4. G. Levy and G. Nelson, Handbook of Carbon-13 Nuclear Magnetic Resonance [Russian translation], Mir, Moscow (1975).
5. A. A. Ponomarev, M. V. Noritsina, and A. P. Kriven'ko, Khim. Geterotsikl. Soedin., No. 6, 923 (1966).
6. A. A. Ponomarev, A. P. Kriven'ko, and M. V. Noritsina, Khim. Geterotsikl. Soedin., No. 6, 787 (1970).
7. Tatsuya Shono, Voshihiro Matsumura, and Kanji Tsubata, J. Am. Chem. Soc., 103, 1172 (1981).

BISINDOLES.

25.* PROPERTIES OF 3H,8H-INDOLO[4,5-e]- AND -[5,4-e]INDOLE

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Electrophilic-substitution reactions for 3H,8H-indolo[4,5-e]- and -[5,4-e]-indole were studied. Mono- and disubstituted compounds were isolated as a result of formylation and acetylation, whereas only monosubstitution products were isolated in the case if diazo coupling. It is shown that in the dimethylaminomethylation of 3H,8H-indolo[4,5-e]indole steric factors hinder the formation of a disubstituted compound, while the formation of β-substitution products is hindered in the case of diazo coupling of 3H,8H-indolo[4,5-e]- and -[5,4-e]indole.

In this research we investigated the behavior of isomeric 3H,8H-indolo[4,5-e]- (I) and 3H,8H-indolo[5,4-e]indole (II) in electrophilic-substitution reactions, and the results were compared with analogous data for 1H,6H-indolo[7,6-g]indole (III) [3, 4].

Quantum chemical calculations of the indoloindole I and II molecules (Fig. 1) by the self-consistent-field (SCF) MO method within the CNDO/2 method [5] for a planar structure by means of the program of Maslov [6] (for I) and by means of the program developed in the NMR laboratory of Moscow State University [7] (for II) showed that, as in the case of indoloindole III [4], high electron densities are observed in the β positions of the pyrrole rings.

In the Vilsmeier formylation of indoloindoles I and II using a threefold excess of the complex, indolo[4,5-e]indole I gives a mixture of two dialdehydes, viz., 1,9-diformyl- (IV) and 1,10-diformyl-3H,8H-indolo[4,5-e]indole (V), while indolo[5,4-e]indole II like III [3], forms only a symmetrical dialdehyde, viz., 1,6-diformyl-3H,8H-indolo-[5,4-3]indole (VI). As in the case of indoloindole III [4], the use of equimolar ratios of the reagents leads to the formation of primarily α- and β-monoaldehydes, viz., 2-formyl- (VII) and 1-formyl-3H,8H-indolo[4,5-e]indole (VIII), although the formation also of diformyl derivatives IV and V is observed chromatographically.

Mixtures of acetyl derivatives are formed in the acetylation of indoloindoles I and II with acetic anhydride in the presence of acetic acid. The following compounds were isolated by column chromatography: 3-acetyl-8H- (IX), 2-acetyl-3H,8H- (X), and 2,8-diacetyl-3H-indolo[4,5-e]indole (XI) and 2-acetyl- (XII) and 1-acetyl-3H,8H-indolo[5,4-e]indole (XIII). Acetylation with acetyl chloride in the presence of $AlCl_3$ in the case of indoloindole I proceeds more selectively with the formation of primarily 2-acetyl derivative X, whereas the use of indoloindole II under these conditions gives acetyl derivatives XII and XIII. In contrast to III [3], the incorporation of an acetyl group into the naphthalene

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*See [1] for Communication 24.

