water. The aqueous mixture was made alkaline with sodium bicarbonate solution and extracted with chloroform. The chloroform extracts were combined, dried with magnesium sulfate, and evaporated at reduced pressure. The residue was crystallized from benzene to give 0.7 g (67%) of IIa. Compounds IIb-d were obtained by a similar method (Table 1).

β-Thiosemicarbazones IIa-d. These compounds were obtained by the method in [1]. It is expedient to obtain them from thoroughly purified starting substances. The properties are presented in Table 2.

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DIINDOLYLS.

8.* SYNTHESIS OF DI(5-INDOLYL) OXIDE

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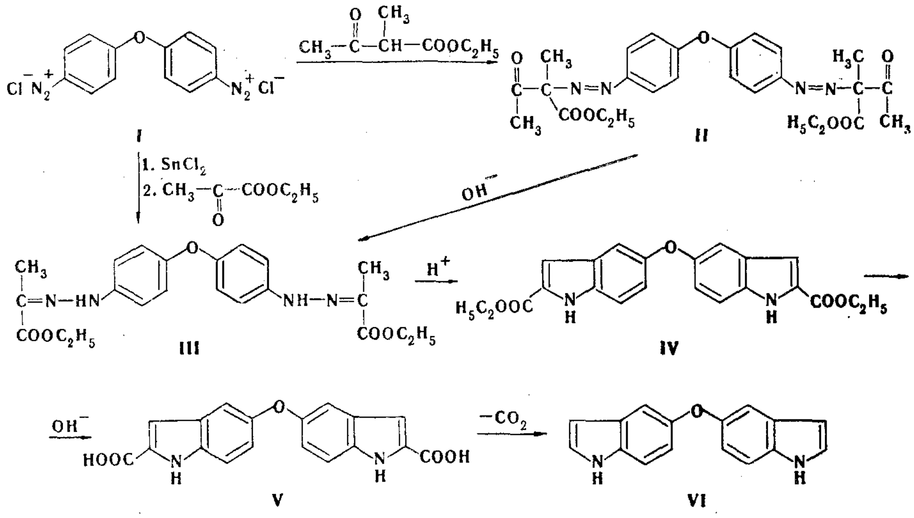
UDC 547.759.1/2.5

Bis(2-carbethoxy-5-indolyl) oxide was obtained by cyclization of ethyl pyruvate 4,4'-diphenyloxydihydrazone. 5-Phenoxy-2-carbethoxyindole was also isolated from the reaction products. Saponification of these esters gave the corresponding acids, the thermal decarboxylation of which yielded di(5-indolyl) oxide and 5-phenoxyindole.

We have previously reported the synthesis of some uncondensed diindolyls [1-3]. Continuing our research in this area we have obtained the parent compound of a new heterocyclic system, viz., di(5-indolyl) oxide, via the scheme



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*See [1] for Communication 7.

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TABLE 1. Parameters of the PMR Spectra in d_6-DMSO at 20°C

Compound	Chemical shifts, δ, ppm									Spin–spin coupling constants, J, Hz
	1H	2H	3H	4H	6H	7H	C_6H_5	CH_2CH_3	CH_3CH_2	
IV	11,8, br s*	—	7,02, d	7,13, dd	6,99, dd	7,42, octet†	—	4,31 q	1,33, q	$J_{37} \simeq J_{47} = 0,5$; $J_{46} = 2,3$; $J_{67} = 8,8$; $J_{CH_3CH_2} = 7,1$
V	11,7, br s*	—	6,96, d	7,11, dd	6,97, dd	7,39, octet†	—	—	—	$J_{37} \simeq J_{47} = 0,5$; $J_{46} = 2,4$; $J_{67} = 8,7$
VI‡	10,9, br s*	7,28, br s	6,30, Octet†	7,03, dd	6,79, dd	7,33, octet†	—	—	—	$J_{13} = 2,3$; $J_{23} = 2,9$; $J_{37} \simeq J_{47} = 0,5$; $J_{46} = 2,3$; $J_{67} = 8,7$
VIII‡	11,8, br s*	—	6,8—7,3	7,14, dd	6,89, dd	7,43, octet†	6,8–7,3	—	—	$J_{37} \simeq J_{47} = 0,5$; $J_{46} = 2,3$; $J_{67} = 8,7$
IX	11,0, br s*	~7,3, m	6,36, dd	7,16, dd	6,79, dd	7,38, octet†	6,8–7,4	—	—	$J_{23} = 3,0$; $J_{37} \simeq J_{47} = 0,6$; $J_{46} = 2,4$; $J_{67} = 8,6$

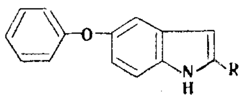
*Rapidly deuterated.

