STUDIES IN THE BENZ- AND NAPHTHAZOLE SERIES

XXXI.* STRUCTURE AND PROPERTIES OF 1-BENZAZOLYL-3-METHYL(PHENYL)-5-NAPHTHYLFORMAZANS

G. N. Lipunova, E. P. Motyleva, and N. P. Bednyagina

UDC 547.785.5.787

A series of 1-benzazolyl-3-methyl(phenyl)-5-[α(β)-naphthyl]formazans was synthesized. A steric effect of the naphthyl group on the structure (tautomerism and state of the intramolecular hydrogen bond) of the azohydrazone grouping was noted. Some tetrazolium salts were obtained by the reaction of the formazans with N-bromosuccinimide. It was established that benzoxazolylformazans are cleaved to 2,5-disubstituted tetrazoles in the process. A method is proposed for the preparation of disubstituted tetrazoles by oxidative cleavage of 1-benzoxazolyl-3,5-diarylformazans.

A series of formazans (III-XIV) (Table 1) containing benzazolyl (benzimidazolyl, benzothiazolyl, and benzoxazolyl) and naphthyl groups in the 1 and 5 positions, respectively, and a methyl or phenyl group in the 3 position, was synthesized to study the effect of the naphthyl group (as compared with a phenyl group) on intramolecular hydrogen bonding (IHB) and tautomerism of the azohydrazone group.

As seen from the data in Table 1, formazans that have a benzimidazolyl group in the 1 position (XI-XIV) have the same color, regardless of the substituent in the 3 position and the substituent in the 5 position, and the IR spectra contain the same ν_{NH} frequencies at approximately 3445-3450 cm^{-1}, typical for the imino form (C) [2,3].

Formazans that contain a benzothiazolyl group attached to N_1 and a phenyl group attached to C_3 (III and IV), like 1-benzothiazolyl-3,5-diphenylformazan (XXI) [2], have chelate structures (their deep color and the absence of a ν_{NH} band). 1-Benzothiazolyl-3-methylformazans (V and VI) do not have IHB and are found in the amino form (B), for which a higher color and a ν_{NH} frequency of about 3340-3350 cm^{-1} are characteristic. In contrast to this, 1-(2-benzothiazolyl)-3-methyl-5-phenylformazan has two frequencies – both the amino and imino forms [2].

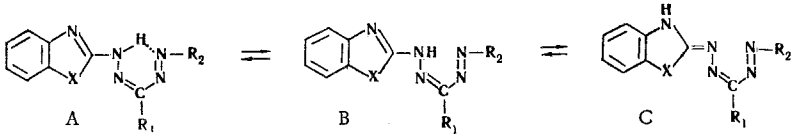
Compounds VII and VIII, which have a phenyl group attached to C_3, apparently have extremely weak IHB or are partially opened, judging from the appearance of a ν_{NH} band of low intensity. Compounds IX and X, which have a methyl group attached to C_3, have, like 1-(2-benzoxazolyl)-3-methyl-5-phenylformazan [2], an open structure and contain a tautomeric mixture of amino and imino forms (B and C), as is apparent from the presence of two ν_{NH} frequencies – high and low – in the IR spectrum.

Thus, the effect of an α(β)-naphthyl group reduces to steric hindrance to the formation of IHB. No appreciable difference in the effects of the α- or β-naphthyl groups on the structures and chromaticity of the formazans was noted. The steric effect of the naphthyl groups is expressed more weakly than the effect of an o-tolyl group. Thus, 1-benzothiazolyl(benzoxazolyl)-3,5-diphenylformazans have chelate structures [2], while 1-benzothiazolyl(benzoxazolyl)-3-phenyl-5-(o-tolyl)formazans (I and II) exist as an equilibrium mixture of forms B and C.

*See [1] for communication XXX.

S. M. Kirov Ural Polytechnical Institute, Sverdlovsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 831-835, June, 1971. Original article submitted March 9, 1970.

