Fig. 2. IR spectra of formazans X-XIX.

Whereas only an absorption band at 3340-3360 cm^{-1}, which characterizes ν_{NH} of the amino form, is observed in the IR spectra of hydrazones of the aryl series (I, II) in $CHCl_3$ solution, the IR spectra of hydrazones of benzothiazole and benzoxazole (III-VI) contain two ν_{NH} bands, the higher-frequency band of which is related to ν_{NH} of the imine form.

It should be noted that the intensity of the low-frequency band increases sharply on passing from hydrazones of salicylaldehyde to hydrazones of o-methoxyaldehyde, whereas the intensity of the high-frequency band decreases. This can be explained either by a shift of the amine—imine equilibrium to favor the amine form or by a change in the polarity of the N—H bonds, which gives rise to the corresponding changes in the intensity of the ν_{NH} band. Only one high-frequency band is observed in the IR spectra of benzimidazole hydrazones (VII-X) in CCl_4, i.e., in solution these compounds exist in the imine form. The appearance of a second tautomeric form is observed in chloroform solutions of VIII and IXa, since a low-frequency band is also observed in the IR spectra (Fig. 1).

Primarily two absorption bands at 300-390 nm (Table 1) are observed in the electronic spectra of the hydrazones in CCl_4. One observes a bathochromic shift of the long-wave band for all of the hydrazones in

TABLE 1. Characteristics of the Hydrazones and Formazans

Compound	mp, °C[a]	Empirical formula	Found, %			Calculated, %			UV spectrum, λ_{max}, nm			pK_a[c] NH—H	pK_a[c] OH—H
			C	H	N(S)	C	H	N(S)	CCl_4	alcohol	alcoholic NaOH[b]		
I	140	$C_{13}H_{12}N_2O$	73,8	5,8	13,2	73,6	5,7	13,2	300 350	300 350	375		11,62
II	60	$C_{14}H_{14}N_2O \cdot 0{,}2C_2H_5OH$	73,2	6,1	12,1	73,2	6,1	12,2					
III	250	$C_{14}H_{11}N_3OS$	62,5	4,3	15,5 (11,7)	62,5	4,1	15,6 (11,9)	330[d] 355	330[d] 355	400	12,60	10,27
IV	235	$C_{15}H_{13}N_3OS$	63,8	4,5	14,8 (11,0)	63,6	4,6	14,8 (11,3)	350	350	400	12,10	
V	245	$C_{14}H_{11}N_3O_2$	66,4	4,5	16,4	66,4	4,4	16,6	310 340	310 340	380	12,75	10,02
VI	210	$C_{15}H_{13}N_3O_2$	67,3	5,0	15,7	67,4	4,9	15,7	340	330	380	11,75	
VII	145	$C_{21}H_{18}N_4O \cdot 0{,}5C_2H_5OH$	72,7	5,3	15,3	72,4	5,7	15,4	305 360 380	325 360 370	400	13,01	10,82
VIII	190	$C_{22}H_{20}N_4O$	73,8	5,9	15,6	74,2	5,6	15,7	350 365 390[d]	360	375 400[d]	13,06	
IX	190	$C_{20}H_{16}N_4O \cdot 0{,}5C_3H_7OH$	72,2	5,3		72,1	5,6		355 380[d]	295 300 360	400	12,69	10,73
X	196	$C_{19}H_{16}N_4O$	72,1	5,1	17,8	72,1	5,1	17,7	545	405 505	425		10,81
XI	134	$C_{20}H_{18}N_4O \cdot 0{,}5H_2O$	71,2	5,5		70,8	5,6		410 480[d]	410	410 500[d]		
XII	173	$C_{20}H_{15}N_5OS$	64,1	4,2	(8,9)	64,3	4,3	(8,6)	500	360 400[d]	500	12,12	9,17
XIII	103	$C_{21}H_{17}N_5OS \cdot 0{,}5C_5H_5N$	66,0	4,9	(7,4)	66,0	4,7	(7,5)	400 480[d]	400	520	10,13	
XIV	130	$C_{21}H_{17}N_5OS$	65,4	4,6		65,1	4,4		500	485	525	10,37	
XV	230	$C_{20}H_{15}N_5O \cdot 0{,}5C_2H_3OH$	66,6	4,7	18,2	66,3	4,7	18,5	500	330 400[d]	475	12,11	10,02
XVI	150	$C_{21}H_{17}N_5O_2 \cdot 2H_2O$	64,7	4,9		64,8	4,9		350 480[d]	350	500	9,80	
XVII	165	$C_{27}H_{23}N_6O$	72,3	5,1		72,5	5,1		440[d]	420	410 530	13,20	11,07
XVIII	117	$C_{28}H_{24}N_6O$	73,3	5,4		73,0	5,2		440[d]	465	535	11,82	
XIX	110	$C_{26}H_{20}N_6O$	71,9	5,0		72,2	4,6		500— 560	520 560[d]	390 525	13,16	11,02

