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FORMATION OF DERIVATIVES OF INDOLE AND 1-HYDROXYINDOLE UPON REACTION OF 4-OXO-5-HYDROXIMINO-4,5,6,7-TETRAHYDROBENZOFURAZAN AND -TETRAHYDROBENZOFUROXAN WITH ENAMINES

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Upon reaction of 4-oxo-5-hydroximino-4,5,6,7-tetrahydrobenzofurazan and -tetrahydrobenzofuroxan with enamines, derivatives of N-oxides of tetrahydropyrrolo[2,3-e]benzofurazan are formed. Upon action of acids on these compounds, we observe formation of derivatives of indole and 1-hydroxyindole, annelated with the furazan and furoxan rings.

The reaction of isonitroso ketones in the presence of ammonia with ketones or with ketimines has been known for a long time and is used for synthesis of 2H-imidazoles [1, 2]. Studying the properties of the compounds 4-oxo-5-hydroximino-4,5,6,7-tetrahydrobenzofurazan (I) and 4-oxo-5-hydroximino-4,5,6,7-tetrahydrobenzofuroxan (II) which we recently described in [3], we observed that they easily react with acetone in the presence of ammonia at room temperature with formation of colorless crystalline compounds (IIIa and IVa), having a structure different from 2H-imidazole. The UV spectra of the products obtained are close to the UV spectra of the starting isonitroso ketones (Table 1, see [3]). In the PMR spectra of compounds IIIa and IVa, we observe signals from the protons of the methyl group as a singlet at 1.89 ppm, signals at 1.6-3.1 ppm as a complex multiplet which may be assigned to protons of the cyclohexane ring, and also signals in the region 6.70 ppm (for IIIa) and 6.81 ppm (for IVa) from protons of the hydroxyl groups, which disappear upon addition of CD_3OD. Their ^{13}C NMR spectra have signals from the sp^2-hybridized carbon atoms at 156.5, 152.0, 134.9 ppm for IIIa and 160.0, 112.6, 135.4 ppm for IVa. The signals at 69.9 and 70.8 ppm can be assigned to the sp^3-hybridized carbon atom bonded to the hydroxyl group, and the signals in the 88.7 ppm region can be assigned to the sp^3-hybridized carbon atom bonded to the amino group. The signals from the carbon atoms of the CH_2 groups are found at 16.3, 30.0, 42.5 ppm for compound IIIa and at 16.3, 29.3, 41.8 ppm for compound IVa, and for the methyl groups at 12.6 and 12.8 ppm. In the mass spectra of the products IIIa and IVa, there are molecular ion peaks M^+ 224 and 240, respectively. Based on these data and also the results of elemental analysis for compounds IIIa and IVa, a possible oximinoenamine structure (A) was rejected. We could not choose between the possible cyclic oxazine (B) or pyrrolobenzofurazan (C) structures based on the data given above. Therefore, we studied compound IIIa by x-ray diffraction. The structure of the molecule is shown in Fig. 1. The furazan ring is planar within ± 0.003 Å. The dihydropyrrole ring has the envelope form; the deviations of the $C_{(3)}$ atom from the plane of the double bond are equal to 0.479(5) and 0.481(5) Å respectively for two independent molecules. The conformation of the six-membered ring is intermediate between half-chair and sofa, the deviations of the $C_{(4)}$ and $C_{(5)}$ atoms are equal to 0.266(6), 0.156(6), and $-0.492(8)$, $-0.577(7)$ Å. The bond lengths in the molecule are close to the expected values [4]. We note the shortening of the $C_{(4)}-N_{(4)}$ bond to 1.415(4), 1.426(4) Å compared with the expected value of 1.469(10) Å [4]. In the crystal, the molecules are joined into pairs by strong hydrogen bonds $O_{(2)}-H...O_{(3)}$ with parameters O...H 1.66(4), 1.64(4), O...O 2.638(3), 2.615(3) Å, O–H...O 174(3), 170(3) Å. The amine group participates in formation of weak intra- and intermolecular hydrogen bonds of the type N–H...O.

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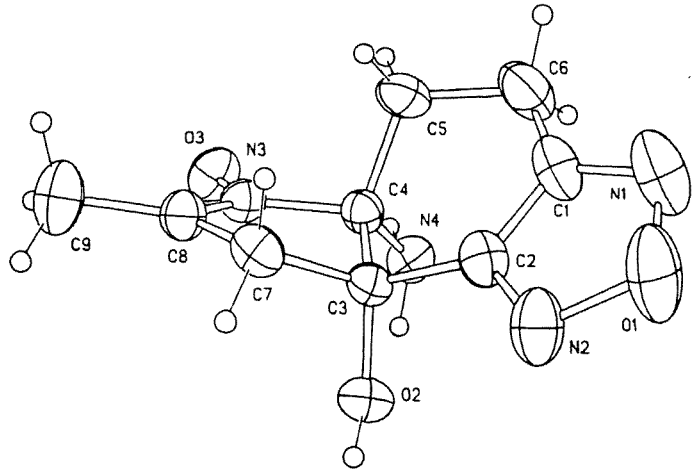


Fig. 1. Projection of a three-dimensional model of 5a-amino-8a-hydroxy-4,5,5a,8a-tetrahydro-8H-pyrrolo[2,3-e]benzofurazan-6-oxide (IIIa).