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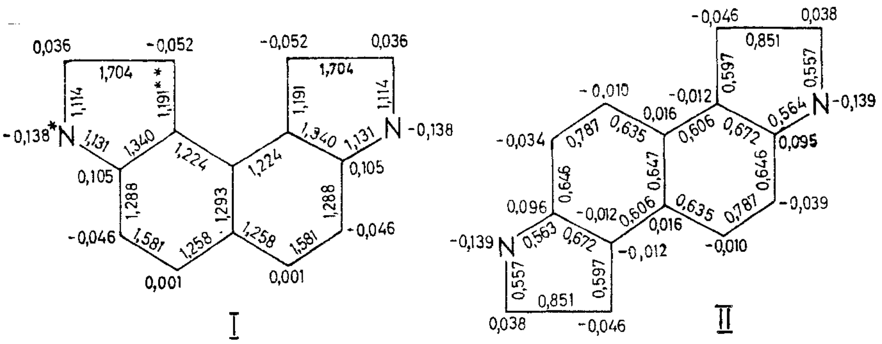
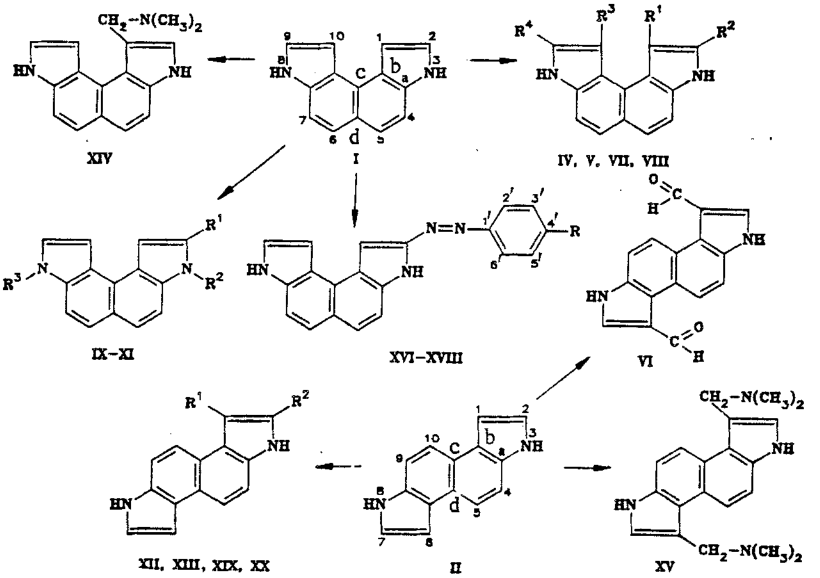


Fig. 1. Molecular diagrams of indoloindoles I and II (one asterisk is used to designate the charge densities on the atoms, while two asterisks are used to designate the Wilberg indexes [11]).

part of the molecule is not observed. The difficulty encountered in the formation of diacetyl derivatives of indoloindole II can be explained by deactivation of the aromatic ring by the electron-acceptor substituent [3]. In contrast to indoloindole II, an acetyl group is not incorporated into the β position of indoloindole I, evidently because of the steric hindrance created by the drawn-together pyrrole rings.

A monosubstitution product – 1-dimethylaminomethyl-3H,8H-indolo[4,5-e]indole (XIV) was isolated in the Mannich reaction in acetic acid in the case of indoloindole I, whereas 1,6-bis(dimethylaminomethyl)-3H,8H-indolo[5,4-e]indole (XV) was isolated in the case of indoloindole II. The difficulty encountered in the incorporation of a dimethylaminomethyl group into the second pyrrole ring of indoloindole I can be explained by steric hindrance.



IV R^1=R^4=CHO; R^2=R^3=H; V R^1=R^3=CHO, R^2=R^4=H; VII R^1=R^3=R^4=H, R^2=CHO; VIII R^1=CHO, R^2=R^3=R^4=H; IX R^1=R^3=H, R^2=COCH$_3$; X R^1=COCH$_3$, R^2=R^3=H; XI R^1=R^3=COCH$_3$, R^2=H; XII R^1=H, R^2=COCH$_3$; XIII R^1=COCH$_3$, R^2=H; XVI R=H; XVII R=Cl; XVIII R=NO$_2$; XIX R^1=N=NC$_6$H$_5$, R^2=H; XX R^1=H, R^2=N=NC$_6$H$_5$

In contrast to III [3], the diazo coupling of indoloindole I in a neutral medium at a molar ratio of the substrate and the diazonium salt of 1:3 proceeds anomalously and leads to the formation of primarily monosubstituted 2-phenylazo derivatives, viz., 2-phenylazo- (XVI), 2-(p-chlorophenylazo)- (XVII), and 2-(p-nitrophenylazo)-3H,8H-indolo[4,5-e]indole (XVIII). Under similar conditions indoloindole II reacts with benzenediazonium chloride to give two substances, viz., 1-phenylazo- (XIX) and 2-phenylazo-3H,8H-indolo[5,4-e]indole (XX) in a ratio of 1:4.5, whereas it reacts with p-nitrobenzenediazonium chloride to give polymeric compounds. The formation of monosubstituted compounds can be explained by the weak electrophilicity of the ArN$_2^+$ ion [3], while the formation of 2-substituted derivatives

TABLE 1. Chemical Shifts of the Protons and Spin-Spin Coupling Constants (SSCC) in the PMR Spectra of I, II, IV-VIII, and XII-XV (in d_6-DMSO) and IX-XI (in d_6-acetone)