---

[a] Compounds I, III-VI, VIII, and IX were recrystallized from pyridine–water, VII, XIII-XV, and XVII-XIX were recrystallized from alcohol, X was recrystallized from chloroform–alcohol, XI was recrystallized from $CHCl_3$–heptane, XII was recrystallized from octane, and XVI was recrystallized from aqueous alcohol.

[b] pH 13-14.

[c] The pKa values were determined with an accuracy up to ±0.06.

[d] Shoulder.

alcoholic alkali solutions, and this made it possible to spectrophotometrically determine the ionization constants. Two-step ionization is observed for the salicylaldehyde hydrazones (except for I), and two ionization constants are determined. The exponent of the first ionization constant (10-11) characterizes ionization involving the hydroxy group and is close to the pK_a value of phenol or one unit higher. The acidity of the hydroxy group increases for the hetarylhydrazones, evidently due to the acceptor character of the heteroring. The exponent of the second ionization constant ranges from 12 to 13 and is close to the pK_a values of o-methoxybenzaldehyde hydrazones, in which there is only one acidic group (NH); we assigned it to the ionization constant of the amino group. We were unable to determine the pK_a (NH) values for arylhydrazones I and II, since they evidently undergo conversion to azo compounds in alkaline media, as in [7].

Benzimidazolylhydrazones VII-IX have the highest pK_a (NH) values. A difference in the acidity of the amino group as a function of the structure of the aldehyde fragment is observed for benzothiazolyl (benzoxazolyl) hydrazones: The pK_a values of III and V are ~ 0.5-1 higher than the pK_a values of methoxy analogs IV and VI.

The shift of the amine–imine equilibrium as a function of the solvent and the substituent attached to C_3 and N_5 shows up even more distinctly in the case of formazans.

The presence of an o-hydroxy group in 1,5-diphenyl-3-(o-hydroxyphenylformazan leads to cleavage of the IHB in the formazan grouping. Thus, in contrast to triphenylformazan, a broad absorption band at 3200-3400 cm^{-1} is observed in the IR spectrum of formazan X in concentrated CCl_4 and $CHCl_3$ solutions, and a narrow absorption band at 3350 cm^{-1}, which can be assigned to the stretching vibrations of a free NH group, and a band at 3200 cm^{-1}, assigned to a hydroxyl group tied up in an IHB, appear when the solution is diluted to a concentration of 10^{-3} mole/liter. A rather strong N–H...N or N–H...O intermolecular hydrogen bond is evidently characteristic for this compound in concentrated solutions.

An intense narrow ν_{NH} band is observed in the IR spectra of 1,5-diphenyl-3-(o-methoxyphenyl)formazan in CCl_4 and $CHCl_3$; this provides evidence for its existence in solution in an open amine form that is not tied up by hydrogen bonds. At the same time, the ν_{NH} band in this region, as in the case of triphenylformazan, is absent in the IR spectrum of 1,5-diphenyl-3-(p-methoxyphenyl)formazan [2]. Rotation of the o-methoxyphenyl group relative to the C–C bond and removal of the phenyl ring from conjugation with the formazan grouping evidently lead to the conformational isomer (the anti-trans form) in which the formation of an IHB is impossible, as in the case of 1,5-diphenyl-3-(2,6-dimethoxyphenyl)formazan [2].

The ν_{NH} bands of the amine and imine forms show up distinctly in the IR spectra of the 3-(o-hydroxyphenyl)formazans of the benzothiazole and benzoxazole series (XII, XV). Moreover, a sharp increase in the intensity of the ν_{NH} band at 3330-3365 cm^{-1}, which is associated with a shift in the equilibrium to favor the amine form, is observed on passing from CCl_4 to $CHCl_3$ for XV. The imine form disappears completely in the case of 1-phenyl-3-(o-methoxyphenyl)-5-benzothiazolyl(benzoxazolyl)formazans XIII and XVI. It is interesting to note that doubling of the ν_{NH} band (Fig. 2), which can be explained by the appearance in solution of two three-dimensional isomers in the amine form, is observed in the spectra of these compounds.

