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BISINDOLES.

6,* SYNTHESIS AND INVESTIGATION OF SOME PROPERTIES OF 2-FORMYL-, 3-FORMYL-, AND 3,8-DIFORMYL-1H,6H-INDOLO[7,6-g]INDOLES

Sh. A. Samsoniya, M. V. Trapaidze,
L. N. Kurkovskaya, Dzh. A. Kereselidze,
and N. N. Suvorov

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The formylation of 1H,6H-indolo[7,6-g]indole under the conditions of the Vilsmeier reaction at a molar ratio of the indoloindole and the Vilsmeier complex of 1:1 has made it possible to raise the yield of 3-formyl-1H,6H-indolo[7,6-g]indole to 43% and to also isolate 2-formyl-1H,6H-indolo[7,6-g]indole. The 1H,6H-indolo[7,6-g]indole molecule was subjected to quantum-chemical calculation by the CNDO (complete neglect of differential overlap) MO method. The formylindoloindoles were condensed with aniline, thiosemicarbazide, nitromethane, nitroethane, and hydroxylamine. The configurations of the isomeric dioximes of 3,8-diformyl-1H,6H-indole[7,6-g]indole were established by PMR spectroscopy.

In the present research we investigated the chemical properties of our previously obtained [2] 3-formyl (I, obtained in 2% yield) and 3,8-diformyl-1H,6H-indolo[7,6-g]indoles (II) under the conditions of the Vilsmeier reaction. To raise the yield of aldehyde I we carried out the formylation at a molar ratio of 1H,6H-indolo[7,6-g]indole (III) [3, 4] and the Vilsmeier complex of 1:1 at 55-60°C. Aldehyde I was obtained in 43% yield. Under these conditions we were also able to isolate 2-formyl-1H,6H-indolo[7,6-g]indole (IV) (the spectral data are presented in Table 2), the formation of which was previously not observed [2]. The 2 position of indoloindole III is also reactive in the case of acetylation with acetic anhydride in acetic acid [2]. To explain the results of the experimental studies we carried out the quantum-chemical calculation of the indoloindole molecule III by the CNDO (complete neglect of differential overlap) MO method [5] (see the diagram presented below). The formation of 2-substituted compounds along with 3-substituted compounds in the acylation of I can be explained by the presence of sufficiently high π-electron density in the 2 position of indoloindole molecule III. The absence of products of formylation in the naphthalene part of the molecule (in the 5 or 10 position) is probably associated with more pronounced steric hindrance (because of the large volume of the Vilsmeier complex) in the case of formylation

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*See [1] Communication 5.

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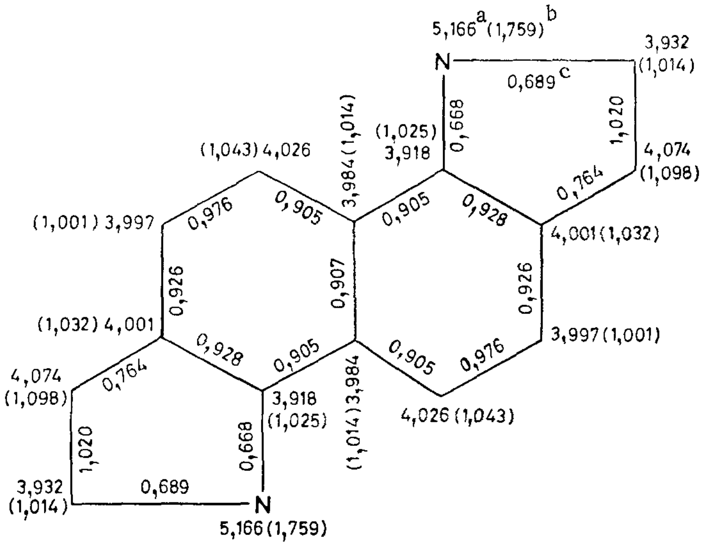

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[a] Total (σ + π) charges. [b] π-Electron densities.
[c] Bond orders.

than in the case of acetylation under the conditions of the Friedel-Crafts reaction. In the latter case we isolated 3,10-diacethyl-1H,6H-indole[7,6-g]indole [2].

It is known [6] that in the formylindole series the 3-formyl isomers are more resistant to electron impact than the 2-formyl isomers. This principle is also observed in the mass spectra of the isomeric 2-formyl- and 3-formyl-1H,6H-indolo[7,6-g]indoles IV and I. The stabilities with respect to electron impact (W_M) are, respectively, 20.7 and 39.3 for IV and I [7]. It is apparent from the scheme of the fragmentation of aldehydes IV and I that the pathway of fragmentation of formyl derivatives IV and I is common to the 2- and 3-formyl isomers and that the differences consist only in the relative intensities of the peaks of the primary fragment ions.