Compound	δ, ppm										J, Hz
	1-H	2-H	3-H	4-H	5-H, д	6-H	7-H	8-H	9-H	10-H	
I	7,24 m	7,43 dd	11,4 br s	7,47 dd	7,60	7,60 d	7,47 dd	11,4 br s	7,43 dd	7,24 m	$J_{12}=J_{23}=2{,}6$; $J_{13}=2{,}2$; $J_{14}=0{,}4$; $J_{45}=8{,}9$
I*	7,34 m	7,43 dd	10,5 br s	7,50 dd	7,64	7,64 d	7,50 dd	10,5 br s	7,43 dd	7,34 m	$J_{12}=2{,}9$; $J_{13}=1{,}7$; $J_{14}=0{,}8$; $J_{23}=2{,}7$; $J_{45}=8{,}6$
II	6,90 dd	7,25 dd	11,0 br s	7,52 br d	7,85	6,90 dd	7,25 dd	11,0 br s	7,52 br d	7,85 d	$J_{12}=3{,}0$; $J_{13}=2{,}0$; $J_{23}=2{,}6$; $J_{45}=9{,}0$
IV	9,81 s (CHO)	8,26 d	12,3 br s	7,58 d	7,85	7,78 d	7,55 dd	12,6 br s	10,35 s (CHO)	7,80 dd	$J_{23}=2{,}4$; $J_{45}=9{,}1$; $J_{67}=9{,}0$; $J_{710}=0{,}5$; $J_{810}=1{,}4$
V	10,0 s (CHO)	8,13 s	NH→ND	7,65 d	7,80	7,80 d	7,65 d	NH→ND	8,13 s	10,0 s (CHO)	$J_{45}=J_{67}=8{,}8$
VI	9,95 s (CHO)	8,27 s	12,2 br s	7,70 d	9,56	9,95 s (CHO)	8,27 s	12,2 br s	7,70 d	9,56 d	$J_{45}=J_{910}=9{,}1$; $J_{23}=0$ (fast NH→ND)
VII	8,11 d	10,58 s (CHO)	12,3 br s	7,53 d	7,74	~7,6		11,3 br s	7,25 dd	7,00 m	$J_{13}=1{,}6$; $J_{89}=J_{910}=2{,}9$; $J_{810}=1{,}7$; $^5J_{710}=0{,}7$; $J_{45}=9{,}0$
VIII	9,86 s (CHO)	8,11 d	12,1 br s	7,43 d	7,79	~7,6		11,3 br s	7,29 dd	7,45 m	$J_{23}=2{,}0$; $J_{45}=8{,}8$; $J_{910}=2{,}8$; $J_{89}=2{,}5$; $^5J_{710}=0{,}9$; $J_{810}=1{,}8$
IX	7,60 d	7,85 d	2,76 s (CH$_3$)	8,47 d	7,81	~7,6		10,8 br s	~7,3		$J_{12}=3{,}1$; $J_{45}=8{,}3$
X	8,13 dd	2,67 s (CH$_3$)	11,0 br s	7,52 dd	7,79	7,64 d	7,53 d	10,7 br s	~7,4		$J_{13}=1{,}8$; $^5J_{14}=0{,}4$; $J_{45}=8{,}9$; $J_{67}=8{,}5$
XI	8,17 dd	2,64 s (CH$_3$)	11,2 br s	7,62 dd	7,75	7,86 d	8,54 dd	2,80 s (CH$_3$)	7,93 d	7,70 dd	$J_{13}=2{,}0$; $J_{45}=J_{67}=9{,}0$; $^5J_{14}=0{,}7$; $^5J_{710}=0{,}5$; $J_{910}=3{,}1$
XII	7,84 d	2,58 s (CH$_3$)	11,7 br s	7,65 d	8,09	6,97 dd	7,35 dd	11,2 br s	7,58 d	8,00 d	$J_{13}=1{,}9$; $^5J_{14}=0{,}5$; $J_{67}\approx J_{78}=2{,}9$; $J_{68}\approx 2$; $J_{45}=J_{910}=8{,}8$
XIII	2,60 s (CH$_3$)	8,29 d	11,9 br s	7,63 d	8,09	6,99 dd	7,30 dd	11,1 br s	7,58 d	9,47 d	$J_{23}\approx 2$; $J_{45}=J_{910}=8{,}8$; $J_{67}\approx J_{78}\approx 2{,}9$; $J_{68}\approx 2$
XIV	3,90 s (CH$_2$); 2,31 s (CH$_3$)	7,24–7,22	11,1 br s	7,36 d	7,51	7,52 d	7,38 d	11,1 br s	7,24–7,22	7,80 m	$J_{45}=J_{67}=8{,}2$; $J_{810}=2{,}4$; $J_{910}=3$
XV	3,72 s (CH$_2$); 2,26 s (CH$_3$)	7,12 d	10,8 br s	7,46 d	8,29	3,72 s (CH$_2$); 2,26 s (CH$_3$)	7,12 d	10,8 br s	7,46 d	8,29 d	$J_{23}\approx J_{78}\approx 2$; $J_{45}=J_{910}=9{,}0$

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*In d_6-acetone.

