or 33% aqueous methylamine solution (experiment No. 6) was heated in an autoclave test tube, after which the mixture was extracted with ethyl acetate, and the solution was dried with magnesium sulfate. The solvent was removed by evaporation, and the residue was crystallized to give amine IIe or IIf. The same amine, as well as an aminoindole that did not contain a carbethoxy group in the 3 position, was additionally obtained from the mother liquor after separation on Al_2O_3.

Method for the Preparation of Aminoindoles IIg, h. A mixture of 2.25 mmole of hydroxyindole Ic, 4 g of potassium metabisulfite, and 15 ml of 15% aqueous dimethylamine solution (experiment No. 7) or 15% aqueous diethylamine solution (experiment No. 8) was heated in an autoclave test tube, after which the mixture was extracted with ethyl acetate, and the extract was dried with magnesium sulfate. The solvent was removed by evaporation, and the residue was separated preparatively by chromatography on Al_2O_3. The isolated aminoindole was then recrystallized. The yield given is based on the converted hydroxyindole.

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PYRROLOCARBAZOLES.

1. SYNTHESIS AND SOME PROPERTIES OF 3H-PYRROLO[2,3-c]CARBAZOLE

T. E. Khoshtariya, M. I. Sikharulidze,
L. G. Tret'yakova, T. K. Efimova,
and N. N. Suvorov

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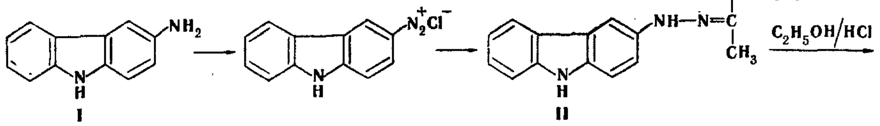
3H-Pyrrolo[2,3-c]carbazole was synthesized from 3-aminocarbazole by means of the Japp–Klingemann reaction. The structure of this heterocycle was proved by a study of the absorption, fluorescence, IR, PMR, and mass spectra. A great analogy between 3H-pyrrolo[2,3-c]carbazole and carbazole as compared with indole in the case of formation of hydrogen bonds was observed; this was indicated by the shift of the absorption band of the NH group in the IR spectra of the investigated compound in the presence of various proton-acceptors.

Despite the large number of studies devoted to the synthesis of indole derivatives, no data on the preparation and properties of 3H-pyrrolo[2,3-c]carbazole are available in the literature.

We accomplished the synthesis of this compound by means of the Japp–Klingemann reaction [1]:



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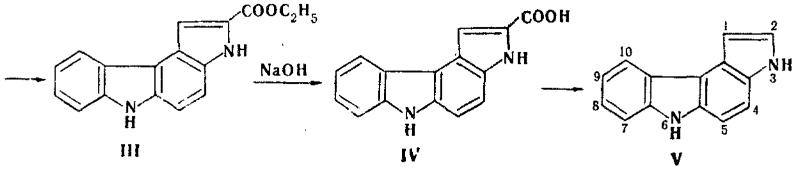
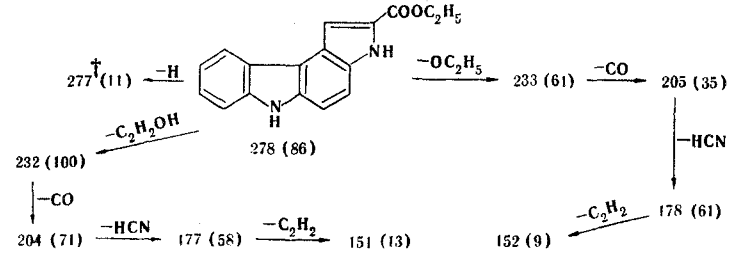


By diazotization of 3-aminocarbazole (I) and subsequent reaction of the resulting diazonium salt with methylacetoacetic ester we obtained hydrazone II in the form of two geometrical isomers, which we were able to separate by preparative column chromatography into syn-IIa and anti-IIb forms.