Compound I

$$\begin{tikzcd}
M^+\ 234\ (32{,}8) \arrow[r, "-H", "m^*\ 232"'] \arrow[d, "CO"] & 233^a(8{,}5)^b \arrow[r, "(CO)", "m^*\ 180{,}3"'] & 205\ (7{,}9) \arrow[r, "(HCN)", "m^*\ 154{,}6"'] & 178\ (8{,}3) \arrow[r, "(HCN)", "m^*\ 128{,}1"'] & 151\ (2{,}7) \\
206\ (6{,}8) \arrow[r, "(HCN)"] & 179\ (2{,}3) \arrow[r, "(HCN)"] & 152\ (1{,}2)
\end{tikzcd}$$

Compound IV

$$\begin{tikzcd}
M^+\ 234\ (17{,}2) \arrow[r, "-H", "m^*\ 232"'] \arrow[d, "CO"] & 233^a\ (2{,}2)^b \arrow[r, "(CO)", "m^*\ 180{,}3"'] & 205\ (4{,}9) \arrow[r, "(HCN)", "m^*\ 154{,}6"'] & 178\ (5{,}0) \arrow[r, "(HCN)", "m^*\ 128{,}1"'] & 151\ (2{,}1) \\
206\ (5{,}5) \arrow[r, "(HCN)"] & 179\ (1{,}8) \arrow[r, "(HCN)"] & 152\ (1{,}0)
\end{tikzcd}$$

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[a] Here and subsequently, the m/e values are presented.
[b] Here and subsequently, the intensities relative to the total ion current are presented.

Aldehydes I and II readily undergo condensation with aniline and thiosemicarbazide to give the corresponding Schiff bases, viz., 3-formyl-1H,6H-indolo[7,6-g]indole anil (V), 3,8-diformyl-1H,6H-indolo[7,6-g]-indole dianil (VI), 3-formyl-1H,6H-indolo[7,6-g]indole thiosemicarbazone (VII), and 3,8-diformyl-1H,6H-indolo[7,6-g]indole thiosemicarbazone (VIII).

TABLE 1. Chemical Shifts (δ, ppm) and Spin–Spin Coupling Constants (J, Hz) of Dioximes XVIa and XVIb in d_6-DMSO at 60°C

Compound	1-H	2-H	4-H*	5-H*	—CH=N—	O—H	J, Hz
XVIa	11,9 br s	7,56 d	8,16 d	8,04 d	8,32 s	10,20 s	$J_{1,2}=26$, $J_{4,5}=88$
Mixture XVIa+XVIb	11,8 br s syn	7,56 d syn	8,16 d syn	8,03 d syn	8.34 s syn	10,15 s syn	$J_{1,2}=26$, $J_{4,5}=89$
	12,0 br s anti	8,21 d anti	8,13 d anti	8,06 d anti	7,81 s anti	10,76, br s anti	$J_{1,2}=26$, $J_{4,5}=89$

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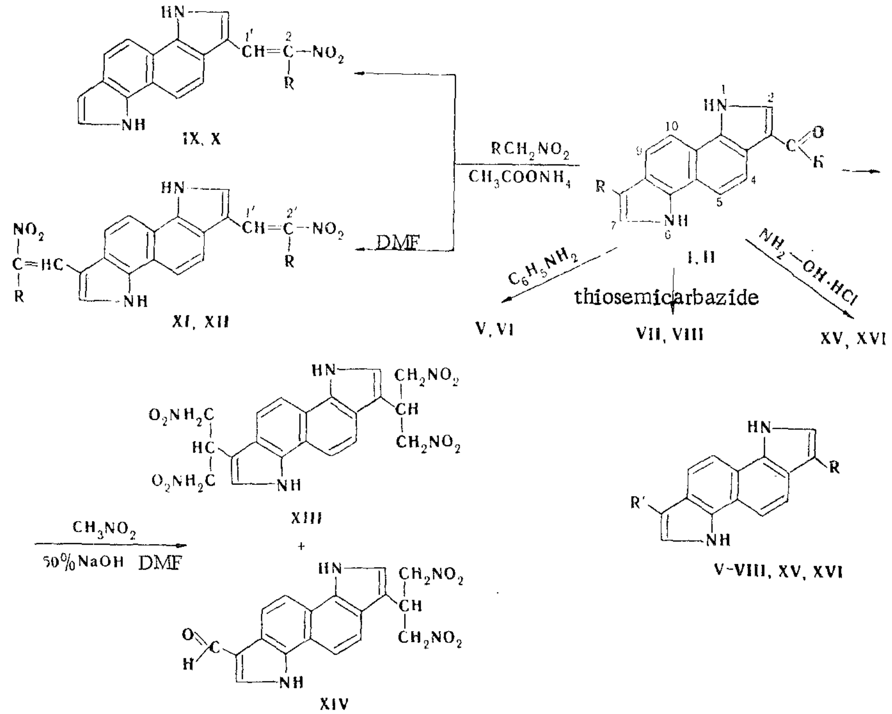
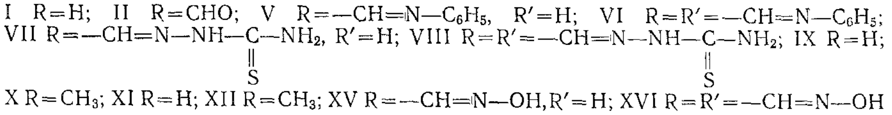
*Directly opposite assignments are possible.