TABLE 2. Chemical Shifts of the Protons and Spin-Spin Coupling Constants (SSCC) in the PMR Spectra of XVI-XX (in d_6-acetone)

Compound	δ, ppm											J, Hz
	1-H, dd	2-H	3-H, br s	4-H	5-H, d	6-H	7-H	8-H, br s	9-H, d	10-H, d	Ph	
XVI	8,08	—	11,2	7,55 dd	7,82	7,4÷7,6		10,7	7,4— 7,6		7,87÷8,09	$J_{13}=1,8$; $^5J_{14}=0,7$; $J_{45}=8,9$
XVII	8,11	—	11,2	7,55 dd	7,82	7,5÷7,6		10.6	~7,4		7,86 (2'H) d 7,51 (3'H) d	$J_{13}=2,1$; $J_{45}=8,8$; $J_{AB}=8,6$; $^5J_{14}=0,5$
XVIII	8,23	—	11,3	7,51 dd	7,86	~7,6		10,7	7,4—7,5		7,99 (2'H) d 8,36 (3'H) d	$J_{13}=1,9$; $^5J_{14}=0,7$; $J_{45}=8,9$; $J_{AB}=9,1$
XIX	—	8,0m	11,2	7,75 d	8,14	7,10 m	7,41m	10,6	7,71	9,12	7,95 (2'H, 6'H); 7,5÷7,6 (3'H—5'H)	$J_{45}=J_{910}=8,8$
XX	7,88	—	11,1	7,75 dd	8,13	7,07 dd	7,44 dd	10,6	7,71	8,23	7,90 (2'H, 6'H); 7,5÷7,6 (3'H—5'H)	$J_{13}=2,4$; $^5J_{14}\approx0,8$; $J_{45}=J_{910}=8,8$; $J_{67}=3,0$; $J_{68}=2,2$; $J_{78}=2,9$

TABLE 3. Chemical Shifts of the Carbon Nuclei in the ^{13}C NMR Spectra of I, II, and V (in d_6-DMSO) and XVIII (in d_6-acetone)

Compound	δ*, ppm											
	$C_{(1)}$	$C_{(2)}$, d	$C_{(4)}$, d	$C_{(5)}$, d	$C_{(6)}$, d	$C_{(7)}$, d	$C_{(9)}$, d	$C_{(10)}$	$C_{(a)}$, s	$C_{(b)}$, s	$C_{(c)}$, s	$C_{(d)}$, s
I	102,57 d	122,99	109,76	122,76	122,76	109,76	122,99	102,57 d	133,15	123,22	122,04	121,29
II	101,24 d	123,31	112,66	118,17	101,24	123,31	112,66	118,17 d,	132,61	125,16	123,48	123,48
V	118,40 d, 183,70 s (CHO)	133,04	111,21	125,01	125,01	111,21	133,04	118,40 d, 83,70 s (CHO)	135,81	127,26	123,71	122,41
XVIII**	114,82 d	145,70	111,74	124,90	124,30	110,61	131,69	103,55 d	137,56	135,56	125,54	123,33

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*The multiplicity of the signals for the off-resonance spectrum is presented.

**$J_{C_1H_1}$ = 173.5 Hz (with complete suppression of the protons); $C_{(1')}$ 148.53, $C_{(2')}$ 123.33, $C_{(3')}$ 125-54, $C_{(4')}$ 149.26 ppm.