†The existence of three different constants is signified.

‡At 60°C.

We synthesized dihydrazone III both by the Japp–Klingemann method and through the corresponding dihydrazine in ~50% yields (based on the starting diamine) in both cases. The yield of bis(2-carbethoxy-5-indolyl) oxide (IV) obtained from crude dihydrazone III reaches 70% and does not depend on the method used to prepare the starting dihydrazone.

The formation of 5-phenoxy-2-carbethoxyindole (VII) in 1-2% yield is observed in the cyclization of dihydrazone III. The splitting out of one hydrazone group evidently occurs as a consequence of decomposition of the azo form of the hydrazone at elevated temperatures; this does not contradict the literature data [4, 6].



VII–IX

VII $R = COOC_2H_5$; VIII $R = COOH$; IX $R = H$

Saponification of esters IV and VII leads to the corresponding acids V and VIII, the thermal decarboxylation of which yielded di(5-indolyl)oxide (VI) and 5-phenoxyindole (IX).

The PMR spectra are in agreement with the proposed structures of IV-IX (Table 1). The molecular weights of IV, VI, VII, and IX determined by mass spectrometry are in agreement with the calculated values, and the character of the subsequent fragmentation does not contradict the proposed structures [7] (see the experimental section). The fragmentation of the molecular ions of the indicated compounds under the influence of electron impact does not differ fundamentally from the scheme of the fragmentation of indole itself.

It is apparent from Table 2, in which the frequencies of absorption of the NH group for associates of indole and diindolyl VI with several acceptors are presented, that the absorption bands of associated groups of indole and diindolyl VI are virtually the same. Thus indole and diindolyl VI display almost identical donor properties in the formation of complexes by means of hydrogen bonds.

A comparison of the UV spectra of VI, IX, and indole (see Fig. 1) shows that the positions of the long-wave maxima of the indicated three compounds differ only slightly and are observed basically at 280 nm. The short-wave portions of the spectra of VI and IX are identical (227 nm) and differ only slightly from the spectrum of indole (215 nm). The spectrum of VI differs from the spectrum of IX with respect to a slight increase in the intensities of the absorption bands.

EXPERIMENTAL

The course of the reactions and the purity of the compounds were monitored and the R_f values were determined on Silufol UV-254. Silica gel (100-250 μ) was used as the solvent for preparative column chromatography. The IR spectra of the compounds were recorded with a UR-20

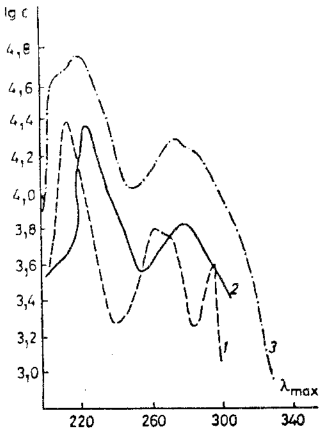


Fig. 1. Electronic spectra: 1) indole; 2) IX; 3) VI.

spectrometer. The UV spectra of solutions in ethanol were recorded with a Specord spectrophotometer. The PMR spectra were recorded with a Varian CFT-20 spectrometer (80 MHz) with tetramethylsilane as the internal standard. The accuracy in the measurement of the chemical shifts was 0.02 ppm, and the accuracy in the measurement of the spin—spin coupling constants (SSCC) was 0.1 Hz. The mass spectra were recorded with an MKh-1303 mass spectrometer with direct introduction of the samples into the ion source at an ionizing-electron energy of 50 eV.

Ethyl Pyruvate 4,4'-Diphenyloxydihydrazone (III). A) A 27.3-g (0.1 mole) sample of diaminodiphenyl oxide dihydrochloride was suspended in a mixture of 150 ml of concentrated HCl and 25 ml of water, and the suspension was cooled to —5°C and diazotized with a solution of 16.8 g (0.22 mole) of $NaNO_2$ in 75 ml of water. After 30 min, the solution was added in a fine stream with stirring to a cooled (to —10°C) solution of 135.5 g (0.6 mole) of $SnCl_2$ in 200 ml of HCl at such a rate that the temperature did not exceed —5°C. The mixture was then stirred for 2 h, and the precipitate was removed by filtration, squeezed on the filter, and recrystallized from 0.5 liter of water.