As in the case of 3-formylindoles [8,9], the condensation of aldehyde I with nitromethane and nitroethane proceeds smoothly to give 3-(2-nitrovinyl)-1H,6H-indole[7,6-g]indole (XI) and 3-(2-methyl-2-nitrovinyl)-1H,6H-indolo[7,6-g]indole (X). In the preparation of the dinitrovinyl derivatives 3,8-bis(2-nitrovinyl)-1H,6H-indole[7,6-g]indole (XI) and 3,8-bis(2-methyl-2-nitrovinyl)-1H,6H-indolo[7,6-g]indole (XII) the best results are obtained when dimethylformamide (DMF), a stoichiometric amount of nitroalkane, and ammonium acetate as the catalyst are used, whereas in the condensation of II with nitroethane the best results are obtained when a system containing pyridine and a catalytic amount of piperidine is also used. Absorption maxima are observed in the visible region in the electronic spectra of IX-XII (see Table 2).

The protons of the ethylene group in the PMR spectra of IX and XI form an AB system with spin–spin coupling constants 13.5 and 13.4 Hz, and this confirms the trans configuration of these compounds.





I R=H; II R=CHO; V R=—CH=N—C_6H_5, R'=H; VI R=R'=—CH=N—C_6H_5; VII R=—CH=N—NH—$\underset{\underset{S}{\|}}{C}$—$NH_2$, R'=H; VIII R=R'=—CH=N—NH—$\underset{\underset{S}{\|}}{C}$—$NH_2$; IX R=H; X R=$CH_3$; XI R=H; XII R=$CH_3$; XV R=—CH=N—OH, R'=H; XVI R=R'=—CH=N—OH