As in the case of 1,5-diphenyl-3-(o-methoxyphenyl)formazan, we made a comparison of the spectra of XIII with the spectra of its 3-(p-methoxyphenyl) analog XVI and showed that the position of the methoxy group gives rise to a sharp difference in the intensity of the ν_{NH} band.

Regardless of the solvent, benzimidazole formazans with an o-hydroxy group (XVII, XIX) exist in the imine form, and the presence of a methoxy group in place of a hydroxy group leads to the appearance in $CHCl_3$ solution of the amine form, just as we observed for the corresponding hydrazone.

An o-hydroxy group in the phenyl ring attached to the meso-carbon atom, tied up by IHB, not only leads to cleavage of the IHB in the formazan ring and to a shift in the tautomeric equilibrium to favor the imine form but is also responsible for the deep color of 3-(o-hydroxyphenyl)formazans in nonpolar solvents (CCl_4 and benzene). The negative solvatochromism of these compounds in polar solvents [alcohol and dimethyl sulfoxide (DMSO)] is apparently explained by cleavage of the IHB and possible rotation of the o-hydroxyphenyl group relative to the C–C bond; this should lead to removal of this residue from conjugation with the formazan grouping. This solvent effect on the color shows up particularly clearly for 1,5-diphenyl-3-(o-hydroxyphenyl)-formazan. A long-wave absorption band at 545 nm is observed in the spectrum of a CCl_4 solution of this compound, whereas in alcohol the intensity of this band decreases, and the intensity of the absorption band at 405 nm increases; however, in DMSO there is only one absorption band at 400 nm, which is close in position and intensity to the absorption of this compound in alcoholic alkali. In contrast to 3-(o-hydroxyphenyl)formazans, their 3-(o-methoxy) analogs have identical colors in various solvents (Table 1).

The electronic spectra of alcoholic alkali solutions of the formazans are characterized by a bathochromic shift of the absorption bands as compared with the spectra of the formazans, except for X, for which a hypsochromic shift is observed. The ionization constants of the formazans were determined spectrophotometrically. As in the case of the corresponding hydrazones, two ionization constants were obtained for 1-phenyl-3-(o-hydroxyphenyl)-5-benzazolylformazan. The first constant characterizes ionization of the hydroxy group and ranges from 10^{-9} to 10^{-11}. The second constant pertains to ionization of the NH group and ranges from 10^{-12} to 10^{-13}. In the case of 1,5-diphenyl-3-(o-hydroxyphenyl)formazan we were able to determine only the pK_a value of the hydroxy group, as in the case of the hydrazone. It is interesting to note that the pK_a(NH) values of 5-benzazolyl-3-(o-hydroxyphenyl)formazans are ~2 units higher than the pK_a(NH) values of their methoxy analogs. The low acidity of the NH group in o-hydroxyphenylformazans can be explained by the electron-donor effect of the ionized o-hydroxy group.

The presence of an o-hydroxy(methoxy) group in the phenyl ring attached to C_3 in the formazans affects their properties. Thus, in contrast to triphenylformazan, 1,5-diphenyl-3-[o-hydroxy(methoxy)phenyl]formazans

(X, XI) in solution in benzene and carbon tetrachloride do not have photochromic properties. The impossibility of red-yellow transitions can be explained by the fact that a chelate formazan ring with an IHB is absent in formazans X and XI. Stable verdazyls, to which triphenylformazan is readily converted, also cannot be isolated in the case of formazan X. Highly colored methylation products are formed as a result of the reaction. 1-Phenyl-3-[o-hydroxy(methoxy)phenyl]-5-(2-benzimidazolyl)formazans (XVII, XVIII) have red-blue irreversible photochromism: A red solution of formazan XVII in CCl_4 is rapidly converted to a blue solution, and a red solution of formazan XVIII is rapidly converted to a green solution. The color also changes from red to green when a chloroform solution of formazan XVII or an alcohol (acetone) solution of formazan XVIII is heated. According to the results of elementary analysis, the green precipitate is the product or reaction with the solvent.