TABLE 1. Characteristics of Synthesized Compounds

Compound	Empirical formula	mp, °C*	UV spectrum, λ_{max}, nm (lg ε)	Yield, %
IIIa	$C_9H_{12}N_4O_3$	188...190	228 (3,99)	72
IIIb	$C_{10}H_{14}N_4O_3$	168...170	232 (4,01)	32
IIIc	$C_{14}H_{14}N_4O_3$	206...208	226 (4,15); 297 (4,30)	84
IVa	$C_9H_{12}N_4O_4$	141...142	233 (3,90); 271 (3,73)	63
IVb	$C_{10}H_{14}N_4O_4$	183...185	235 (3,90); 259 (4,02)	23
IVc	$C_{14}H_{14}N_4O_4$	204...206	226 (4,09); 284 (4,37)	59
Va	$C_{13}H_{18}N_4O_4$	142...144	225 (3,85); 253 (4,02)	85
Vb	$C_{14}H_{20}N_4O_4$	133...135	225 (3,90); 254 (4,02)	33
VIa	$C_{13}H_{18}N_4O_5$	140...143	237 (3,88); 273 (4,01)	84
VIb	$C_{14}H_{20}N_4O_5$	148...151	233 (3,96); 275 (4,06)	37
VII	$C_{16}H_{22}N_4O_4$	151...153	227 (3,70); 255 (3,88)	95
VIII	$C_{16}H_{22}N_4O_5$	183...185	238 (3,84); 275 (4,07)	80
IXa	$C_9H_7N_3O$	183...185	302 (3,66); 345 (4,38); 377 (3,73)	36
IXb	$C_{10}H_9N_3O$	181...183	235 (4,15); 248 (4,19); 315 (3,55); 390 (3,60)	10
IXc	$C_{14}H_9N_3O$	215...217	232 (4,03); 292 (4,43); 400 (3,70)	35
Xa	$C_9H_7N_3O_2$	201...203	258 (4,34); 300 (3,75); 415 (3,92)	32
Xb	$C_{10}H_9N_3O_2$	197...198	252 (4,19); 306 (3,66); 425 (3,88)	8
Xc	$C_{14}H_9N_3O_2$	201...204	233 (4,29); 323 (3,72); 382 (3,85); 428 (4,24)	47
XI	$C_{10}H_9N_3O_2$	228...230	242 (4,30); 335 (3,65); 399 (3,78)	32
XII	$C_{10}H_9N_3O_3$	124...126	238 (4,13); 338 (3,58); 384 (3,66)	46
XIII	$C_{12}H_{11}N_3O_2$	201...204	241 (4,08); 336 (3,48); 399 (3,60)	40
XIV	$C_{12}H_{11}N_3O_3$	146...149	268 (4,26); 301 (3,83); 424 (4,06)	59

*Compounds IIIa-c, IVa-c, Va, b, VIa, b, VII, and VIII were recrystallized from acetonitrile; compounds IXa-c, Xa-c, XI, XII, XIII, and XIV were recrystallized from alcohol.

Based on these data, compound IIIa is 5a-amino-8a-hydroxy-7-methyl-4,5,5a,8a-tetrahydro-8H-pyrrolo[2,3-e]-benzofurazan-6-oxide, and compound IVa accordingly is 5a-amino-8a-hydroxy-7-methyl-4,5,5a,8-tetrahydro-8H-pyrrolo[2,3-e]-benzofurazan-3,6-dioxide.

TABLE 2. PMR Spectra and Mass Spectra of Derivatives of N-Oxides of Tetrahydropyrrolo[2,3-e]benzofurazan