TABLE 2. Spectral Characteristics of IV-VI and IX-XIV

Compound	IR spectrum, cm^{-1}	UV spectrum, λ_{max}, nm (log ε)	PMR spectrum, δ, ppm (solvent, temp., °C)	J, Hz
IV	3450, 3330 (NH); 1650 sh. 1630 (C=O)	206 (3,19), 245 sh (3,58), 254 (3,66), 275 sh (3,37), 287 (3,52), 366 (3,42)	11,5 br s (1H), 7,47 d (3H), 8,32 dd (4H), 7,80 d (5H), 11,2 br s (6H), 7,44 dd (7H), 6,67 dd (8H), 8,08 dd (9H), 7,78 d (10H), 9,84 s (CHO)(d_6-acetone, 20)	$J_{13}=2,2$; $J_{14}=0,8$; $J_{45}=8,6$; $J_{67}=2,5$; $J_{68}=2,0$; $J_{69}=0,8$; $J_{78}=2,9$; $J_{910}=8,9$
V	3380, 3390 (NH); 1590, 1620 (C=N)	205 (4,51), 266 (4,92), 294 (4,54), 324 (4,52)	11,5 br s (1H), 7,90 d (2H), 8,65 d (4H), 8,11 dd (5H), 11,1 br s (6H), 7,19—7,39 (7H), 6,64 dd (8H), 7,99 d (9H), 7,74 dd (10H), 7,19—7,39 (Ph), 8,78 s (—CH=N—) (d_6-acetone, 20)	$J_{12}=2,1$; $J_{45}=8,5$; $J_{510}=0,8$; $J_{68}=1,9$; $J_{78}=2,9$; $J_{910}=9,0$
VI	3370—3380 (NH); 1590, 1620 (C=N)	204,5 (3,65), 266,6 (3,72), 330 (3,67)	12,4 br s (1H), 7,98 d (2H), 8,56 d (4H)*, 8,19 d (5H)*, 8,77 (—CH=N—), 7,18—7,41 (Ph) (d_6-DMSO, 60)	$J_{12}\doteq 1,6$; $J_{45}=8,6$
IX	3415, 3380 (NH); 1620 (C=C); 1515, 1320—1350 (NO_2)	206 (4,04), 267 (4,58), 283 sh (3,99), 294 (4,02), 350 (3,93), 414 (4,11)	11,9 br s (1H), 8,16 d (2H), 8,09 d (4H), 8,24 dd (5H), 11,2 br s (6H), 7,41 dd (7H), 6,66 dd (8H), 7,80 d (9H), 8,00 dd (10H), 8,03 d (1′H), 8,45 d (2′H) (d_6-acetone, 20)	$J_{12}=2,8$; $J_{45}=8,5$; $J_{510}=0,5$; $J_{67}=2,5$; $J_{68}=2,0$; $J_{78}=3,0$; $J_{910}=8,7$; $J_{1'2'}=13,5$
X	3400, 3370 (NH); 1640 (C=C); 1500, 1300 sh 1320 (NO_2)	207 (4,31), 264 (4,84), 269 (4,86), 296 (4,28), 352 (4,44), 410 (4,60)	11,9 br s (1H), 8,60 d (2H), 8,02 d (4H), 8,17 dd (5H), 11,1 br s (6H), 7,40 dd (7H), 6,65 dd (8H), 7,81 d (9H) 8,00 dd (10H), 7,93 d (1′H), 2,63 d (CH_3) (d_6-acetone, 20)	$J_{21'}=0,6$; $J_{45}=8,8$; $J_{510}=0,5$; $J_{67}=2,5$; $J_{68}=2,0$; $J_{78}=3,1$; $J_{910}=8,7$
XI	3300 (NH); 1600 (C=C); 1500, 1240 (NO_2)	204 (4,24), 261 sh (4,39), 269 (4,67), 292,5 (4,13), 348 (4,09), 415 (4,38)	12,8 br s (1H), 8,24 br s (2H), 8,15 d (4H)*, 8,23 d (5H)*, 8,07 d (1′H), 8,47 d (2′H) (d_6-DMSO, 60)	$J_{45}=8,2$; $J_{1'2'}=13,4$
XII	3290 (NH); 1630 (C=C); 1515, 1265 (NO_2)	204,8 (3,45), 262 sh (3,56), 271,8 (3,64), 295 (3,27), 351 (3,20), 420 (3,43)	12,7 br s (1H), 8,51 br s (2H) 7,96 d (4H)*, 8,25 d (5H)*, 7,91 br s (1′H), 2,54 s (CH_3) (d_6-DMSO, 60)	$J_{45}=8,6$
XIII	3410 (NH); 1550 (NO_2)	209 (4,56), 256 sh (4,78), 266 (4,97), 288 sh (4,45), 296 (4,41), 309 sh (4,26), 337 (4,11), 351 (4,03)	11,3 br s (1H), 7,49 d (2H), 7,89 d (4H)*, 8,06 d (5H)*, 4,83 quint (—CH<), 5,18 d (—CH_2—)(d_6-acetone, 20)	$J_{12}=2,0$; $J_{45}=8$; $J_{CHCH_2}=6$
XIV	3200—3400 (NH); 1650 (C=O); 1555 (NO_2)	205,5 (4,19), 233 sh (4,22), 259 (4,80), 280 (4,51), 334 (3,82), 350 (3,52),	11,4 br s (1H), 7,55 d (2H), 8,00 d (4H)*, 8,07 d (5H)*, 12,1 br s (6H), 8,24 d (7H), 8,42 d (9H)*, 8,20 d (10H)*, 10,19 s (CHO), 4,96 quint (—CH<), 5,22 d (—CH_2—) (d_6-acetone, 20)	$J_{12}=2,0$; $J_{45}=8,5$; $J_{67}=2,5$; $J_{910}=9$; $J_{CHCH_2}=7$

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*Directly opposite assignments of the indicated signals are possible.