A warm solution (50°C) of 30.3 g (0.1 mole) of 4,4'-dihydrazinodiphenyl oxide dihydrochloride in 0.5 liter of water was added in a fine stream with stirring to a mixture of 30 g (0.26 mole) of ethyl pyruvate in 30 ml of water and 30 ml of isopropyl alcohol. The solution became turbid, and a yellow precipitate formed. The mixture was stirred for 1 h, after which it was extracted with ether. The extract was washed successively with 2% $NaHCO_3$ solution and water until the wash waters were neutral and dried over Na_2SO_4. The white precipitate that formed after evaporation of the ether was washed with hexane and dried to give 22 g (51%) of a product with mp 134-135°C.

B) A 54.6-g (0.2 mole) sample of diaminodiphenyl oxide dihydrochloride was diazotized by the method presented above, and the resulting solution was added in portions to a cooled (to —5°C) solution of 57.6 g (0.4 mole) of methyl acetoacetate in 120 ml of pyridine and 200 ml of water. A red oil was liberated. The reaction mixture was stirred for 2 h, after which it was poured over 0.5 kg of ice, and the aqueous mixture was extracted with chloroform. The extract was washed with cold water and dried over $MgSO_4$. The chloroform was removed by distillation, and the residual mass was dissolved in a mixture of 0.5 liter of water and 0.5 liter of dioxane. A 100-ml sample of 10% aqueous KOH solution was added, and the mixture was stirred for 1-2 min. It was then extracted with ether, and the extract was dried over $MgSO_4$. The yellow precipitate that formed after partial evaporation of the ether was removed by filtration, washed with hexane, and dried to give 41 g (48%) of a product with mp 134-135°C and R_f 0.25 [benzene—acetone (5:1)]. IR spectrum (in mineral oil): 1680 (C=O) and 3320 cm^{-1} (NH). UV spectrum, λ_{max} (log ε): 222 (4.13), 243 (4.02), shoulder, 310 (4.32) shoulder, and 445 nm (4.50). Found: C 61.5; H 6.8; N 13.7%. $C_{22}H_{26}N_4O_5$. Calculated: C 61.9; H 6.1; N 13.1%.

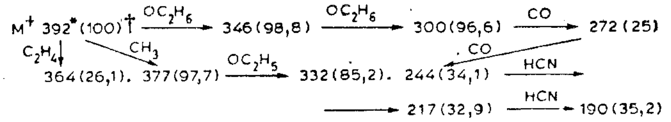
Bis(2-carbethoxy-5-indolyl) Oxide (IV). A 4.26-g (0.01 mole) sample of dihydrazine III was mixed with 50 g of polyphosphoric acid (PPA), during which the mixture warmed up spontaneously. The mixture was stirred at 90°C for 10 min, after which it was cooled and poured into cold water. The resulting precipitate was removed by filtration, washed with water,

TABLE 2. Absorption Band of the NH Group of Indole and Di(5-indolyl) Oxide in the Presence of Some Acceptors

Acceptor	ν, cm^{-1}	
	indole	di(5-indolyl) oxide
Chloroform	3430, 3495	3430, 3490
THF	3310	3305
Ether	3330	3330
Dioxane	3335	3335
Acetonitrile	3400	3390

dried, and purified with a column (elution with chloroform) to give 2.6 g (67%) of a product with mp 180-181°C and R_f 0.47 [benzene—acetone (5:1)]. IR spectrum (in chloroform): 1710 (C=O) and 3470 cm^{-1} (NH); (in mineral oil): 1710 (C=O) and 3330 cm^{-1} (NH). UV spectrum, λ_{max} (log ε): 227 (4.51) and 298 nm (4.51). Found: C 67.3; H 5.2; N 7.1%; M^+ 392. $C_{22}H_{20}N_2O_5$. Calculated: C 67.3; H 5.1; N 7.1%; M 392.

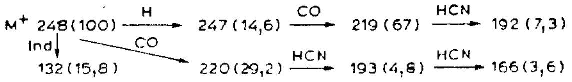
Fragmentation scheme:



Bis(2-carboxy-5-indolyl) Oxide (V). A 3.9-g (0.01 mole) sample of IV was suspended in 1 liter of 10% KOH solution, and the suspension was refluxed with stirring for 3 h. The resulting solution was filtered and acidified to pH 1, and the white precipitate was removed by filtration, washed with water, and dried to give 2.35 g (70%) of a product with mp 265-266°C and R_f 0.58 (in ether). IR spectrum (in mineral oil): 1685 (C=O) and 3360 cm^{-1} (NH). UV spectrum, λ_{max}: 227 and 298 nm. Found: N 8.5%. $C_{18}H_{12}N_2O_5$. Calculated: N 8.3%.