Compound	PMR spectrum, δ, ppm*		Mass spectrum, m/z (I rel %)**
	OH, s	other protons	
IIIa	6,70	1,89 (3H, s, CH_3); 1,70 - 2,40 (2H, m, CH_2); 2,70 - 3,10 (4H, m, $2CH_2$)	224 (30) M^+, 153 (100), 136 (26), 108 (17), 81 (30)
IIIb	6,70	0,90 (3H, d, CH_3); 1,90 (3H, s, CH_3); 2,30 - 2,50 (2H, m, CH_2); 2,70 - 3,00 (2H, m, CH_2); 3,30 (1H, q, CH)	238 (14) M^+, 153 (100), 136 (20), 87 (18), 81 (17)
IIIc	6,80	1,70 - 2,40 (2H, m, CH_2); 2,76 (2H, m, CH_2); 2,90 (2H, m, CH_2); 3,50 (2H, d, NH_2); 7,40 - 7,50 (3H, m, C_6H_5); 8,20 - 8,40 (2H, m, C_6H_5)	286 (23) M^+, 254 (100), 153 (93), 103 (27)
IVa	6,81	1,89 (3H, s, CH_3); 1,70 - 2,40 (2H, m, CH_2); 2,80 - 3,30 (4H, m, $2CH_2$)	240 (11) M^+, 153 (47), 125 (19), 82 (30), 73 (43), 57 (60), 54 (18), 52 (16), 42 (100)
IVb	6,81	1,05 (3H, d, CH_3); 1,90 (3H, s, CH_3); 1,60 - 2,00 (2H, m, CH_2); 2,20 - 2,40 (2H, m, CH_2); 3,20 (1H, g, CH)	254 (10) M^+, 169 (20), 152 (100)
IVc	6,92	1,70 - 2,80 (6H, m, $3CH_2$); 3,55 (2H, d, NH_2); 7,40 - 7,60 (3H, m, C_6H_5); 8,30 - 8,50 (2H, m, C_6H_5)	302 (18) M^+, 270 (41), 169 (20), 152 (100), 103 (30), 77 (30)
Va	6,80	1,44 (3H, s, CH_3) 2,50 - 3,60 (14H, m, $7CH_2$)	294 (11) M^+, 277 (20), 189 (60), 167 (19), 127 (48), 112 (24), 87 (79), 82 (26), 70 (48), 57 (100)
	6,90	1,70 (3H, s, CH_3)	
Vb	6,82	0,59 (3H, t, CH_3) 1,50 - 1,60 (16H, m, $8CH_2$)	308 (3) M^+, 203 (18), 167 (18), 141 (15), 126 (31), 87 (54), 82 (35), 57(87)
	6,94	0,97 (3H, t, CH_3)	
VIa	6,88	1,50 (3H, s, CH_3) 2,30 - 3,60 (14H, m, $7CH_2$)	170 (15), 127 (50), 69 (20), 57 (48), 44 (100)
	6,96	1,62 (3H, s, CH_3)	
VIb	6,86	0,69 (3H, t, CH_3) 1,50 - 3,50 (16H, m, $8CH_2$)	324 (3) M^+, 153 (18), 141 (25), 126 (20), 87 (49), 83 (28), 72 (20), 57 (83)
	7,00	0,95 (3H, t, CH_3)	
VII	6,60	1,00 - 3,60 (21H, m, $10CH_2$, CH)	334 (2) M^+, 229 (73), 167 (100), 166 (92), 152 (27), 108 (17), 87 (30), 81 (27), 69 (23), 57 (48)
VIII	6,65	1,00 - 3,60 (21H, m, $10CH_2$, CH)	350 (2) M^+, 213 (17), 167 (47), 166 (48), 152 (16), 124 (16), 111 (24), 98 (62), 88 (50), 69 (60), 57 (82)

*Molecular ion peaks and peaks with intensity greater than 15% are given.

**No molecular ion peak is observed.

The data obtained were unexpected to us, since we assumed that the amino group is in the 7 position of the ring (structure C) rather than the 5a position. We may hypothesize that compound IIIa is formed from the initially formed compound C. Upon reaction of compound C with ammonia, addition of the latter to the nitrone group occurs, followed by cleavage of ammonia with formation of a more stable compound where the amino- and oxy groups participate in the formation of an intramolecular hydrogen bond.

Upon reaction of isonitroso ketones I and II with methyl ethyl ketone and acetophenone in the presence of ammonia, products are formed which based on spectral and analytical data were assigned the structure of the corresponding pyrrolobenzofurazans (IIIb, c and IVb, c).

We should note that the UV spectra of compounds IIIc and IVc are typical for the UV spectra of phenylnitrones [5] (see Table 1), which is additional evidence that their amino group is in the 5a position of the ring.

Based on the data presented, we may hypothesize that in the reaction under consideration, the corresponding enamine is initially formed from the ketone and the amine, and then this enamine reacts with the isonitroso ketone with formation of pyrrolobenzofurazans IIIa-c and IVa-c.

