mm). IR spectrum: 3350 (OH) and 2210 cm^{-1} (C≡C). PMR spectrum, δ: 2.69 (1H, s, OH), 1.89 and 1.60 (2H, d, J = 1.1 Hz, 3-H), 1.45 [6H, s, C(CH$_3$)$_2$], 1.35 (3H, s, CH$_3$), and 1.16 ppm [9H, s, C(CH$_3$)$_3$]. Found: C 74.1; H 10.8; N 7.3%. C$_{12}$H$_{21}$NO. Calculated: C 73.8; H 10.8; N 7.2%.

1-tert-Butylamino-2-methyl-4-phenyl-3-butyn-2-ol Hydrochloride (XId). Hydrogen chloride was passed through a solution of 1.5 g (6.5 mmole) of amino alcohol Xd for 30 min, and the resulting precipitate was washed with acetone to give 1.6 g (91%) of hydrochloride XId with mp 161-163°C.

1-tert-Butyl-2-methyl-2-(phenylethynyl)aziridine (XIIId). A mixture of 1 g (3.7 mmole) of hydrochloride XId, 0.58 g (4.8 mmole) of thionyl chloride, and 20 ml of chloroform was maintained at room temperature for 24 h, after which it was evaporated, and the residue was washed with ether. A 0.62-g (11 mmole) sample of potassium hydroxide and 10 ml of ethanol were added to crude hydrochloride XIId, and the mixture was stirred for 1 h. The precipitate was removed by filtration, and the filtrate was evaporated. The residue was chromatographed with a column packed with aluminum oxide by elution with pentane, and the pentane solution was evaporated to give 0.24 g (30%) of aziridine XIIId. IR spectrum: 3090 (ring C–H) and 2230 cm^{-1} (C≡C). PMR spectrum, δ: 7.29 (5H, m, C$_6$H$_5$), 2.06 and 1.72 (2H, d, J = 1.2 Hz, 3-H), 1.47 (3H, s, CH$_3$), and 1.23 ppm [9H, s, C(CH$_3$)$_3$]. Found: C 84.2; H 9.0; N 6.8%. C$_{15}$H$_{19}$N. Calculated: C 84.5; H 8.9; N 6.6%.

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DIMERIZATION OF BIRADICALOID HETEROCYCLIC COMPOUNDS.

NITRO DERIVATIVES OF PYRROLO[1,2-a]BENZIMIDAZOLE

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V. V. Kuz'menko, A. A. Bumber,
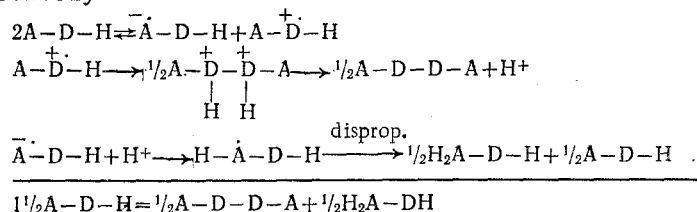N. A. Klyuev, A. N. Suslov,
and A. I. Chernyshev

A new type of easily dimerized heterocyclic compound, viz., nitro derivatives of 2-phenylpyrrolo[1,2-a]benzimidazole, was discovered. The reaction proceeds by heating the latter in acetic acid. A radical mechanism for the dimerization that takes into account partial protonation of the starting compound is discussed on the basis of electrochemical data, the high π-donor capacity of 2-phenyl-4-methylpyrrolo[1,2-a]benzimidazole, the coloration that is characteristic for self-complexes, and EPR spectroscopy.