TABLE 1



Comp.	X	R_1	R_2	Mp, °C	Empirical formula	Found, %			Calc., %			λ_{max}, nm		ν_{NH}
						C	H	N	C	H	N	alcohol	alcohol–NaOH	
I	S	C_6H_5	o-Tolyl	195—198	$C_{21}H_{17}N_5S \cdot H_2O$*	65,28	4,86	—	64,80	4,88	—	570	522	3425
II	O	C_6H_5	o-Tolyl	172—174	$C_{21}H_{17}N_5O$	70,80	4,89	20,37	70,98	4,78	19,71	432	494	3309; 3421; 3321
III	S	C_6H_5	α-Naphthyl	178—179	$C_{24}H_{17}N_5S$	70,75	4,13	16,47	70,76	4,17	17,20	478	546	absent
IV	S	C_6H_5	β-Naphthyl	190—192	$C_{24}H_{17}N_5S$	70,66	4,36	16,45	70,76	4,17	17,20	480	540	absent
V	S	CH_3	α-Naphthyl	163—165	$C_{19}H_{15}N_5S \cdot 1/2\ H_2O$	64,32	4,52	18,82	64,40	4,52	19,77	442	550	3344
VI	S	CH_3	β-Naphthyl	133—135	$C_{19}H_{15}N_5S \cdot 1/2\ H_2O$	64,84	4,67	18,84	64,40	4,52	19,77	430	536	3348
VII	O	C_6H_5	α-Naphthyl	156—158	$C_{24}H_{17}N_5O$	73,53	4,55	17,01	73,66	4,34	17,90	440	520	3350 †
VIII	OS	C_6H_5	β-Naphthyl	127—130	$C_{24}H_{17}N_5O \cdot 2\ H_2O$	67,56	4,93	—	67,45	4,91	16,39	476	506	3360 †
IX	OS	CH_3	α-Naphthyl	121—124	$C_{19}H_{15}N_5O \cdot 1/2\ H_2O$	67,90	4,77	20,93	67,45	4,73	20,71	424	516	3445; 3346
X	OS	CH_3	β-Naphthyl	137—140	$C_{19}H_{15}N_5O \cdot 1/2\ H_2O$	67,07	5,16	20,03	67,45	4,73	20,71	426	506	3445; 3360
XI	$NCH_2C_6H_5$	C_6H_5	α-Naphthyl	170—171	$C_{31}H_{24}N_6 \cdot H_2O$	77,19	5,27	—	77,50	5,00	17,50	428	550	3471
XII	$NCH_2C_6H_5$	C_6H_5	β-Naphthyl	120—125	$C_{31}H_{24}N_6 \cdot 1/2\ H_2O$	75,86	5,40	—	76,07	5,11	17,68	480	542	3445
XIII	$NCH_2C_6H_5$	CH_3	α-Naphthyl	134—135	$C_{26}H_{22}N_6 \cdot 1/2\ H_2O$	72,85	5,00	20,03	73,06	5,38	19,67	490	550	3447
XIV	$NCH_2C_6H_5$	C_6H_5	β-Naphthyl	127—130	$C_{26}H_{22}N_6 \cdot 1/2\ H_2O$	74,65	5,50	19,50	63,06	5,38	19,67	476	544	3445

* Found %: S 8.62. Calculated %: S 8.23.

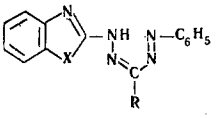
† Of low intensity.

TABLE 2. Characteristics of 1-Phenyl-3-[α(β)-naphthyl]-tetrazoles

Comp.	Mp, °C	λ_{max}, nm	IR spectrum,* cm^{-1}	Empirical formula	Found %			Calc. %			Yield, %	
					C	H	N	C	H	N	A	B
XVII	78	290—300	1212; 1075; 1029; 767	$C_{17}H_{12}N_4$	75,18	4,61	21,03	74,88	4,78	20,70	70	97
XVIII	125	290—300	1217; 1072; 1023; 710	$C_{17}H_{12}N_4$	74,55	4,52	21,27	74,88	4,78	20,70	55	90
XX	98 (101 [11])	270	1219; 1079; 1022; 767	$C_{13}H_{10}N_4$	—	—	—	—	—	—	—	—

*The bands that pertain to the vibrations of the tetrazole ring [6,7] are presented.