TABLE 4. Characteristics of IV-XX

Compound	mp, °C	R_f*	Found, %			Empirical formula	Calc., %			Yield, %
			C	H	N (Cl)		C	H	N (Cl)	
IV	298...299	0,37	73,2	4,0	10,2	$C_{16}H_{10}N_2O_2$	73,3	3,8	10,7	26
V	327...328	0,66	73,3	4,0	10,8	$C_{16}H_{10}N_2O_2$	73,3	3,8	10,7	58
VI	350 (dec.)	0.48	73,2	3,9	10,0	$C_{16}H_{10}N_2O_2$	73,3	3,8	10,7	98
VII	225...226	0,5	76,5	4,5	11,7	$C_{15}H_{10}N_2O$	76,9	4,3	12,0	13
VIII	211...212	0,24	77,0	4,7	11,6	$C_{15}H_{10}N_2O$	76,9	4,3	12,0	48
IX	146...147	0,54	77,2	4,6	11,6	$C_{16}H_{12}N_2O$	77,4	4,8	11,3	10
X	240...241	0,45	77,6	5,4	11,4	$C_{16}H_{12}N_2O$	77,4	4,8	11,3	14
XI	259...260	0,37	74,1	4,9	9,2	$C_{18}H_{14}N_2O_2$	74,5	4,8	9,7	21
XII	214...215	0,35	77,3	4,8	11,0	$C_{16}H_{12}N_2O$	77,4	4,8	11,3	6
XIII	231...232	0,72	77,1	4,9	11,6	$C_{16}H_{12}N_2O$	77,4	4,8	11,3	6
XIV	260 (dec.)	0,75	77,8	6,4	15,7	$C_{17}H_{17}N_3$	77,6	6,5	16,0	88
XV	260 (dec.)	0,39	74,9	6,9	17,7	$C_{20}H_{24}N_4$	75,0	7,5	17,5	88
XVI	194...195	0.35	77,7	4,7	17,7	$C_{20}H_{14}N_4$	77,4	4,5	18,1	73
XVII	216...217	0,45	69,8	4,2	16,1 (9,8)	$C_{20}H_{13}ClN_4$	69,7	3,8	16,3 (10,3)	76
XVIII	258...259	0,21	67,1	3,2	19,4	$C_{20}H_{13}N_5O_2$	67,6	3,7	19,7	83
XIX	123...124	0,31	77,7	4,4	18,8	$C_{20}H_{14}N_4$	77,4	4,5	18,1	9
XX	191...192	0,35	77,4	4,2	18,2	$C_{20}H_{14}N_4$	77,4	4,5	18,1	42

*Obtained in benzene–acetone (1:1) for IV and V, in ethyl acetate for VI, in benzene–ether (1:1) for VII-XI, in benzene–ether (2:1) for XII, in ether for XIII, in ethanol–ammonia (5:1) for XIV, in ethanol–ammonia (4:1) for XV, in benzene for XVI-XVIII and XX, and in benzene–ether (4:1) for XIX.

can be explained by the steric effect of the pyrrole and naphthalene rings in indoloindoles I and II, respectively.

In the case of symmetrical substitution in the indoloindole molecules the signals of the chemically equivalent protons in the PMR spectra coincide, and one set of signals is displayed, while two sets of signals are observed in the case of unsymmetrical substitution (Tables 1 and 3).

The assignment of the signals in the PMR spectra of the synthesized compounds was made on the basis of the shift of the signals and the change in their multiplicity as compared with unsubstituted heterocycles I and II as a consequence of the effect of the electron-acceptor groups in the α or β positions of the pyrrole rings. The complete assignment of the lines in the PMR spectra proved to be possible owing to the presence of long-range ^5J spin-spin coupling constants (SSCC) of the transoid type [8] and the different degree of deuteration of the protons of the NH groups on exchange with the D_2O contained in the deuterated solvent, as in the case of derivatives of indoloindole III [3]. The rate of the NH→ND exchange varies as a function of the nature and position of the substituents; this leads to a change in the multiplicity of the signals of the protons that couple with NH on the background of the doublets ($J_{NH,CH}$ = 1.4-3 Hz), and broadened signals ($J_{ND,CH} \approx 0$) appear. In the ^{13}C NMR spectra of indoloindoles I and II (Table 2) the shifts of the $C_{(1)}$ nuclei virtually do not differ from the shift of the $C_{(\beta)}$ nucleus of indole [9]. Four doublet signals of CH groups and four singlets from quaternary carbon atoms are present in the high-resolution ^{13}C NMR spectra of I and II. A signal of carbon atoms of a formyl group at 183.7 ppm is observed in the ^{13}C NMR spectrum of dialdehyde V. The assignment of the remaining signals was made on the basis of a comparison with the spectrum of unsubstituted indoloindole I. As expected, the presence of a formyl group in the 1 position gives rise to a greater weak-field shift of the signal of the $C_{(1)}$ atom as compared with the $C_{(2)}$ atom [$\Delta\delta_{C_{(1)}} \approx$ 16 ppm, $\Delta\delta_{C_{(2)}} \approx$ 10 ppm].

The correctness of this assignment is demonstrated by the appearance of the signal of the $C_{(2)}$ atom in the form of a doublet in the off-resonance spectrum. In the case of the assumption of alternative substitution of the formyl group in the 2 position it is impossible to explain the observed shifts of the signals of the $C_{(2)}$ and $C_{(1)}$ nuclei.