In fact, upon reaction of isonitroso ketones I and II with acetone and methyl ethyl ketone in the presence of a secondary amine (morpholine), the corresponding pyrrolobenzofurazans are formed in high yield (Va, b and VIa, b). In the PMR and ^{13}C

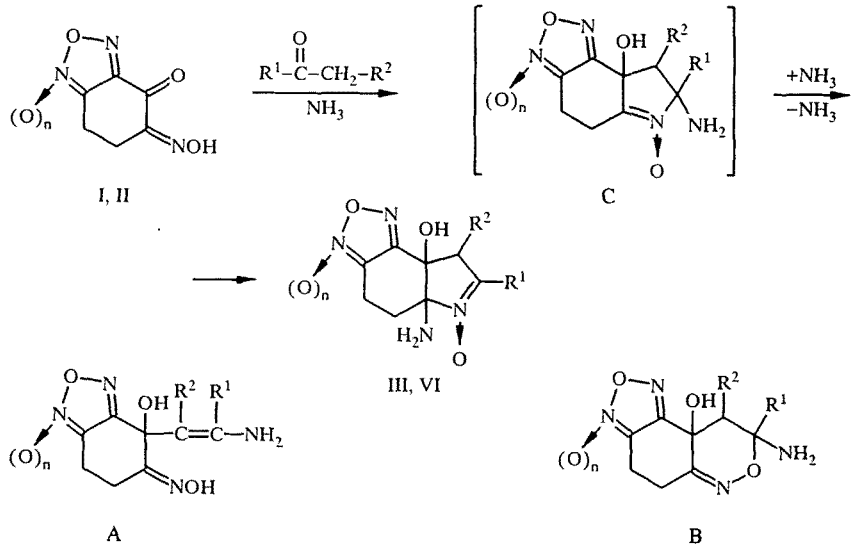
TABLE 3. PMR Spectra of Derivatives of Pyrrolo[2,3-e]benzofurazan

Compound	PMR spectrum, δ, ppm*		Mass spectrum, m/z (I_{rel}, %)*2
	OH, NH br.s	other protons	
IXa	11,97	2,41 (3H, s, CH_3); 6,65 (1H, s, Harom) 7,38 (1H, d, Harom) 7,62 (1H, d, H arom)	173 (88) M^+, 156 (100), 142 (16), 52 (16), 42 (18)
IXb	11,80	2,30 (3H, s, CH_3); 2,35 (3H, s, CH_3); 7,32 (1H, d, H arom)7,55 (1H, d, H arom)	187 (80) M^+, 170 (100), 155 (30), 142 (30), 44 (40)
IXc	12,57	7,30 - 7,70 (8H, m, H arom)	235 (86) M^+, 218 (100), 205 (16), 177 (15), 151 (15), 77 (25), 51 (17)
Xa	12,56	2,45 (3H, s, CH_3); 6,95 (1H, s, H arom) 7,24 (1H, d, Harom) 7,88 (1H, d, H arom)	189 (74) M^+, 129(100), 104(15), 75(24)
Xb	11,60	2,20 (3H, s, CH_3); 2,23 (3H, s, CH_3); 6,66 (1H, d, Harom)7,20 (1H, d, H arom)	203(100) M^+, 186(30), 143(90), 128(30), 115(25)
Xc	12,48	6,80 - 7,95 (8H, m, H arom)	251(82) M^+, 191(100), 163(18), 77(15)
XI	11,47	2,30 (3H, s, CH_3); 2,37 (3H, s, CH_3); 7,33 (1H, d, Harom) 7,62 (1H, d, H arom)	203 (100) M^+, 186 (26), 171 (16), 157 (17), 149 (31), 145 (53), 131 (16), 104 (20), 77 (17)
XII	11,60	2,59 (6H, s, $2CH_3$); 6,76 (1H, d, Harom) 7,34 (1H, d, H arom)	219 (100) M^+, 202 (23), 159 (76), 142 (27), 115 (21), 89 (18), 75 (16)
XIII	11,10	1,54 (4H, m, $2CH_2$); 2,50 (4H, m, $2CH_2$); 7,04 (1H, d, H arom) 7,36 (1H, d, H arom)	229 (100) M^+, 212 (19), 171 (30), 149 (15), 44 (28)
XIV	11,49	1,80 (4H, m, $2CH_2$); 2,50 (4H, m, $2CH_2$); 6,80 (1H, d, H arom) 7,36 (1H, d, H arom)	245 (100) M^+, 228 (49), 185 (49), 170 (21), 157 (20), 140 (22), 45 (68)

*In all cases, for H_{arom}, the spin–spin coupling constant J_{AB} = 10 Hz.