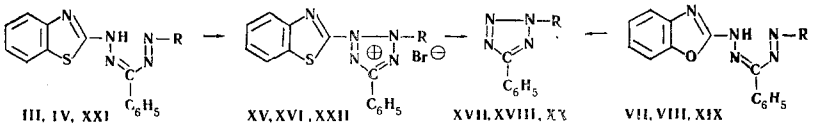
TABLE 3. π-Electron Charge on C_2 of the Heterocycle for 1-Benzazolylformazans



X	R	π-Electron charge on C_2 of the heterocycle
$NCH_2C_6H_5$	CH_3	+0,113
$NCH_2C_6H_5$	C_6H_5	+0,101
S	CH_3	+0,118
S	C_6H_5	+0,104
O	CH_3	+0,146
O	C_6H_5	+0,133

Products III-XIV form sodium salts in solution, and the sodium salts of the α-naphthylformazans (as expected, in view of the higher degree of conjugation) are more deeply colored than the salts of the β-naphthylformazans. All of the investigated formazans are good complexing agents.

The reaction with N-bromosuccinimide, which gives tetrazolium salts [4,5], was investigated in detail for the above series of formazans. It is known that the stability of tetrazolium salts obtained from 1-benzazolyl-3,5-diphenylformazans depends on the nature (electronegativity) of the benzazole and decreases on passing from benzothiazole to benzoxazole. The tetrazolium salts from 1-benzoxazolyl-5-phenylformazans have not been obtained at all [5], since they decompose at the instant of formation. We have now ascertained that the final products of their cleavage are 2,5-disubstituted tetrazoles. The structure of the cleavage products as tetrazoles is proved by their alternative synthesis by acid cleavage of the stable 2-benzothiazolyl-3-naphthyl(phenyl)-5-phenyltetrazolium bromides (XV, XVI, and XXII). Instances of cleavage of tetrazolium salts are reported in the case of arylformazans [8] and benzimidazolylformazans [9]. The scheme of the mechanism is presented in [9], and two cleavage products – the substituted tetrazole and 2-chlorobenzimidazole – were isolated.



III, IV, XXI XV, XVI, XXII XVII, XVIII, XX VII, VIII, XIX

III R-α-naphthyl IV R-β-naphthyl; XXI R-phenyl; XV R-α-naphthyl; XVI R-β-naphthyl; XXII R-phenyl; XVII R-α-naphthyl; XVIII R-β-naphthyl; XX R-phenyl; VII R-α-naphthyl; VIII R-β-naphthyl; XIX R-phenyl.

The instability of the tetrazolium salts of benzoxazolylformazans can be explained using the results of quantum-mechanical calculations of a series of 1-(2-benzazolyl)-5-phenylformazans [10] (Hückel method).

The molecular diagrams indicate that the maximum overall positive charge is localized on the C_2 carbon (in the heterocycle) of benzoxazolylformazans (Table 3).

The positive charge on the nitrogen atoms in the tetrazolium salts that arises as a consequence of the acceptor character of the heterocycle is to a great extent localized on N_2, which also leads to heterolytic cleavage of the $\gtrless C-\underset{|}{N}-$ bond.

The preparation of tetrazoles by oxidative cleavage of 1-benzoxazolyl-5-arylformazans (by passing the step involving the tetrazolium salt) may serve as a preparative method for the synthesis of diverse 2,5-disubstituted tetrazoles.

EXPERIMENTAL

1-(2-Benzothiazolyl)-3-phenyl-5-(o-tolyl)formazan (I). A solution of diazonium compound obtained from 0.015 mmole of o-toluidine was added to a cooled solution of 0.01 mmole of benzaldehyde benzothiazolylhydrazone in alcohol and 2 ml of concentrated HCl. The mixture was neutralized with 2 N NaOH to pH 6 to give 80% of fine, lustrous, black crystals with mp 195-198° [alcohol–chloroform (1 : 1)].

1-Benzoxazolyl-3-phenyl-5-(o-tolyl)formazan (II). This compound was similarly obtained in 85% yield as dark-brown, lustrous crystals.

Formazans III-X. These were similarly obtained in 50-70% yields. Their melting points and analyses are presented in Table 1.