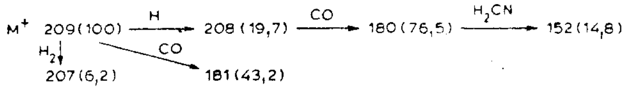
Di(5-indolyl) Oxide (VI). A 1-g (0.025 mole) sample of V was heated at 280°C for 10-15 min until CO_2 evolution ceased, and the mixture was purified with a column (elution with benzene) to give 0.23 g (31%) of a product with mp 130-131°C and R_f 0.31 (chloroform). IR spectrum (in mineral oil): 3350 and 3420 cm^{-1} (NH). UV spectrum, λ_{max} (log ε): 206 (4.66) shoulder, 224 (4.73), and 276 nm (4.29). Found: C 77.0; H 5.1; N 11.8%; M^+ 248. $C_{16}H_{12}N_2O$. Calculated: C 77.4; H 4.8; N 11.3%; M 248.

Fragmentation scheme:



5-Phenoxy-2-carbethoxyindole (VII). This compound was isolated in 1-2% yield in the synthesis of IV by means of a column (elution with chloroform) and had mp 113-114°C and Rf 0.31 (in benzene). IR spectrum (in mineral oil): 1690 (C=O) and 3330 cm^{-1} (NH); (in chloroform): 1710 (C=O) and 3480 cm^{-1} (NH). UV spectrum, λ_{max} (log ε): 227 (4.41) and 295 nm (4.24). Found: C 72.9; H 5.7; N 5.1%; M^+ 281. $C_{17}H_{15}NO_3$. Calculated: C 72.6; H 5.3; N 5.0%; M 281.

Fragmentation scheme:



5-Phenoxy-2-carboxyindole (VIII). A 2.8-g (0.01 mole) sample of VII was suspended in 0.5 liter of 10% KOH solution, and the suspension was refluxed with stirring for 3 h. The resulting solution was filtered, and the filtrate was acidified to pH 1. The precipitate was removed by filtration, washed with water, and dried to give 2 g (80%) of a product with

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[*] Here and subsequently, the m/e values are presented.

[†] Here and subsequently, the relative intensities with respect to the maximum peak are presented.

mp 209-210°C. IR spectrum (in mineral oil): 1680 (C=O) and 3400 cm^{-1} (NH); (in chloroform): 1710 (C=O) and 3460 cm^{-1} (NH). UV spectrum, λ_{max} (log ε): 227 (4.35) and 298 nm (4.31). Found: C 70.6; H 4.6; N 5.5%. $C_{15}H_{11}NO_3$. Calculated: C 71.1; H 4.3; N 5.5%.

5-Phenoxyindole (IX). A 2.5-g (0.01 mole) sample of VIII was heated at 240°C until CO_2 evolution ceased (7-10 min), after which the residue was purified with a column (elution with benzene) to give 0.8 g (40%) of a product with mp 110-111°C and Rf 0.66 (in chloroform). IR spectrum (in mineral oil): 3440 cm^{-1} (NH). UV spectrum, λ_{max} (log ε): 227 (4.37) and 277 nm (3.82). Found: C 80.7; H 5.0; N 7.0%; M^+ 209. $C_{14}H_{11}NO$. Calculated: C 80.4; H 5.2; N 6.7%; M 209.

Fragmentation scheme:

$$\begin{tikzcd}
M^{+}\ 209(100) \arrow[r, "H"] \arrow[d, "H_2"'] \arrow[dr, "CO"] & 208(19{,}7) \arrow[r, "CO"] & 180(76{,}5) \arrow[r, "H_2CN"] & 152(14{,}8) \\
207(6{,}2) & 181(43{,}2) & &
\end{tikzcd}$$

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INVESTIGATION OF THE STATE OF A SYMMETRICAL tert-BUTYL-SUBSTITUTED MACROHETEROCYCLIC COMPOUND IN SOLUTION BY PMR SPECTROSCOPY

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UDC 541.571.35/9:543.42.23

The PMR spectra of the macroheterocyclic compound obtained by the reaction of 5-tert-butyl-1,3-diiminoisoindoline with 1,3-phenylenediamine in refluxing butyl alcohol and purified by chromatography on aluminum oxide were recorded. It is shown that the compound does not contain a unified conjugated macroring system. The dependence of the chemical shift of the protons of the endocyclic imino groups on the nature of the solvent was investigated. It is shown that the formation of compound—solvent intermolecular hydrogen bonds is complicated by steric factors.

Macroheterocyclic compounds (MHC) that have structures similar to that of phthalocyanine, in which one or two isoindole fragments are replaced by residues of aromatic amines, find practical application as stabilizers and dyes for polymeric materials [1, 2]; this is responsible for the interest in the structures of these compounds and the peculiarities of the behavior of their molecules in solutions.

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