**Molecular ion peaks and peaks with intensity greater than 15% are given.

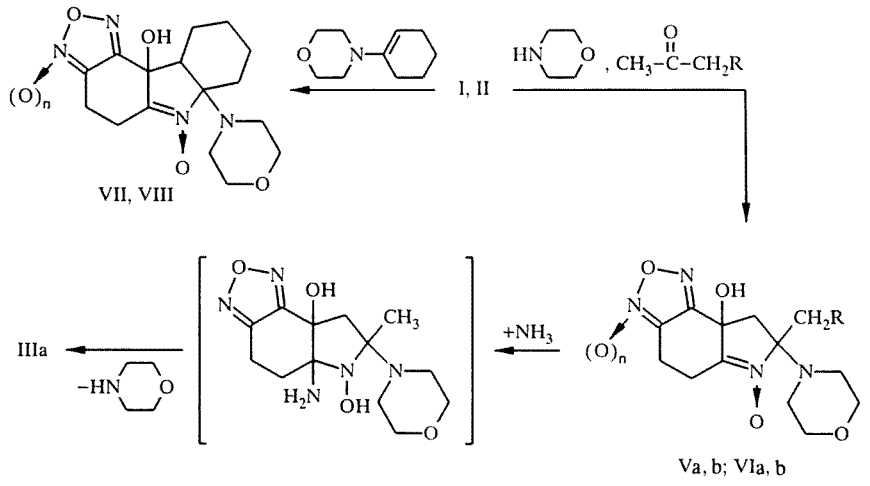
NMR spectra of these products, we observe a double set of signals. This can be explained by the presence in compound Va, b and VIa, b and also IIIa, c and IVa, c of two asymmetric carbon atoms, leading to a mixture of diastereomers. However, in the case of compounds IIIa, c and IVa, c, one diastereomer is formed preferentially, probably due to the participation of their



I–IV a $R^1 = CH_3$, $R^2 = H$; b $R^1 = R^2 = CH_3$; c $R^1 = C_6H_5$, $R^2 = H$

I, III n = 0; II, IV n = 1

oxy- and amino groups in the formation of an intramolecular hydrogen bond. Compounds Va, b and VIa, b are obtained as a mixture of diastereomers which we could not separate. Based on the PMR spectral data, we arrived at the conclusion that in pyrrolobenzofurazans Va, b and VIa, b, the morpholine residue is located at the 7 position of the ring, since the chemical shifts of the protons of the methyl and methylene groups are characteristic for analogous groups bonded to sp^3-hybridized carbon atoms [6]. In the case of methyl ethyl ketone, in contrast to the analogous reaction in the presence of ammonia, the product of closure of the pyrrole ring at the methyl group rather than at the methylene group is formed, which can be explained by the effect of steric factors.

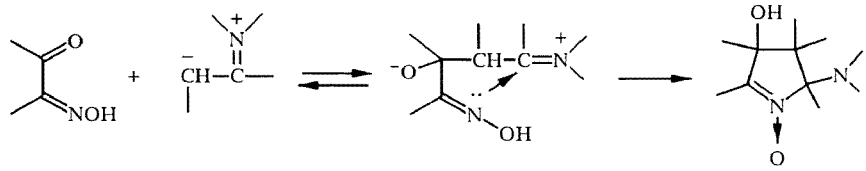


V, VI a R = H, b R = CH_3; V, VII n = 0; VI, VIII n = 1

In the reaction of isonitroso ketones I and II with an enamine (1-(N-morpholinyl)cyclohexene), products VII and VIII are formed in high yields, which according to analytical and spectral data have a structure analogous to compounds Va, b and VIa, b. In compounds IIIb, IVb, VII, and VIII there are three asymmetric carbon atoms, and we might expect formation of a mixture of diastereomers. However, in their ^{13}C NMR spectra we observe a single set of signals from the carbon atoms, which allowed us to hypothesize that only one diastereomer forms in the given reaction. We did not determine the configuration of the products obtained.

The hypothesis above that in compound C addition of ammonia to the nitrone group is possible with cleavage of another ammonia molecule and formation of compounds IIIa-c and IVa-c is supported by the fact that upon treatment of morpholinyl-pyrrolobenzofurazan Va with ammonia, the aminopyrrolobenzofurazan IIIa was isolated quantitatively.

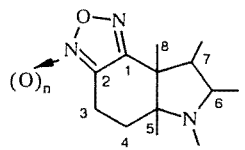
Formation of pyrrolobenzofurazans can be explained by a scheme including nucleophilic addition of enamine at the carbonyl group of the isonitroso ketone, transfer of a proton, and finally nucleophilic attack of the oxime nitrogen atom at the carbon atom, leading to the closure of the pyrrole ring.



Studying the properties of the synthesized compounds IIIa-c, IVa-c, VII and VIII, we observed that under the action of acid they are converted to indole derivatives. In the case when R^2 = H, the reaction products are indole derivatives, while when $R^2 \neq$ H they are 1-hydroxyindole derivatives, compounds which at present are not readily available and have not been well studied [7]. For $R^1 = R^2 = CH_3$, derivatives of both indole and 1-hydroxyindole are isolated.

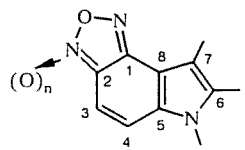
The indicated conversion can be explained by the fact that upon protonation, the following occur in succession: deamination, dehydration, and aromatization, leading to 1-hydroxyindoles.