1-Benzimidazolyl-3-phenyl-5-(α-naphthyl)formazan (XI). Sodium acetate (1.6 g) was added to a solution of 0.005 mole of benzaldehyde benzyl-2-benzimidazolylhydrazone in 60 ml of alcohol and 30 ml of pyridine and, at 8-10°, a diazonium solution obtained from 0.007 mole of α-naphthylamine was added to the mixture. The resulting precipitate was crystallized from alcohol to give 50% XI.

Formazans XII-XIV. These were obtained in the same way as XI (Table 1).

2-Benzothiazolyl-3-(α-naphthyl)-5-phenyltetrazolium Bromide (XV). A 0.13-g sample of III was dissolved on heating in 5 ml of ethyl acetate, and the solution was cooled to room temperature and mixed with a warm solution of 0.18 g of N-bromosuccinimide in 7 ml of ethyl acetate. The resulting precipitate was crystallized from 50% alcohol to give 53% of XV with mp 182°. Found %: Br 17.36; S 6.75. $C_{24}H_{16}BrN_5S$. Calculated %: Br 16.46; S 6.20.

2-Benzothiazolyl-3-(β-naphthyl)-5-phenyltetrazolium Bromide (XVI). A 0.13-g sample of IV was dissolved in 5 ml of $CHCl_3$, and a solution of 0.18 g of N-bromosuccinimide in 7 ml of $CHCl_3$ was added to it. After 1 h, ether was added to precipitate 55% of a yellow substance with mp 172-175° (from 50% alcohol). Found %: Br 37.05. $C_{24}H_{16}BrN_5S \cdot 2HBr$. Calculated %: Br 37.03.

2-(α-Naphthyl)-5-phenyltetrazole (XVII). A. A 0.6-g sample of XV was dissolved in 10 ml of ethanol and refluxed with 30 ml of concentrated HBr for 3 h. The solution was neutralized with 2 N NaOH to pH ~ 7 and diluted with water. The resulting precipitate was crystallized from aqueous alcohol (with charcoal decolorization) to give colorless needles.

B. A 1.5-g sample of VII was dissolved by heating in the minimum amount of ethyl acetate and, at 20°, a solution of 1.5 g of N-bromosuccinimide in 30 ml of ethyl acetate was added. The resulting yellow precipitate was crystallized from an aqueous alcoholic alkaline solution and then from aqueous alcohol. An additional quantity of XVII was isolated from the mother liquors by evaporation to give an overall yield of 97%.

2-(β-Naphthyl)-5-phenyltetrazole (XVIII). A. A 0.8-g sample of XVI was dissolved in 20 ml of alcohol and refluxed with 30 ml of concentrated HBr for 3 h. The reaction mixture was neutralized with 30% NaOH to pH ~ 7. The oil that separated began to crystallize when water was added. The product was recrystallized from aqueous alcohol.

B. Compound XVII was similarly obtained by method B in 90% yield.

The characteristics of the tetrazoles are presented in Table 2.

LITERATURE CITED

1. N. V. Serebryakova, G. N. Lipunova, N. P. Bednyagina, and L. F. Lipatova, Khim. Geterotsikl. Soedin., 1403 (1970).
2. N. P. Bednyagina and G. N. Lipunova, Khim. Geterotsikl. Soedin., 877 (1969).
3. A. P. Zeif, L. N. Shchegoleva, G. N. Lipunova, N. P. Bednyagina, and A. P. Novikova, Zh. Organ. Khim., 6, 1332 (1970).
4. R. Kuhn and W. Münzing, Ber., 86, 858 (1963).
5. N. P. Bednyagina and G. N. Lipunova, Khim. Geterotsikl. Soedin., 902 (1968).
6. Yu. N. Sheinker, I. Ya. Postovskii, N. P. Bednyagina, I. B. Sinyavina, and L. F. Lipatova, Dokl. Akad. Nauk SSSR, 141, No. 6, 1388 (1961).
7. E. Lieber, D. R. Levering, and I. Patterson, Anal. Chem., 23, 1594 (1951).
8. E. Wedekind, Ber., 29, 1846 (1896).
9. Yu. A. Sedov and I. Ya. Postovskii, Zh. Organ. Khim., 5, 781 (1969).
10. G. N. Lipunova, Master's Thesis [in Russian], Sverdlovsk (1969).
11. O. Dimroth, Ber., 40, 2402 (1907).