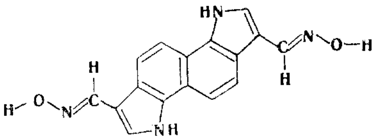
Substances with elementary compositions and spectral data that correspond to products of the addition of nitromethane to the unsaturated nitro compounds formed during the reaction, i.e., 3,8-bis(1,3-dinitroisopropyl)-1H,6H-indolo[7,6-g]indole (XIII) and 3-(1,3-dinitroisopropyl)-8-formyl-1H,6H-indolo[7,6-g]indole (XIV), were isolated in low yields (5-8%) when the condensation of dialdehyde II was carried out with a large excess of nitromethane in DMF in the presence of catalytic amounts of 50% NaOH. Similar addition of nitromethane to 3-(2-nitrovinyl)indole is known [10]. The spectral data for the compounds obtained are presented in Table 2.

The condensation of I with hydroxylamine in ethanol in the presence of sodium bicarbonate leads to the formation of a mixture of 3-formyl-1H,6H-indolo[7,6-g]indole oxime isomers (XV), which we were unable to separate into the individual isomers.

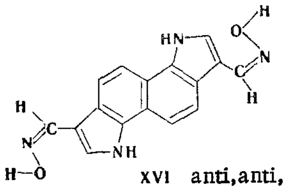
The condensation of dialdehyde II with hydroxylamine occurs only when a strongly oximating reagent, viz., a mixture of hydroxylamine hydrochloride with pyridine, is used [11, 12]. A mixture of geometrical isomers of 3,8-diformyl-1H,6H-indolo[7,6-g]indole dioxime (XVI) is formed as a result of this reaction. Both isomers were isolated when this mixture was subjected to chromatography. The PMR spectrum of XVIa, which has a high R_f value (see Table 1), contained one set of signals corresponding to a symmetrical molecule. It was consequently an individual isomer with identical configurations and conformations of the two aldoxime groups.

The PMR spectrum of XVIb, which has a lower Rf value, contained two sets of signals of approximately equal intensities. Since XVIb is an individual compound according to the data from thin-layer chromatography (TLC), one may assume that partial isomerization of dioxime XVIb occurs in solution in d_6-DMSO, and signals of the protons of both isomers are observed in the PMR spectrum. A change in only the intensities of the signals is observed in the PMR spectrum of a pre-prepared mixture of isomers XVIa and XVIb, and this could be a consequence of a change in the ratio of the isomers in the mixture. On the basis of this spectrum we made an independent assignment of the signals for isomers XVIa and XVIb (see Table 1). It is apparent from Table 1 that the more chromatographically labile XVIa isomer has a syn,syn configuration, while the less labile XVIb has an anti,anti configuration.

The chemical shifts of the signals of the 4-H and 5-H protons in the PMR spectrum of the mixture of isomers XVIa and XVIb coincide, and the position of the heteroring C=C and C=N bonds relative to one another in the isomers consequently does not change, i.e., the aldoxime groups in both isomers have the same conformation. Since a change in the configuration of the aldoxime groups does not affect the position of the 4-H proton, it may be concluded that a cisoid conformation, which is sterically more favorable than a transoid conformation of the aldoxime groups, is realized in both isomers.



XVI a syn,syn, cisoid



XVI anti,anti, cisoid

EXPERIMENTAL

The course of the reaction and the purity of the compounds were monitored on Silufol UV-254. The IR spectra of mineral oil suspensions were recorded with a UR-20 spectrometer. The UV spectra of solutions of the compounds in ethanol were recorded with a Specord spectrophotometer. The PMR spectra were recorded with a Varian CFT-20 spectrometer with tetramethylsilane as the internal standard; freshly prepared solutions of XVIa, b were recorded. An increase in the temperature did not affect the chemical shifts of the signals. The mass spectra were recorded with an MKh-1303 spectrometer with a modified system for introduction of the samples (direct introduction into the ion source) at an ionizing-electron energy of 50 eV. The quantum-chemical calculations were made with the program of V. G. Maslov [13] with a BESM-6 computer in the Institute of Applied Mathematics of Tbilisi State University.