TABLE 4. Chemical Shifts in ^{13}C NMR Spectra of Derivatives of N-Oxides of Tetrahydropyrrolo[2,3-e]benzofurazan, ppm



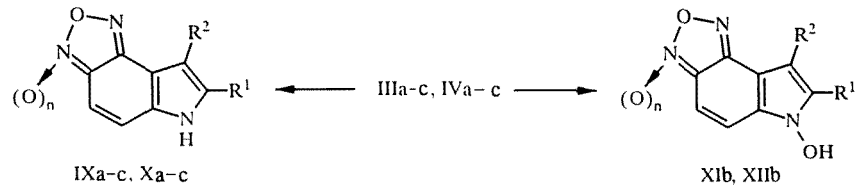
Compound	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	$C_{(8)}$	C_6H_5, CH_2	CH_3
IIIa	152,0	156,5	30,0	16,3	88,7	134,5	42,5	69,9		12,6
IIIb	152,7	154,5	31,8	16,2	88,3	139,6	47,9	72,5		13,6, 11,2
IIIc	152,1	156,2	30,3	16,6	91,4	132,2	41,8	69,6	129,9, 129,5, 126,9, 128,4	
IVa	160,0	112,6	29,3	16,3	88,7	135,4	41,8	70,8		12,8
IVb	158,0	113,0	31,1	16,0	88,2	139,9	47,7	73,2		13,7, 11,2
IVc	159,3	112,4	29,6	16,5	91,2	132,0	40,4	70,3	130,0, 129,5, 126,8, 128,5	
Va	151,7 151,9	155,4 156,7	22,9 23,9	17,1 17,4	139,0 139,6	93,5 93,7	42,7 43,3	68,4 69,0	45,1, 66,6 46,3, 66,6	16,5, 16,6
Vb	151,9 152,0	155,6 156,5	26,5 27,0	16,5 17,3	139,8 140,0	96,7 97,1	39,5 40,1	68,5 69,3	45,5, 66,7 , 17,6 46,5, 66,7, 18,7	7,5, 8,0
VIa	159,0 159,0	112,0 112,2	22,9 23,8	17,3 17,2	138,7 139,0	93,6 93,8	41,8 42,3	69,3 69,8	45,2 , 66,7 46,2, 66,7	15,1, 15,4
VIb	159,1 160,0	112,0 112,1	26,5 26,9	15,0 15,2	138,9 138,9	96,8 97,1	38,7 39,1	69,4 70,0	45,5, 66,7, 17,0 46,5, 66,7, 17,3	7,5, 8,0
VII	151,6	155,7	29,3	16,4	139,5	93,5	40,9	71,4	45,2, 67,1, 17,7, 20,1, 21,2, 22,2	
VIII	159,5	112,0	29,3	15,2	138,7	93,6	40,4	72,0	45,3, 67,1, 17,4, 20,1, 21,5 22,2	

TABLE 5. Chemical Shifts in ^{13}C NMR Spectra of Synthesized Derivatives of Indole



Compound	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$*	$C_{(6)}$*	$C_{(7)}$*	$C_{(8)}$*	CH_3, CH_2, C_6H_5
IXa	144,0	148,1	123,0	106,0	135,0	132,5	108,8	102,3	12,9
IXb	144,9	148,1	123,0	106,0	130,8	130,6	109,2	111,3	9,9, 10,7
IXc	144,9	148,2	123,1	107,9	134,2	131,2	109,8	101,7	137,3, 129,0, 127,6, 124,9
Xa	148,6	112,2	120,3	100,8	135,5	133,2	102,3	110,3	12,8
Xb	149,0	112,0	120,0	101,6	131,6	131,4	110,3	110,4	9,8, 10,5
Xc	148,8	112,2	120,3	104,5	134,9	130,9	100,0	111,0	137,5, 128,8, 124,8, 127,6
XIb	144,5	148,3	119,7	105,4	128,9	127,7	103,5	107,3	8,1, 10,1
XIIc	148,9	112,4	117,4	102,3	129,8	128,8	104,3	106,7	8,3, 10,4
XIII	144,6	148,5	119,9	105,8	131,7	128,4	102,5	110,2	22,8, 22,2, 22,0, 20,5
XIV	149,0	112,3	117,5	102,4	132,1	129,2	103,4	109,2	22,5, 22,0, 21,7, 20,3

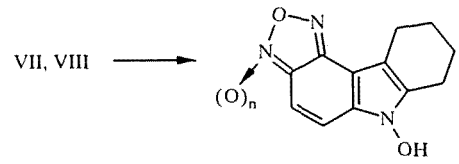
*The reverse assignment of the signals from the carbon atoms $C_{(5)}$ and $C_{(6)}$ and also $C_{(7)}$ and $C_{(8)}$ is possible.