The UV spectrum of isomer II differs from the spectrum of isomer IIb with respect to a certain increase in intensity and a considerable bathochromic shift of the absorption bands, particularly the long-wave band (a shift of 42 nm). In conformity with the literature data [2], it may be assumed that the indicated changes in the spectrum are due to the existence of intramolecular hydrogen bonds and that isomer IIa is the syn form. The IR spectrum of isomer IIa contains the absorption band of an NH group at 3280 cm^{-1}, while that of isomer IIb contains the band of this group at 3340 cm^{-1}. The absorption band of the carbonyl group of the syn isomer is found at 1680 cm^{-1} in the case of a chloroform solution and at 1660 cm^{-1} in the case of a suspension in mineral oil; in the case of the anti isomer this band shows up at 1710 cm^{-1} (for a suspension in mineral oil). The PMR signal of the proton of the NH group of isomer IIa (12.2 ppm) is shifted to weak field relative to the corresponding signal of the proton of isomer IIb (9.06 ppm) because of the formation of a strong intramolecular hydrogen bond, and this confirms the syn structure of isomer IIa.*

Ethyl 3H-pyrrolo[2,3-c]carbazole-2-carboxylate (III) is formed by cyclization of the resulting mixture of hydrazones with an alcohol solution of hydrogen chloride. The form of the PMR spectrum indicates an angular structure for III: an AB system of 4-H and 5-H protons with a characteristic (for an ortho orientation) spin–spin coupling constant (SSCC) J = 8.8 Hz is observed on the background of the split signals of the 7-H, 8-H, and 9-H protons. Confirmation of the correctness of this assignment was obtained by recording the spectrum of III in a mixture of $(CD_3)_2CO$ and C_6D_6. Under these conditions we observed an increase in the relative chemical shift ($\Delta\delta_{AB}$), which was accompanied (in accordance with our expectations) by an increase in the relative intensities of the outer A'B' peaks and a decrease in the intensities of the inner A and B peaks.

The mass spectrum of III contains an intense molecular-ion peak [M^+] at 278, and the character of the subsequent fragmentation, which was confirmed by the metastable transitions, does not contradict the proposed structure:



The maximum peak in the mass spectrum of 3H-pyrrolo[2,3-c]carbazole (V) is the molecular-ion [M^+] peak at 206. During ionization of the molecule, the C–N bond is cleaved, and the molecule undergoes subsequent fragmentation to give (M–H) (29) and (M–HCN) (9) ions, which were confirmed by metastable transitions. The loss of H, HCN, and C_3H_3N particles from the molecular ion gives a carbazole ion, the subsequent fragmentation of which proceeds in manner described in [3].

The UV spectra of 3H-pyrrolo[2,3-c]carbazole in alcohol and heptane differ only slightly from one another, and this indicates that this compound does not have a significant capacity for the formation of associates with the solvent.

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*The authors thank K. F. Turchin for his consultation in the interpretation of the PMR spectra.

†Here and subsequently, we present the m/e values; the relative intensities with respect to the total ion current are given in parentheses.

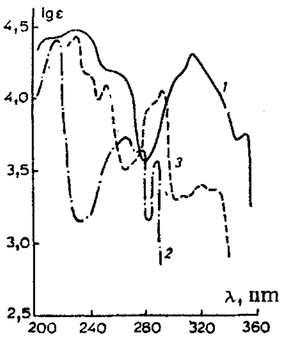

Fig. 1

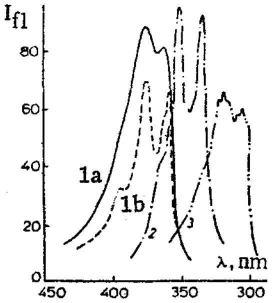

Fig. 2

Fig. 1. UV absorption spectra in alcohol: 1) 3H-pyrrolo[2,3-c]carbazole; 2) indole; 3) carbazole.

Fig. 2. Fluorescence spectra: 1) 3H-pyrrolo[2,3-c]-carbazole [a) at room temperature; b) at −70°C]; 2) carbazole; 3) indole.

TABLE 1. Absorption Band of the Associated NH Group of Pyrrolocarbazole, Indole, and Carbazole in the Presence of Some Proton Acceptors

Acceptor	ν, cm^{-1}		
	3H-Pyrrolo [2,3-c] carbazole	indole	carbazole
Chloroform	3490*	3495*	3480*
Mineral oil	3420†, 3340†	3410†	3340†
Acetonitrile	3400, 3430	3415	3430
Pyridine	3415	3385	3415
Acetone	3310	3240	3320
Tetrahydrofuran	3420	3320	3415
Dioxane	3330	3320	—
	3340	3330	3340

*Free.
†Associated.

The long-wave band in the UV spectra of V (Fig. 1) is more intense and is shifted to the long-wave region as compared with the spectrum of carbazole. The fluorescence spectrum of V recorded in alcohol at room temperature is shifted significantly to the long-wave side as compared with the spectrum of indole (Fig. 2). It is interesting that at − 70°C the spectrum becomes only somewhat more structured, whereas the position of the maxima does not change.