2-Formyl-1H,6H-indole[7,6-g]indole (IV). A 1.48-ml (0.019 mole) sample of DMF was cooled to −5°C, 0.46 ml (4.9 mmole) of $POCl_3$ was added dropwise, and the mixture was stirred at 20°C for 1 h. It was again cooled to −5°C, and a solution of 0.82 g (4 mmole) of 1H,6H-indole[7,6-g]indole in 12 ml of DMF was added relatively rapidly, during which the temperature rose to 10°C. The mixture was stirred at 55-60°C for 1 h, during which a yellow precipitate formed. The reaction was poured into ice water, and the aqueous mixture was made alkaline to pH 10 with 10% NaOH solution. The mixture was then heated to the boiling point and allowed to stand overnight. The precipitate was washed to neutrality and dried to give 1 g of a mixture of formyl-1H,6H-indole [7,6-g]indoles. This mixture was separated into individual compounds with a column (on SiO_2, elution with benzene—ether (2:1)]. Workup gave 20 mg of IV with R_f 0.85 (ether) and 0.4 g (43%) of I with R_f 0.49 (ether). A small amount of 3,8-diformyl-1H,6H-indolo[7,6-g]indole [2] was also eluted from the column (with ethyl acetate) with difficulty. Compound IV was obtained as yellow crystals with mp 250°C (dec.) and R_f 0.63 [ether—benzene (2:1)]. Found: C 76.6; H 5.2; N 12.0%; M^+ 234. $C_{15}H_{10}N_2O$. Calculated: C 76.9; H 4.3; N 12.0%; M 234.

3-Formyl-1H,6H-indolo[7,6-g]indole Anil (V). A 2-ml sample of freshly distilled aniline was added to 70 mg (0.3 mmole) of aldehyde I, and the mixture was heated at 100°C for 1 h. The crystals that precipitated after cooling were washed with ethanol and ether and dried to give 70 mg (78%) of colorless crystals with mp 304°C (dec.). Found: C 80.9; H 5.4; N 13.9%; M^+ 309. $C_{21}H_{15}N_3$. Calculated: C 81.6; H 4.9; N 13.6%; M 309.

3,8-Diformyl-1H,6H-indolo[7,6-g]indole Dianil (VI). A 10-ml sample of freshly distilled aniline was added to 0.13 g (0.5 mmole) of II, and the mixture was refluxed for 30 min. It was then diluted with 30 ml of ethanol, and the crystals that precipitated after cooling were washed with ethanol and ether and dried to give 0.15 g (75%) of white crystals of VI with mp 337°C (dec.). Mass spectrum: 412 (100); 335 (14.6), 308 (25.8), 213 (12.9), 204 (33.4), 177 (4.3), 150 (4.3). Found: N 13.4%; M^+ 412. $C_{28}H_{20}N_4$. Calculated: N 13.6%; M 412.

3-Formyl-1H,6H-indolo[7,6-g]indole Thiosemicarbazone (VII). A warm solution of 80 mg (0.3 mmole) of aldehyde I in 12 ml of ethanol was added to a solution of 90 mg (1 mmole) of thiosemicarbazide in a mixture of 3 ml of water and 2 ml of ethanol, and a few drops of an alcohol solution of HCl (pH 4-5) were added. The mixture was then stirred at 55°C for 1 h and filtered while hot. The precipitate was washed with ethanol, water, isopropyl alcohol, and ether and dried to give the product in quantitative yield. The yellowish crystals had mp 230°C (dec.) IR spectrum: 3420, 3410 (indole NH); 3300 (unsymmetrical NH_2); 3280 (hydrazone NH); 3170 (symmetrical NH_2); 1600, 1620 (C=N); 1535, 1285 cm^{-1} (C=S). Found: C 62.3; H 5.1; N 22.7; S 10.5%. $C_{16}H_{13}N_5S$., Calculated: C 62.2; H 4.2; N 22.8; S 10.4%.

3,8-Diformyl-1H,6H-indolo[7,6-g]indole Bis(thiosemicarbazone) (VIII). This compound was similarly obtained by refluxing a mixture of 0.13 g (0.5 mmole) of II in 150 ml of ethanol and 0.18 g (2 mmole) of thiosemicarbazide in 10 ml of ethanol and 10 ml of water for 1 h. Workup gave 0.13 g (65%) of light-yellow crystals with mp 257°C (dec.). IR spectrum: 3495 (unsymmetrical NH_2); 3430 (indole NH); 3365 (hydrazone NH); 3275-3320 (symmetrical NH_2); 1590, 1620 (C=N); 1560, 1290 cm^{-1} (C=S). Found: N 27.6; S 15.1%. $C_{18}H_{16}N_8S_2$. Calculated: N 2.75; S 15.7%.

3-(2-Nitrovinyl)-1H,6H-indolo[7,6-g]indole (IX). A mixture of 70 mg (0.3 mmole) of I, 40 mg (0.6 mmole) of anhydrous ammonium acetate, and 6 ml of nitromethane was refluxed for 2 h, after which it was allowed to stand overnight in a refrigerator. The precipitated crystals were washed successively with a small amount of alcohol and water and dried to give 80 mg (97%) of dark-red crystals with mp 206°C (dec.) and R_f 0.68 (ether). Found: C 68.8; H 4.2; N 14.4%. $C_{16}H_{11}N_3O_2$. Calculated: C 69.3; H 4.0; N 15.2%.