EXPERIMENTAL

The IR spectra of saturated solutions of the hydrazones and formazans in carbon tetrachloride and chloroform in the LiF region were recorded with a UR-20 double-beam IR spectrometer in an 1-cm thick cuvette. The electronic spectra of $5 \cdot 10^{-5}$ M solutions of the compounds were recorded with SF-10, Specord UV-vis, and SF-4 spectrophotometers. The ionization constants of the hydrazones and formazans were measured spectrophotometrically – the pK_a(OH) values in a 50% alcohol-buffer solution (ammonium acetate buffer) and the pK_a(NH) values by means of prepared alkaline solutions with known pH values [8].

Salicylaldehyde Phenylhydrazone (I). A saturated alcohol solution of 5.6 ml (0.06 mole) of salicylaldehyde was added to a saturated alcohol solution of 5 ml (0.05 mole) of phenylhydrazine, and the mixture was heated for 20-30 min. It was then cooled, and the light-yellow precipitate was removed by filtration and crystallized twice from pyridine–water (1 : 1) to give a product with mp 140° (mp 142° [9]).

The heterocyclic hydrazones (85-90% yields) of salicylaldehyde (III, V, VII, and IX) and o-methoxybenzaldehyde (IV, VI, and VIII) were similarly obtained.

o-Methoxybenzaldehyde Phenylhydrazone (II). A saturated alcohol solution of 8.4 g (0.06 mole) of o-methoxybenzaldehyde was added to 5 ml (0.05 mole) of phenylhydrazine. At the end of the spontaneous reaction, the solution was evaporated, and the residue was triturated. The residue was then analyzed without additional purification. The hydrazone was quite soluble in ether, alcohol, benzene, chloroform, and pyridine.

1,5-Diphenyl-3-(o-hydroxyphenyl)formazan (X). A cooled (to 0°) solution of benzenediazonium chloride, obtained from 4.1 ml (0.045 mole) of aniline in 20 ml of HCl (1 : 1) and 3 g (0.045 mole) of sodium nitrite in 20 ml of water, was added gradually to a cooled solution of 6.3 g (0.03 mole) of salicylaldehyde phenylhydrazone (I) in pyridine, and the mixture was allowed to stand at 5-10° for 1 h. The formazan was then precipitated by the addition of ice. Recrystallization from chloroform–alcohol (1 : 1) gave a product with mp 196° (mp 164-165° [10]) in 85% yield.

1,5-Diphenyl-3-(o-methoxyphenyl)formazan (XI) was similarly obtained and crystallized from chloroform–heptane (1 : 3).

1-Phenyl-3-(o-hydroxyphenyl)-5-benzothiazolylformazan (XII). A cooled (to 0°) solution of benzenediazonium chloride, obtained as described above, was added gradually to a cooled solution of 6.5 g (0.03 mole) of hydrazone III in alcohol–pyridine (1 : 1), and the mixture was allowed to stand at 5-10° and pH 8 for 1 h. It was then acidified to pH 6-7 and treated with ice. The precipitated formazan was separated and crystallized from octane. The yield was 80%.

Formazans XIII-XIX were similarly obtained. A green precipitate was obtained after crystallization of formazan XVII from chloroform. Found: C 67.5; H 4.7%. $(C_{27}H_{23}N_6)_3 \cdot CHCl_3$. Calculated: C 67.1; H 4.7%.

LITERATURE CITED

1. G. Arnold and C. Schiele, Spectrochim. Acta, Part A, 25, 685 (1969).
2. W. Ottig and F. A. Neugebauer, Z. Naturf., B, 23, 1064 (1968).
3. N. P. Bednyagina and G. N. Lipunova, Khim. Geterotsikl. Soedin., No. 5, 877 (1969).
4. N. P. Bednyagina, I. Ya. Postovskii, A. D. Garnovskii, and O. A. Osipov, Usp. Khim., 47, 1052 (1975).
5. A. P. Zeif, L. N. Shchegoleva, T. N. Lipunova, A. P. Novikova, and N. P. Bednyagina, Zh. Organ. Khim., 6, 1332 (1970).
6. I. I. Mudretsova and S. L. Mertsalov, Khim. Geterotsikl. Soedin., No. 12, 1666 (1975).
7. Yu. P. Kitaev and B. I. Buzykin, Hydrazones [in Russian], Nauka, Moscow (1974), p. 70.
8. A. Albert and E. Serjeant, Ionization Constants of Acids and Bases, Methuen (1962).
9. G. C. Knöpfer, 1, 916 (1909).
10. F. R. Fichter and I. C. Fröhlich, 2, 426 (1903).