IXa-c, Xa-c

IIIa-c, IVa-c

XIb, XIIb



XIII, XIV

IX–XII a $R^1 = CH_3$, $R^2 = H$; b $R^1 = R^2 = CH_3$; c $R^1 = C_6H_5$, $R^2 = H$
IX, XI, XIII n = 0; X, XII, XIV n = 1

Formation of indole derivatives is probably explained by the fact that the presence of a hydrogen atom in the 8 position of the ring facilitates loss of an oxygen atom in the N-oxide group. A correct explanation of the observed fact has not yet been found.

TABLE 6. Coordinates ($\times 10^4$) and Equivalence Temperature Factors (Å^2, $\times 10^3$) of Atoms of the Two Crystallographically Independent IIIa Molecules

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
$C_{(1)}$	3050(1)	-4778(3)	4542(2)	48(1)
$C_{(2)}$	3457(1)	-4254(3)	5142(2)	35(1)
$C_{(3)}$	3928(1)	-4825(2)	5688(2)	29(1)
$C_{(4)}$	3945(1)	-6027(2)	5347(2)	31(1)
$C_{(5)}$	3361(1)	-6528(3)	5204(3)	44(1)
$C_{(6)}$	3021(2)	-5979(3)	4385(3)	58(1)
$C_{(7)}$	3867(1)	-4936(3)	6775(2)	35(1)
$C_{(8)}$	4138(1)	-6009(2)	7013(2)	35(1)
$C_{(9)}$	4295(2)	-6411(4)	7985(3)	56(1)
$N_{(1)}$	2727(1)	-4044(3)	4131(2)	69(1)
$N_{(2)}$	3385(1)	-3202(2)	5112(2)	51(1)
$N_{(3)}$	4197(1)	-6569(2)	6241(2)	32(1)
$N_{(4)}$	4263(1)	-6176(3)	4520(2)	38(1)
$O_{(1)}$	2930(1)	-3043(2)	4478(2)	72(1)
$O_{(2)}$	4148(1)	-4338(2)	5491(2)	37(1)
$O_{(3)}$	4412(1)	-7547(2)	6145(2)	45(1)
$C_{(1A)}$	3004(1)	-159(3)	7911(2)	43(1)
$C_{(2A)}$	3362(1)	476(2)	7337(2)	32(1)
$C_{(3A)}$	3883(1)	48(2)	6898(2)	29(1)
$C_{(4A)}$	3996(1)	-1144(2)	7237(2)	30(1)
$C_{(5A)}$	3463(1)	-1812(3)	7343(3)	40(1)
$C_{(6A)}$	3101(2)	-1337(3)	8118(3)	54(1)
$C_{(7A)}$	3839(1)	-59(3)	5796(2)	36(1)
$C_{(8A)}$	4205(1)	-1019(2)	5600(2)	34(1)
$C_{(9A)}$	4434(2)	-1317(4)	4666(3)	59(1)
$N_{(1A)}$	2594(1)	449(3)	8186(2)	58(1)
$N_{(2A)}$	3172(1)	1464(2)	7261(2)	49(1)
$N_{(3A)}$	4287(1)	-1589(2)	6367(2)	30(1)
$N_{(4A)}$	4342(1)	-1190(3)	8093(2)	39(1)
$O_{(1A)}$	2689(1)	1480(2)	7787(2)	62(1)
$O_{(2A)}$	4355(1)	675(2)	7183(2)	38(1)
$O_{(3A)}$	4571(1)	-2502(2)	6475(1)	38(1)

EXPERIMENTAL

The IR spectra were recorded on the UR-20 in KBr (concentration 0.25%). The UV spectra were recorded on the Specord UV-vis in ethanol. The PMR spectra were obtained on the Varian A-55-60 in DMSO-d_6. The ^{13}C NMR spectra were taken on the Bruker WP-200 in DMSO-d_6. The mass spectra were recorded on the Finnegan MAT MS 8200 by direct injection of the sample into the ion source for ionizing potential of 70 eV. The ionization chamber temperature was 120-200°C. The x-ray diffraction study was carried out on the Syntex 2_1 diffractometer. The crystals were of monoclinic syngony: a = 23.882(6), b = 12.207(3), c = 13.940(3) Å, β = 92.17(2)°, V = 4061(2) Å^3 , space group C2/c, $C_9H_{12}N_4O_3$, M = 224.23, Z = 16, d_{calc} = 1.467 g/cm^3, λ Cu(Kα), graphite monochromator. The intensities of 2576 independent reflections with $2\theta > 14°$ were measured by $\theta/2\theta$ scanning. Corrections for absorption were introduced empirically. The structure was deciphered by the direct method using the program SHELX-86 and least-squares refined in the full-matrix anisotropic – isotropic approximation to wR2 = 0.1145, S = 1.065 for all reflections (R = 0.0435 for 2037 F > 4σ) using the program SHELXL-93 (F^2 refinement). The positions of the hydrogen atoms were found from a difference synthesis. The atomic coordinates obtained are given in Table 6. The melting points were determined on a Kofler microheating stage. The yields, melting points, and spectral data of the synthesized compounds are presented in Tables 1-5.