3-(2-Methyl-2-nitrovinyl)-1H,6H-indolo[7,6-g]indole (X). This compound was similarly obtained in quantitative yield. The yellow crystals had mp 196°C (dec.) and R_f 0.79 (ether). Found: C 70.0; H 4.3; N 13.8%. $C_{17}H_{13}N_3O_2$. Calculated: C 70.1; H 4.5; N 14.4%.

3,8-Bis(2-nitrovinyl)-1H,6H-indolo[7,6-g]indole (XI). A 0.19-g (2.5 mmole) sample of anhydrous ammonium acetate and 0.1 ml (1.5 mmole) of nitromethane were added to 0.13 g (0.5 mmole) of dialdehyde II in 3 ml of DMF, and the mixture was heated at 100°C for 30 min. The precipitated crystals were washed with water and dried to give 50 mg of product. Dilution of the filtrate with water yielded another 60 mg of XI for an overall yield of 0.11 g (65%). The dark-red crystals had mp 280°C (dec.) and R_f 0.83 (ethyl acetate). Found: C 62.5; H 3.7; N 16%. $C_{18}H_{12}N_4O_4$. Calculated: C 62.1; H 3.4; N 16.1%.

3,8-Bis(2-methyl-2-nitrovinyl)-1H,6H-indolo[7,6-g]indole (XII). This compound was similarly obtained by heating a reaction mixture consisting of 0.13 g (0.5 mmole) of dialdehyde II, 0.12 g (1.5 mmole) of ammonium acetate, and 0.4 ml of nitroethane for 1.5 h. Workup gave 0.11 g (55%) of dark-red crystals with mp 232°C (dec.) and R_f 0.86 (ethyl acetate). Found: C 63.4; H 4.5; N 14.7%. $C_{20}H_{16}N_4O_4$. Calculated: C 63.6; H 4.3; N 14.9%.

Condensation of 3,8-Diformyl-1H,6H-indolo[7,6-g]indole with Nitromethane in the Presence of 50% NaOH Solution. A solution of 0.26 g (1 mmole) of dialdehyde II in 20 ml of DMF and four drops of 50% NaOH solution (pH 9) were added to 10 ml of nitromethane, and the mixture was heated at 110-113°C for 4.5 h. It was then diluted with water and acidified with dilute hydrochloric acid to pH 1. The black precipitate was washed with water and dried to give 0.41 g (87%) of product. Two substances were visible on the chromatogram of this precipitate [ethyl acetate—benzene (1:1)]. This mixture was separated into individual compounds with a column [silica gel (100-250 μ), elution with benzene—ether (2:1)].

3,8-Bis(1,3-dinitroisopropyl)-1H,6H-indolo[7,6-g]indole (XIII). This compound [40 mg (9%)] was obtained as yellow crystals with mp 205° (dec.) and R_f 0.66 [ethyl acetate—benzene (1:1)]. Found: C 50.7; H 3.9; N 17.8%. $C_{20}H_{18}N_6O_8$. Calculated: C 51.1; H 3.8; N 17.9%.

3-(1,3-Dinitroisopropyl)-8-formyl-1H,6H-indolo[7,6-g]indole (XIV). This compound [15 mg (5%)] was obtained as a brown powder with mp 210°C (dec.) and R_f 0.33 [ethyl acetate—benzene (1:1)]. Found: N 14.6%. $C_{18}H_{14}N_5O_5$. Calculated: N 15.0%.

3-Formyl-1H,6H-indolo[7,6-g]indole Oxime (XV). A mixture of 0.21 g (0.5 mmole) of I and 0.14 g (2 mmole) of hydroxylamine hydrochloride was dissolved by heating in 12 ml of ethanol, sodium bicarbonate solution was added to pH 5-6, and the mixture was refluxed for 10 h. The solvent was evaporated, and the residue was diluted with water, removed by filtration, and dried to give 0.12 g of a black product. The latter was purified with a column [on silica gel (100-250 μ), elution with benzene—ether (1:1)] to give 70 mg (58%) a mixture of isomeric oximes with R_f 0.73 and 0.53 (ether) with mp 286°C. IR spectrum: 3350 (NH); 3150-3300 (OH); 1630, 1620 sh; 1615 cm^{-1} (C=N). Found: C 69.7; H 4.6; N 16.2%. $C_{15}H_{11}N_3O$. Calculated: C 72.2; H 4.4; N 16.9%. The data presented are for the mixture of isomers.