A single absorption band of an NH group at 3490 cm^{-1} is observed in the IR spectrum of a 0.04 mole/liter solution of V in chloroform. An increase in the concentration of the solution to 0.07 mole/liter leads to the appearance of yet another band at 3420 cm^{-1}. An additional band at 3340 cm^{-1} appears in the case of a 0.12 mole/liter solution. Two bands at 3430 and 3400 cm^{-1} are observed in the case of a suspension in mineral oil.

The complex character of the concentration changes in the absorption band of the NH group in the spectrum is probably explained by the presence in solution of associates with different compositions, each of which has its own NH absorption band; these individual bands are superimposed upon one another.

A comparison of the donor properties of 3H-pyrrolo[2,3-c]carbazole with indole and carbazole indicates a considerably greater similarity to carbazole than to indole (Table 1). Thus the positions of the absorption band of the NH group in the associates of carbazole and V with dioxane, acetonitrile, and acetone virtually coincide but differ considerably from the positions of the corresponding bands in the associates of indole, which are shifted to lower frequencies; this indicates the somewhat more weakly expressed donor properties of 3H-pyrrolo[2,3-c]carbazole during the formation of associates through hydrogen bonds as compared with indole.

EXPERIMENTAL

The IR spectra of the compounds were recorded with a UR-10 spectrometer with NaCl and LiF prisms, a spectral slit width of 4 cm^{-1}, and a scanning rate of 60 cm/sec. In our study of the donor properties of the ring we used solutions with concentrations below 0.08 mole/liter, which excluded the possibility of self-association. The concentration of the acceptors ranged from 0.2-0.08 mole/liter. The UV spectra were recorded with a Specord UV spectrophotometer. The mass spectra were recorded with an MKh-1303 spectrometer with direct introduction of the substances into the ion source; the accelerating voltage was 2 kV, the ionizing voltage was 50 eV, the cathode emission current was 1.5 mA, and the recording temperature was 90°C. The PMR spectra of IIa, IIb, IV, and V were recorded with a CFT-20-16K spectrometer, while the spectrum of III was recorded with a JNM-4H-100 spectrometer. The internal standard for IIa, IIb, and IV was tetramethylsilane, while the internal standard for III and V was hexamethyldisiloxane. The course of the reaction and the purity of the compounds were monitored on Silufol UV-254 plates in a benzene—ether system (7:3).

Ethyl Pyruvate 3-Carbazolylhydrazone (II). A solution of 1.21 g (0.017 mole) of sodium nitrite in 5 ml of water was added dropwise with stirring to a cooled (to 0-5°C) mixture of 3 g (0.016 mole) of 3-aminocarbazole (I) in 35 ml of water and 15 ml of concentrated HCl. After all of the $NaNO_2$ solution had been added (the end of the diazotiazation was verified with starch—iodide paper), the solution was filtered, and the pH of the medium was brought up to five with sodium acetate. The mixture was then poured rapidly into a cooled (to −10°C) mixture of 16.5 ml of water, 16.5 ml of isopropyl alcohol, and 1.26 g (0.017 mole) of potassium hydroxide, to which 16.5 g of ice and 2.6 ml (0.018 mole) of methylacetoacetic ester had been added prior to the addition of the diazonium solution. After addition of the diazonium solution, the reaction mixture was stirred at −5°C for 2 h, and the temperature was then allowed to rise to room temperature without stirring. It was then extracted with benzene, and the benzene solution was dried and evaporated. The resulting mixture of stereoisomers was separated with a column filled with 100/250 μm silica gel (elution with benzene) to give the syn-IIa and anti-IIb forms. The yield of the mixture was 1.5 g (52%). Isomers IIa had mp 169-170°C. IR spectrum: 3280 (NH) and 1660 cm^{-1} (C=O). UV spectrum (in alcohol), λ_{max} (log ε): 205 (3.31), 231 (3.45), 247 (3.32), 258 (3.19), 306 (3.18), 357 (3.19), 391 nm (3.19). Found: C 69.4; H 5.6; N 14.1%. $C_{17}H_{17}N_3O_2$. Calculated: C 69.2; H 5.7; N 14.2%.