In 1978 Gorelik and co-workers [1] found that 1-methyl-2-hydroxybenzindolequinone (I) is converted to dimer II in 65% yield when it is heated in acetic acid:
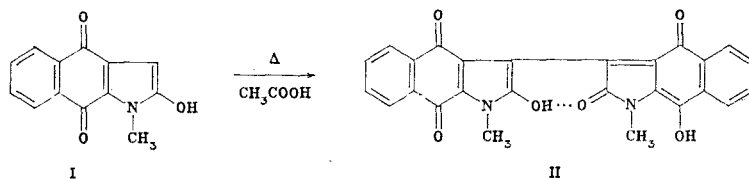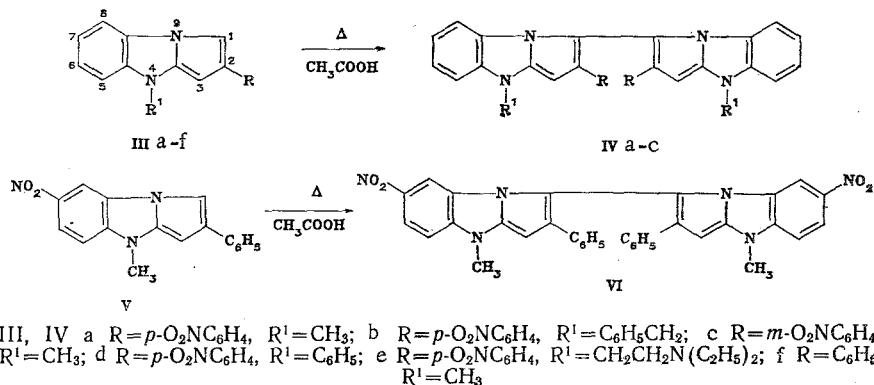
Although a special study was not devoted to the mechanism of this reaction, Shakhno-vich and co-workers [1] pointed out one very important characteristic of I, viz., that it consists of π-donor (2-hydroxypyrrole) and π-acceptor (naphthoquinone) fragments. In principle, electron transfer is possible between these fragments, as a result of which a certain concentration of ion-radical particles, viz., inner ion-radical salts if intramolecular transfer occurs, and cation radicals and anion radicals if intermolecular transfer occurs, is created in the system. Gorelik and co-workers discussed intermolecular transfer and postulated the following dimerization scheme, in which A and D are the acceptor and donor fragments, respectively:

$$2A-D-H \rightleftharpoons \overset{-\cdot}{A}-D-H + A-\overset{+\cdot}{D}-H$$

$$A-\overset{+\cdot}{D}-H \longrightarrow \tfrac{1}{2}A-\overset{+}{\underset{\underset{H}{|}}{D}}-\overset{+}{\underset{\underset{H}{|}}{D}}-A \longrightarrow \tfrac{1}{2}A-D-D-A+H^+$$

$$\underline{\overset{-\cdot}{A}-D-H+H^+ \longrightarrow H-\overset{\cdot}{A}-D-H \xrightarrow{\text{disprop.}} \tfrac{1}{2}H_2A-D-H+\tfrac{1}{2}A-D-H} \quad .$$

$$1\tfrac{1}{2}A-D-H = \tfrac{1}{2}A-D-D-A+\tfrac{1}{2}H_2A-DH$$

In conformity with this scheme, the cation radicals undergo direct dimerization, whereas the anion radicals are protonated to give a neutral radical that undergoes disproportionation to the starting compound and its dihydro derivative. The latter could be isolated from the reaction mixture, and it was thus demonstrated experimentally that the theoretical yield of dimer II should not be greater than 2/3 based on the starting compound.

Compounds of the I type with close-lying higher occupied and lower vacant molecular orbitals are classified as so-called self-complexes [2]. They have also been given the extremely successful and recently popular (in the English literature) name "biradicaloid" compounds [3]. The dimerization of biradicaloid heterocyclic compounds is an extremely interesting area in the chemistry of heterocycles but very little study has been devoted to it. We recently observed a new type of readily dimerized compounds, viz., nitro derivatives of 2-phenylpyrrolo[1,2-a]benzimidazole, which were briefly mentioned in [4]. The present paper is devoted to a more detailed investigation of this reaction in the case of IIIa-f and V.