A shift of the signal of the $C_{(1)}$ nucleus to weak field as compared with the corresponding signal of unsubstituted indoloindole I [$\Delta\delta_{C_{(1)}}$ = 12.25 ppm] is observed in the ^{13}C NMR spectrum of azo derivative XVIII (Table 3). In the case of substitution in the 1 position one would observe, as in the case of indole, a large $J_{C_\alpha H_\alpha}$ SSCC (183 Hz) [9]

TABLE 5. Data from the IR and UV Spectra of IV-XX

Compound	IR spectrum, cm^{-1}		UV spectrum, λ_{max} (log ε)
	N—H	C=O [N=N]	
IV	3220, 3130	1660, 1620 sh	212 (4,66), 255 (4,54), 267 (4,53), 275 sh (4,52), 338 (3,91), 354 (3,88)
V	3200, 3130	1640, 1620 sh	200 (4,27), 222 sh (4,26), 232 (4,28), 282 (4,39), 357 (4,07)
VI	3220	1635...1610	207 (4,62), 212 sh (4,42), 290 (4,55), 321,5 sh (3,98), 329 (3,96), 334 sh (3,87), 351 sh (3,86)
VII	3300, 3250	1640	212 (4,58), 257 (4,62), 285 sh (4,37)
VIII	3315, 3260	1655	204 (4,68), 207 sh (4,60), 238 (3,95), 255 (4,04), 261 (4,02), 285 sh (3,74)
IX	3360, 3330	1660	201 (4,37), 229 (4,43), 245 (4,49), 294 sh (4,41), 301 (4,42), 366 (4,12)
X	3420, 3280	1660...1640	201 (4,27), 229 (4,30), 246 (4,40), 292 sh (4,33), 301 (4,35), 365 (4,06)
XI	3370,3300	1670...1650	202 (4,39), 228 (4,33), 245 (4,35), 286 (4,33)
XII	3360...3320	1650	237,5 sh (4,53), 243 (4,56), 247 sh (4,55), 298,5 (4,09), 370 (4,18)
XIII	3430...3410	1630	204 sh (4,61), 211 (4,68), 231 (4,52), 262 sh (4,16), 275 sh (4,23), 296 (4,46), 332 (4,12), 348 (3,95)
XIV	3400	—	200 (4,35), 217 (4,30), 232 sh (4,26), 255 (4,26), 264 (4,55), 273 (4,67), 303 (3,93), 325 (3,19)
XV	3400	—	210,5 (4,36), 248 (4,46), 310 sh (3,86), 319,5 (4,01), 336 (3,97), 345 (3,72)
XVI	3430	[1400...1370]	202 (4,45), 233 (4,32), 257 (4,37), 270 sh (4,22), 294 (4,05), 306 (4,07), 319 (4,11), 467 (4,36)
XVII	3430	[1390...1370]	202 (4,47), 229 (4,39), 256 (4,44), 270 sh (4,27), 295 (4,09), 305 (4,12), 320 (4,16), 344 (4,07), 480 (4,49)
XVIII	3450...3410	[1370 (N=N); 1530, 1345 (NO_2)]	202 (4,44), 229 (4,33), 253 (4,39), 270 sh (4,18), 294 sh (4,04), 322 sh (3,91), 363 (3,97), 526 (4,45)
XIX	3440...3400	[1300]	241 (4,67), 361 sh (4,13), 337 sh (4,17), 345 sh (4,18), 350 (4,19), 472 (4,61)
XX	3410...3380	[1310]	204 (4,66), 243 (4,57), 253 sh (4,53), 314 sh (4,07)

in the high-resolution spectrum. However, the SSCC here is much smaller ($J_{C_1H_1}$ = 173.5 Hz); this confirms the formation of a 2-substituted compound.

In the mass spectra of the synthesized IV-XX the molecular masses found by mass spectrometry correspond to the calculated values. Splitting out of the substituent (CHO, CH_3CO, CH_2–$N(CH_3)_2$ occurs initially in the fragmentation of the molecular ions; this is followed by its complete loss and ring cleavage with the subsequent detachment of two HCN groups.

EXPERIMENTAL

The course of the reaction and the purity of the compounds were monitored on Silufol-254, and preparative chromatography was carried out on SiO_2 with particle sizes of 100-160 and 100-250 μm. The IR spectra of suspensions of the compounds in mineral oil were recorded with a UR-20 spectrometer. The UV spectra of solutions in ethanol (c = 10^{-5} M) were obtained with a Specord spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded with Varian CFT-20 (80 MHz) and Bruker WP-200SY spectrometers, respectively, with tetramethylsilane as the internal standard. The mass spectra were obtained with MKh-1303 (ionizing-electron energy 50 eV) and Varian MAT 311A (ionizing-electron energy 70 eV) spectrometers, as well as with an R-10-10 B quadrupole chromatographic mass spectrometer* connected to a Sider data-processing system under electron-impact conditions at an ionizing voltage of 70 eV.