3,8-Diformyl-1H,6H-indolo[7,6-g]indole Dioxime (XVI). A mixture of 0.39 g (1.5 mmole) of II, 1.23 g (18 mmole) of hydroxylamine hydrochloride, and 120 ml of pyridine was refluxed for 12 h, after which it was poured into water, and the brown precipitate was separated, washed with water, and dried to give 0.37 g (90%) of a crude product that was identified as a mixture of isomeric dioximes. The isomers were separated with a column [silica gel (100-400 μ)].

syn,syn Isomer (XVIa) of 3,8-Diformyl-1H,6H-indolo[7,6-g]indole Dioxime. This compound [40 mg (9%)], with R_f 0.80 (ethyl acetate), was obtained as white crystals with mp 236°C (dec.). IR spectrum: 3380 (NH), 3200-3400 (OH), and 1625 cm^{-1} (C=N). UV spectrum, λ(log ε): 210 (4.35), 278 (4.78), 319 (4.07), 339 (3.47), 353 nm (4.42). Found: C 65.1; H 4.4; N 18.7%. $C_{16}H_{12}N_4O_2$. Calculated: C 65.8; H 4.1; N 19.2%.

anti,anti Isomer (XVIb) of 3,8-Diformyl-1H,6H-indolo[7,6-g]indole Dioxime. This compound [20 mg (5%)] was eluted with ether—ethyl acetate (1:1). The gray powder had mp 280°C (dec.) and R_f 0.63 (ethyl acetate). IR spectrum: 3380 (NH); 3200, 3300 (OH); 1650 cm^{-1} (C=N). Found: N 20.0%. $C_{16}H_{12}N_4O_2$. Calculated: N 19.2%.

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BISINDOLES.
7.* SYNTHESIS OF DI(5-INDOLYL) SULFONE

I. Sh. Chikvaidze, Sh. A. Samsoniya,
T. A. Kozik, and N. N. Suvorov

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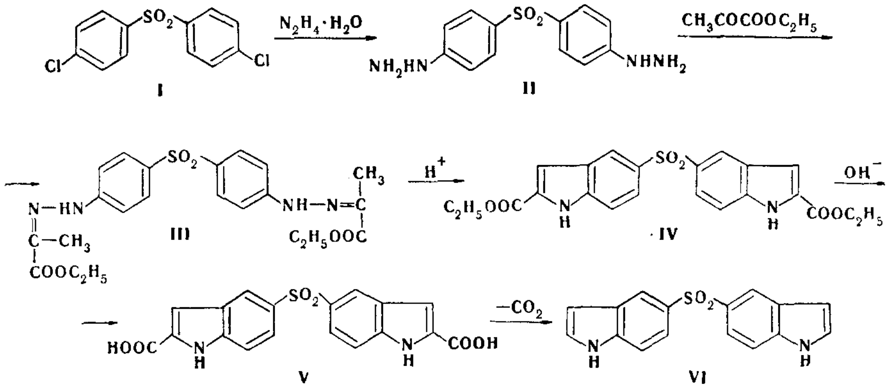
The parent compound of a new heterocyclic system, viz., di(5-indolyl) sulfone, was synthesized by the classical scheme of the Fischer reaction by means of polyphosphoric acid. The starting dihydrazine was obtained from 4,4'-dichlorodiphenyl sulfone.

We have accomplished the synthesis of the parent compound of a new heterocyclic system, viz., di(5-indolyl) sulfone, via the scheme



The presence of the electron-acceptor SO_2 group in I in the para position with respect to the halogens increases the lability of the chlorine atoms to nucleophilic substitution. Thus, in contrast to our earlier studies [2, 3], diazotization of the corresponding diamine with subsequent reduction of the diazonium salt is excluded in the step involving the formation of 4,4'-dihydrazinodiphenyl sulfone (II). Polyphosphoric acid was used as the cyclizing agent in the Fischer reaction. Saponification of ester IV gave acid V, decarboxylation of which leads to the formation of diindolyl compound VI.

The maximum peaks in the mass spectra of IV and VI are the molecular-ion peaks at 440 and 296,† respectively, while the character of the subsequent fragmentation confirms the

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*See [1] for Communication 6.
†Here and subsequently, the m/e values are given for the ion peaks.

Tbilisi State University, Tbilisi 380028. D. I. Mendeleev Moscow Institute of Chemical Technology, Moscow 125047. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1508-1510, November, 1980. Original article submitted April 29, 1980.

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