III, IV a R=p-O$_2$NC$_6$H$_4$, R^1=CH$_3$; b R=p-O$_2$NC$_6$H$_4$, R^1=C$_6$H$_5$CH$_2$; c R=m-O$_2$NC$_6$H$_4$, R^1=CH$_3$; d R=p-O$_2$NC$_6$H$_4$, R^1=C$_6$H$_5$; e R=p-O$_2$NC$_6$H$_4$, R^1=CH$_2$CH$_2$N(C$_2$H$_5$)$_2$; f R=C$_6$H$_5$, R^1=CH$_3$

Let us initially examine the evidence for the biradicaloid nature of nitro derivatives of pyrrolo[1,2-a]benzimidazole. Compounds IIIa-e and V consist of π-donor (pyrrolo[1,2-a]-benzimidazole) and π-acceptor (nitroaryl group) fragments. The degree to which their donor-acceptor properties are manifested can be judged from the electrochemical data that we obtained by means of cyclical voltammetry (Table 1).

It is apparent from Table 1 that IIIa, d and V undergo reversible and, evidently, one-electron reduction to give anion radicals that are stable under cyclical voltammetric conditions. The ease of reduction of IIIa, d, and V is approximately the same and corresponds to the ease of reduction of nitrobenzene and the pyridinium cation [5]. More substantial
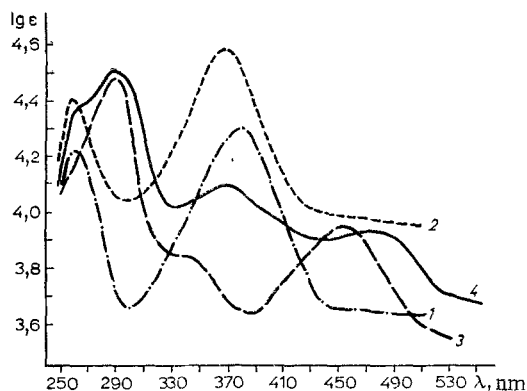
Fig. 1. Electronic absorption spectra for solutions in DMSO: 1) 2-(p-nitrophenyl)-4-methylpyrrolo[1,2-a]benzimidazole (IIIa); 2) 4,4'-dimethyl-2,2'-bis(p-nitrophenyl)-1,1'-bispyrrolo-[1,2-a]benzimidazole (IVa); 3) 4-methyl-2-phenyl-7-nitropyrrolo[1,2-a]benzimidazole (V); 4) 4,4'-dimethyl-2,2'-diphenyl-7,7'-dinitro-1,1'-bispyrrolo[1,2-a]benzimidazole (VI).

TABLE 1. Results of Electrochemical Reduction and Oxidation (in dimethylformamine)

Compound	Reduction				Oxidation			
	change in E* from 0 to −2		change in E* from −2 to 0		change in E from 0 to +1.7		change in E from +1.7 to 0	
	E_{cp},† V	i_{cp}, μA	E_{ap}, V	i_{ap}, μA	E_{ap}, V	i_{ap}, μA	E_{cp}, V	i_{cp}, μA
IIIa	−1,26	4,0	−1,16	4,0	0,82	5,0	—‡	—
IIId	−1,20	4,5	−1,10	4,0	0,86	6,7	0,68	1,6
IIIf	—	—	—	—	0,67	6,6	—	—
V	−1,22	4,0	−1,12	4,0	0,99	5,0	0,85	0,4
IIIa·HClO₄	−1,08	5,0	—	—	0,70	5,0	0,56	2,6
	−1,28	3,6	—	—				
2-Phenylindolizine	—	—	—	—	0,97	7,6	0,90	0,6
Nitrobenzene	−1,20	5,0	−1,10	5,2	—	—	—	—

*The potential of the working electrode in volts.
†The potentials and currents of the cathode peaks (cp) and anode peaks (ap).
‡The dash (—) means that the corresponding peak is absent.