Formylation of 3H,8H-Indolo[4,5-e]indole. A 1.84-ml (24 mmole) sample of absolute DMF was cooled to −5°C, 0.55 ml (6 mmole) of freshly distilled $POCl_3$ was added dropwise, and the mixture was stirred at room temperature for 1 h. A solution of 0.41 g (2 mmole)

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*The spectra were recorded in the Republic Mass-Spectrometry Center of Tbilisi State University of I in 3 ml of DMF was added slowly dropwise, and the mixture was stirred for 2 h at 40°C. It was then treated with cold 10% NaOH solution to pH 10, and the precipitate was removed by filtration, washed with water until the wash water was neutral, and dried to give 0.43 g of a mixture of two aldehydes [TLC, benzene—acetone (1:1)], which were separated with a column.

1,9-Diformyl-3H,8H-indolo[4,5-e]indole (IV). This compound was eluted with benzene—ether (1:3). Workup gave 0.11 g of colorless crystals.

1,10-Diformyl-3H,8H-indolo[4,5-e]indole (V). This compound was eluted with ethyl acetate. Workup gave 0.25 g of colorless crystals.

2-Formyl-3H,8H-indolo[4,5-e]indole (VII) and 1-Formyl-3H,8H-indolo[4,5-e]indole (VIII). These compounds were obtained via the method described above from 0.61 ml (8 mmole) of DMF, 0.18 ml (2 mmole) of $POCl_3$, and 0.41 g (2 mmole) of I in 8 ml of DMF (indoloindole I was added to the Vilsmeier reagent all at once). Workup gave 0.4 g of colorless crystals. The mixture was separated into individual substances with a column [elution with benzene—ether (3:1)]. The yield of VII was 0.05 g. The yield of VIII was 0.19 g.

1,6-Diformyl-3H,8H-indolo[5,4-e]indole (VI). This compound was synthesized from 0.2 g (1 mmole) of II and the Vilsmeier reagent [obtained from 0.56 ml (7.3 mmole) of absolute DMF and 0.16 ml (1.7 mmole) of $POCl_3$] by a method similar to that used to prepare IV and V. Workup gave 0.25 g (98%) of colorless crystals.

Acetylation of 3H,8H-Indolo[4,5-e]- and -[5,4-e]indole. A) A 7.2-ml sample of distilled acetic anhydride and 0.7 ml of glacial acetic acid were added to 0.41 g (2 mmole) of I, and the mixture was refluxed for 20 h. It was then poured into water, and the precipitate was removed by filtration, washed with water until the wash water was neutral, and dried to give 0.42 g of a mixture of several compounds [TLC, benzene—acetone (3:1)], the separation of which was accomplished with a column.

3-Acetyl-3H,8H-indolo[4,5-e]indole (IX). This compound was eluted with benzene. Workup gave 40 mg of colorless crystals.

2-Acetyl-3H,8H-indolo[4,5-e]indole (X). This compound was eluted with benzene—ether (10:1). Workup gave 60 mg of colorless crystals.

2,8-Diacetyl-3H,8H-indolo[4,5-e]indole (XI). This compound was eluted with benzene—ether (10:2). Workup gave 90 mg of colorless crystals.

A 0.2-g (1 mmole) sample of II was acetylated with a mixture of 3 ml of distilled acetic anhydride and 3 ml of glacial acetic acid in the course of 12 h at 115-120°C. The yield was 0.21 g. The mixture obtained was separated with a column.

2-Acetyl-3H,8H-indolo[5,4-e]indole (XII). This compound was eluted with benzene. Workup gave 12 mg of colorless crystals.

1-Acetyl-3H,8H-indolo[5,4-e]indole (XIII). This compound was eluted with benzene—ether (5:1). Workup gave 12 mg of colorless crystals.

B) A 1.44-ml (18 mmole) sample of acetyl chloride was added dropwise at 0°C to a solution of 2.4 g (18 mmole) of anhydrous $AlCl_3$ in 30 ml of methylene chloride at 0°C, and the mixture was stirred for 30 min at 0°C. A solution of 0.41 g (2 mmole) of I in 40 ml of methylene chloride was then added, and the mixture was stirred for 3 h. It was then treated with a mixture of 30 ml of water and 2.4 ml of HCl, and the precipitate was removed by filtration, washed with water until the wash water was neutral, and dried to give a 0.38 g mixture of two compounds [TLC, benzene—acetone (3:1)], the separation of which was accomplished with a column. Elution with benzene—ether (1:1) gave 130 mg (34%) of X.

A 0.2-g (1 mmole) sample of II was acetylated with the complex obtained from 1.2 g (9 mmole) of $AlCl_3$ and 0.72 g (9 mmole) of acetyl chloride by heating at 35° for 3 h. Workup gave 15 mg (9%) of XII and 50 mg (29%) of XIII.