Isomer IIb had mp 175-176°C. IR spectrum: 3340 (NH) and 1710 cm^{-1} (C=O). UV spectrum (in alcohol), λ_{max} (log ε): 205 (3.36), 225 (3.52), 249 (3.37), 284 (3.25), 335 (3.33), 349 nm (3.3). Found: C 69.6; H 5.7; N 13.9%. $C_{17}H_{17}N_3O_2$. Calculated: C 69.2; H 5.7; N 14.2%.

Ethyl 3H-Pyrrolo[2,3-c]carbazole-2-carboxylate (III). One fifth of a 6.8 g (0.02 mole) sample of the hydrazone was added to 25 ml (0.6 mole) of an alcohol solution of HCl heated to 70°C, and the mixture was stirred for 15 min as the temperature was raised to 75-78°C. After the reaction began, the rest of the hydrazone was added at a rate sufficient to maintain gentle boiling. At the end of the addition, the reaction mixture was stirred at 80°C for another 20 min, after which it was cooled to 0-5°C and maintained at this temperature for 12 h. The resulting precipitate was removed by filtration, squeezed thoroughly on the filter, washed with a small amount of cold alcohol and water, and air dried. It was then purified with a column filled with Al_2O_3 (elution with benzene) to give 2.5 g (43%) of a product with mp 251-252°C. IR spectrum: 3410 and 3350 (NH); 1685 cm^{-1} (C=O). UV spectrum (in alcohol), λ_{max} (log ε): 205 (4.09), 208 (4.12), 225 (4.19), 250 (3.00), 294 (3.88), 235 (3.94), 350 nm (3.92). PMR spectrum (in d_6-acetone): 7.74 (1-H, s); 7.54; 7.58 (4-H, 5-H, AB system, J = 8.8 Hz); 7.25-7.6 (7-H, 8-H, 9-H); 8.27 (10-H, m); 1.44 (CH_3CH_2, t); 4.4 ppm (CH_3CH_2, q); PMR spectrum (in d_6-DMSO): 10.63; 11.43 ppm (6-H, 3-H, br s, br s). Found: C 73.7; H 5.4; N 10.1%. $C_{17}H_{14}N_2O_2$. Calculated: C 73.4; H 5.1; N 10.1%.

3H-Pyrrolo[2,3-c]carbazole-2-carboxylic Acid (IV). A suspension consisting of 100 ml of water, 20 ml of alcohol, 0.7 g (0.017 mole) of NaOH, and 1.5 g (0.005 mole) of III was refluxed with stirring for 3-4 h, after which the mixture was cooled and filtered. The filtrate was acidified with dilute HCl (to pH 7-8), and the resulting precipitate was removed by filtration. The filtrate was acidified. The acid was removed by filtration, washed to neutrality with cold water, and dried in a desiccator over P_2O_5 to give 0.6 g

(40%) of a product with mp 265°C (dec.). IR spectrum: 3430 and 3370 (NH); 1690 cm^{-1} (C=O). UV spectrum (in alcohol), λ_{max} (log ε): 205 (4.32), 223 (4.49), 248 (4.35), 273 (4.09), 282 (4.23), 333 (4.27), 346 nm (4.25). PMR spectrum (in d_6-DMSO): 7.1-7.6 (1-H, 4-H, 5-H, 7-H, 8-H, and 9-H); 11.25; 11.89 (3-H, 6-H, br s, br s); 8.26 ppm (10-H, m). Found: N 11.2%. $C_{15}H_{10}N_2O_2$. Calculated: N 11.2%.

3H-Pyrrolo[2,3-c]carbazole (V). A 2-g sample of acid IV was heated in a stream of nitrogen at 250-270°C for 30-40 min, after which the mixture was cooled and purified with a column filled with Al_2O_3 (elution with ether). The ether was removed by distillation to give 1.2 g (60%) of gray crystals with mp 150-151°C; the product gave a dark-blue coloration with Erlich's reagent. IR spectrum: 3400 cm^{-1} (NH). UV spectrum (in alcohol), λ_{max} (log ε): 234 (4.47), 262 (4.22), 271 (4.10), 285 (3.57), 317 (4.30), 353 nm (3.75). PMR spectrum (in d_6-acetone): 7.00 (1-H, m); 7.39 (2-H, m); 9.96; 10.16 (3-H, 6-H, br s, br s); 7.23 (4-H); 7.34 (5-H, d); 7.11-7.32 (7-H, 8-H, 9-H); 8.19 ppm (10-H, m). Found: C 82.1; H 5.0; N 13.5%. $C_{14}H_{10}N_2$. Calculated: C 81.6; H 4.9; N 13.6%.

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