differences are observed in the case of oxidation. The anode oxidation of IIIa and V is completely irreversible, evidently because of fast irreversible dimerization of their cation radicals. However, IIId forms a metastable cation radical, as evidenced by the significant (in height) cathode peak, which corresponds to an oxidation peak. With respect to their ease of oxidation, IIIa, d and V occupy a position between carbazoles ($E_{1/2}^{OX}$ = 1.1 V) and phenothiazines ($E_{1/2}^{OX}$ = 0.6-0.7 V) [6], i.e., they are rather strong π donors. However, it should be noted that the oxidation potentials of IIIa, d and V do not reflect the true π-donor character of the pyrrolobenzimidazole fragment, which is depressed in them because of the effect of the nitro group. We found that 2-phenyl-4-methylpyrrolo[1,2-a]-benzimidazole (IIIf), which does not contain a nitro group, reacts with 1,3,5-trinitrobenzene to give a deeply colored 1:1 molecular complex. Judging from the position of the charge-transfer band in the spectrum of this complex (λ_{max} 585 nm in CHCl₃), the π-donor capacities of pyrrolo[1,2-a]benzimidazoles appreciably surpass the π-donor capacities of even such strong electron donors as phenothiazine (λ_{max} 495) and pyrimidine (λ_{max} 550 nm) [6]. The electrochemical oxidation of IIIf takes place at 0.67 V.

It is natural to expect that when a strong electron donor and a strong electron acceptor are present in IIIa-e and V, they should readily give self-complexes and should be

deeply colored. In fact, in contrast to colorless IIIf, its nitro derivatives IIIa, b, d, e and V are dark red, and IIIc is brick red. The color is due to the typical (for self-complexes) low-intensity and diffuse charge-transfer band, which has the form of end adsorption and extends to 500-600 nm (Fig. 1, curves 1 and 3).

Compounds that form self-complexes often give an EPR signal due to the development of a certain amount of ion-radical particles. N-ω-(3-Indolyl)alkylpyridinium salts, for example, are compounds of this sort [7]. The pyrrolo[1,2-a]benzimidazoles with a nitro group (IIIa-e and V) that we studied also give an extremely intense lone EPR signal with a width of 13.4 Oe in the crystalline state. It is apparent from this that in IIIa-e and V there is only a small energy barrier between the higher occupied and lower vacant molecular orbitals and that they have all of the properties of biradicaloid systems. Unfortunately, not enough data are yet available to draw a conclusion as to whether electron transfer from the donor to the acceptor is an intramolecular or intermolecular process. In the first case (for example, for IIIa) this would lead to the formation of inner ion-radical salts VII, which attest to a low-lying triplet state; in the second case, an ion-radical pair consisting of cation radical VIII and anion radical IX would be obtained. The currently prevailing point of view [2] assumes the possibility of both types of electron transitions; the probability of intermolecular transitions increases as the concentration of the biradicaloid compound increases.