1-(Dimethylaminomethyl)-3H,8H-indolo[4,5-e]indole (XIV). A 0.84-g sample of glacial acetic acid and 0.45 g (6 mmole) of 40% aqueous formaldehyde solution were added slowly to a cooled 0.81 g (6 mmole) sample of 33% aqueous solution of dimethylamine, the resulting mixture was added to 0.41 g (2 mmole) of I, 2 ml of glacial acetic acid was added, and the mixture was stirred at room temperature for 15 min. The reaction mass was diluted with water, and the mixture was washed with ether and made alkaline to pH 10 with 10% NaOH.

The precipitate was removed by filtration, washed with water until the wash water was neutral, and dried in vacuo over KOH to give 0.46 g of XIV in the form of colorless crystals.

1,6-Bis(dimethylaminomethyl)-3H,8H-indolo[5,4-e]indole (XV). This compound was obtained from 0.2 g (1 mmole) of II and a mixture of 0.40 g (3 mmole) of a 33% aqueous solution of dimethylamine, 0.42 g of glacial acetic acid, and 0.22 g (3 mmole) of a 40% aqueous solution of formaldehyde at room temperature in the course of 1 h by a method similar to that used to prepare XIV. The substance obtained was washed with methanol to give 0.28 g of colorless crystals of XV.

2-Phenylazo-3H,8H-indolo[4,5-e]indole (XVI). A solution of 6 mmole of benzenediazonium chloride was added at −5°C to a solution of 0.41 g (2 mmole) of I in 15 ml of dioxane and 8 ml of water while maintaining the solution at pH 7 by the addition of sodium acetate, after which the mixture was stirred for 2 h. It was then poured into ice water, and the aqueous mixture was extracted with ether. The ether extract was washed with 10% NaOH solution and dried with Na_2SO_4, and the solvent was evaporated to give 0.45 g (73%) of product, which was chromatographed with a column by elution with benzene to give orange crystals.

2-(p-Chlorophenylazo)-3H,8H-indolo[4,5-e]indole (XVII). This compound was obtained from 0.41 g (2 mmole) of I and 6 mmole of p-chlorobenzenediazonium chloride by a method similar to that used to prepare XVI. The 0.52 g (76%) of product was purified with a column [elution with benzene—hexane (3:1)] to give red crystals.

2-(p-Nitrophenylazo)-3H,8H-indolo[4,5-e]indole (XVIII). This compound was obtained from 0.41 g (2 mmole) of I and 6 mmole of diazotized p-nitroaniline by a method similar to that used to prepare XVI. Workup gave 0.59 g (83%) of product, which was purified with a column (elution with benzene) to give purple crystals.

1-Phenylazo-3H,8H-indolo[5,4-e]- (XIX) and 2-Phenylazo-3H,8H-indolo[5,4-e]indole (XX). The diazo coupling of 0.13 g (0.6 mmole) of II was carried out with 0.24 g of diazotized aniline hydrochloride under the conditions used to obtain XVI. Workup gave 0.13 g of a mixture of two compounds [TLC, benzene—ether (2:1)], which was separated with a column.

Compound XIX was eluted with benzene to give 12 mg (9%) of orange crystals. Compound XX was eluted with benzene—hexane (2:1) to give 55 mg (42%) of orange crystals.

LITERATURE CITED

1. M. G. Cheshmaritashvili, Sh. A. Samsoniya, E. N. Gordeev, L. V. Vasin, V. A. Shamshina, and N. N. Suvorov, Khim.-farm. Zh., No. 2, 158 (1985).
2. Sh. A. Samsoniya, M. V. Trapaidze, S. V. Dolidze, N. A. Ésakiya, N. N. Suvorov, A. M. Kolesnikov, and F. A. Mikhailenko, Khim. Geterotsikl. Soedin., No. 3, 352 (1984).
3. Sh. A. Samsoniya, M. V. Trapaidze, L. N. Kurkovskaya, L. G. Tret'yakova, T. K. Efimova, and N. N. Suvorov, Khim. Geterotsikl. Soedin., No. 9, 1221 (1979).
4. Sh. A. Samsoniya, M. V. Trapaidze, L. N. Kurkovskaya, Dzh. A. Kereselidze, and N. N. Suvorov, Khim. Geterotsikl. Soedin., No. 11, 1501 (1980).
5. J. A. Pople and D. L. Beveridge, Approximate Molecular Orbital Theory, McGraw-Hill, New York (1970).
6. V. G. Maslov, Zh. Struk. Khim., 18, 414 (1977).
7. Yu. A. Ustynyuk (ed.), Quantum-Chemical Methods of Calculation of Molecules [in Russian], Khimiya, Moscow (1985).
8. S. P. Hiremath and R. S. Hosmane, Adv. Heterocycl. Chem., 15, 277 (1973).
9. R. G. Parker and J. D. Roberts, J. Org. Chem., 35, 996 (1970).