The elemental analysis data of the synthesized compounds correspond to the calculated values.

5a-Amino-7-methyl (IIIa), 5a-Amino-7,8-dimethyl (IIIb), 5a-Amino-7-phenyl-8a-hydroxy-4,5,5a,8a-tetrahydro-8H-pyrrole[2,3-e]benzofurazan-6-oxide (IIIc), 5a-Amino-7-methyl (IVa), 5a-Amino-7,8-dimethyl (IVb), 5a-Amino-7-phenyl-8a- hydroxy-4,5,5a,8a-tetrahydro-8H-pyrrolo[2,3-e]benzofurazan-3,6-dioxide (IVc). A mixture of 10 mmoles isonitroso ketone I or II and 20 ml of the corresponding ketone was saturated with ammonia with rapid stirring. Almost immediately a yellow material precipitated which dissolved when more ammonia was passed through. The solution obtained was stirred without stopping the supply of ammonia until a white maerial began to precipitate, after which the reaction mixture was allowed to stand overnight in a refrigerator. The precipitate was filtered, washed with ether, and dried.

7-(N-morpholinyl)-7-methyl- (Va), 7-(N-morpholinyl)-7-ethyl-8a-hydroxy-4,5,8,8a-tetrahydro-7H-pyrrolo-[2,3-e]benzofurazan-6-oxide (Vb), 7-(N-morpholinyl)-7-methyl- (VIa), 7-(N-morpholinyl)-7-ethyl-8a-hydroxy-4,5,8,8a-tetrahydro-7H-pyrrolo[2,3-e]benzofurazan-3,6-dioxide (VIb). A mixture of 10 mmoles isonitroso ketone I or II and 1 g (11.5 mmoles) morpholine and 20 ml of the corresponding ketone were stirred at room temperature for a day. The precipitate was filtered, washed with ether, and dried.

10b-Hydroxy-6a-(N-morpholinyl)-4,5,7,8,9,10,10a,10b-octahydro-6aH-[1,2,5]oxadiazolo[3,4-c]carbazole-6-oxide (VII), 10b-Hydroxy-6a-(N-morpholinyl)-4,5,7,8,9,10,10a,10b-octahydro-6aH-[1,2,5]oxadiazolo[3,4-c]-carbazole-6-dioxide (VIII). A mixture of 10 mmoles isonitroso ketone I or II, 50 ml methanol and 2 g (12 mmoles) 1-(N-morpholinyl)cyclohexene were stirred at room temperature for a day, after which the white precipitate was filtered, washed with methanol, and dried.

5a-Amino-7-phenyl-8a-hydroxy-4,5,5a,8a-tetrahydro-8H-pyrrolo[2,3-e]benzofurazan-6-oxide (IIIa). A 1 g portion of gaseous ammonia was applied to a solution of 10 mmoles compound Va in 50 ml methanol. The mass was held at room temperature for 2 h. The solvent was distilled under vacuum. The residue was ground with ether. The residue was filtered. The yield was 9.5 mmoles (95%).

7,8-Dimethyl-6-hydroxy-6H-pyrrolo[2,3-e]benzofurazan (XIb), 6-Hydroxy-7,8,9,10-tetrahydro[1,2,5]oxadiazolo-[3,4-c]carbazole (XIII), 7,8-Dimethyl-6-hydroxy- 6H-pyrrolo[2,3-e]benzofurazan-3-oxide (XIIb), 6-Hydroxy-7,8,9,10-tetrahydro[1,2,5]oxadiazolo[3,4-c]carbazole-3-oxide (XIV), 7-Methyl- (IXa), 7,8-Dimethyl- (IXb), 7-Phenyl-6H-pyrrolo-[2,3-e]benzofurazan (IXc), 7-Methyl- (Xa), 7,8-Dimethyl- (Xb), 7-Phenyl-6H-pyrrolo[2,3-e]benzofurazan (IXc), 7-Methyl- (Xa), 7,8-Dimethyl- (Xb), 7-Phenyl-6H-pyrrolo[2,3-e]benzofurazan-3-oxide (Xc). A 1 ml portion of concentrated hydrochloric acid was added to 10 mmoles of compounds VII, VIII, IIIa-c or IVa-c in 30 ml methanol. The mixture was held at 50°C for 2 h and then cooled. Then 1 g potassium carbonate was added. The solvent was driven off and the residue was chromatographed on silica gel (eluent — chloroform).

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