We found that 2-(p-nitrophenyl)-4-methylpyrrolo[1,2-a]benzimidazole (IIIa) and its 4-benzyl (IIIb) and 2-(m-nitrophenyl) (IIIc) analogs undergo dimerization to give IVa-c upon refluxing in glacial acetic acid. Compounds IIId, e, which contain a phenyl or diethylaminoethyl group attached to the N atom, do not undergo dimerization. 2-Phenyl-4-methylpyrrolo[1,2-a]benzimidazole (IIIf) also remains unchanged under these conditions. In addition to this, its 7-nitro derivative V forms dimer VI. The reaction proceeds most readily in the case of IIIa and V. The yields of dimers IVa and VI reach 70% after refluxing for 1.5-2 h. The dimerization of IIIb, c takes place to a considerably lesser extent: the yields of dimers IVb and IVc do not exceed 47% and 25%, respectively, even after heating for 6 h.
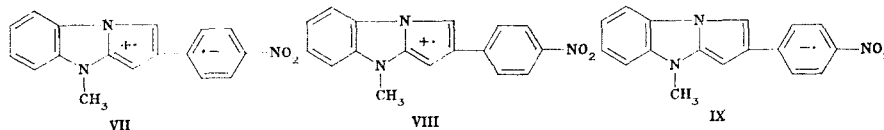
The structures of the dimers obtained were confirmed by the results of elementary analysis and spectroscopic data. The most intense peak in the mass spectra of IVa, c and VI is the molecular-ion peak (M$^+$) with m/z 580. Its fragmentation combines features that are characteristic for bihetaryls [8] and nitro compounds. In particular, the peak with m/z 290 is distinguished by its high intensity. Calculation with the use of the isotope correction showed that 40% of the intensity of this peak is due to a doubly charged ion. The remainder of its intensity is due to cleavage of the interannular bond in the M$^+$ ion. Thus the interannular bond has an appreciable π component even in the case of the apparent noncoplanarity of IV and VI. The mass spectrum of dimer IVb differs substantially from the mass spectra of the other dimers. The molecular-ion peak with m/z 732 has increased intensity, and a peculiarity of its initial fragmentation consists in debenzylation rather than in cleavage of the interannular bond. The stabilities of IV and VI with respect to electron impact are rather high (12-13% of ΣI), and this constitutes evidence for retention of conjugation between the hetaryl rings and the bis system. More detailed characteristics of the mass spectra of IV and VI are presented in Table 2.

The PMR spectral data constitute evidence for the symmetrical structure of the dimers and fusion of III and V in the 1 positions. Thus in the PMR spectrum of IIIa (Fig. 2) the signal of the 3-H proton is located at strongest field at δ 6.0 ppm and has the form of a doublet (J = 1.25 Hz). The splitting is the result of spin-spin coupling with the 1-H proton, the signal of which is also in the form of a doublet at δ 8.0 ppm. The assignment of the signals corresponds to the data in [9] and was confirmed by means of double resonance: In the case of irradiation at the frequency corresponding to the 1-H or 3-H proton the peak corresponding to it vanishes, whereas the peak of the other proton is converted to a singlet. It should also be noted that, according to quantum-mechanical calculations [10, 11], that the most negative π charge in the pyrrolo[1,2-a]benzimidazole molecule is concentrated in the
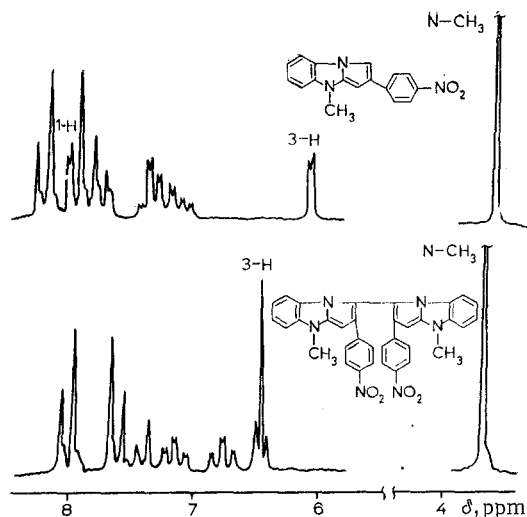
Fig. 2. PMR spectra of solutions in
d$_6$-DMSO.

TABLE 2. Principal Characteristics of the Mass Spectra of Dimers IVa, c and VI

Ion	m/z	Relative intensity (I/I$_{max}$)		
		IVa	IVc	VI
(M+1)	581	38,0	34,6	33,1
M+·	580	100,0	100,0	100,0
(M−NO$_2$)+	534	8,3	—	10,2
A [(M−NO$_2$)−H]+	533	19,6	4,4	23,0
(A−CH$_3$)+	518	3,9	—	—
	291	11,9	—	—
B (M+2) or M+·2	290	25,1	47,0	40,9
(B −NO$_2$)+	244	13,5	—	—
(B −NO$_2$−H)+	243	21,7	51,6	82,0
[(B− NO$_2$)−2H]+	242	4,4	—	—
(C− B−NO$_2$)−H]−CH$_3$	237	11,8	12,7	5,8
(C−H)+	236	13,3	13,8	13,5
(C−.2H)+	235	15,9	21,8	15,5
	230	16,4	11,7	13,5
	229	14,8	11,4	11,9
	228	18,5	24,6	8,2
	222	7,1	14,8	10,4
	132	14,4	2,4	—
	131	11,1	3,9	—

3 position. It is known that a proton bonded to a more pronounced π-surplus center shows up in the PMR spectrum at stronger field [6].

The signal of a 1-H proton vanishes in the PMR spectra of dimers IV, whereas the signal of the 3-H proton becomes a singlet and is shifted slightly (∼0.4 ppm) to weak field (Fig. 2). One's attention is directed to the significantly better resolution of the signals in the PMR spectra of the dimers as compared with the starting compounds. This is evidently due to the noncoplanarity of the dimers, which enables the nitrophenyl ring and the benzene ring of pyrrolo[1,2-a]benzimidazole to have an anisotropic effect on one another.

As expected, the IR spectra of the dimers differ little from one another. An interesting characteristic of dimers IVc and VI is the formation by them of very stable solvates with dimethylformamide (DMF), from which they are crystallized; the dimer:DMF ratio for IVc is 2:1, as compared with 1:2 for VI (determined from the results of elementary analysis and PMR spectroscopic data). Dimers IVa, b and VI in crystalline form are somewhat more deeply colored than the corresponding monomeric compounds. Thus IVa, b are violet red, and VI is dark violet. Only IVc (dark orange) has a somewhat weaker color as compared with IIIc. However, in solutions the long-wave absorption maxima of the dimers are shifted appreciably to the short-wave region as compared with the spectra of the corresponding monomers. This shift is 12 nm for IVa and 25 nm for VI (Fig. 1).
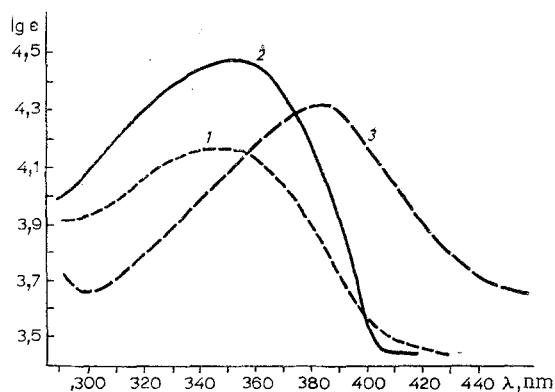
Fig. 3. Electronic absorption spectra
of 4-methyl-2-(p-nitrophenyl)pyrrolo-
[1,2-a]benzimidazole: 1) in CH_3COOH;
2) in CF_3COOH; 3) in DMSO.

From the data presented above it may be concluded that the dimerization of III and V proceeds with the participation of radical particles, most likely cation radicals VIII.* The latter are joined at the 1 positions and then undergo deprotonation in conformity with the scheme proposed by Gorelik and co-workers [1]. However, this conclusion is not unambiguous. The fact is that dimerization occurs in acetic acid and does not take place in trifluoroacetic acid or dioxane. This fact compelled us to make a more detailed study of the behavior of III and V in acetic and trifluoroacetic acids. It is known that pyrrolo-[1,2-a]benzimidazoles are extremely strong bases [9]. The pK_a values of IIIa, IIIb, and IIIc measured in nitromethane are 1.80, 3.80, and 3.48 lower than the pK_a value of diphenylguanidine taken as a standard. When they are extrapolated to aqueous solution, the pK_a values of IIIa-c range from 6.3 to 8.2 (the pK_a of diphenylguanidine in water is 10.12). At such basicities IIIa-c and V should be virtually completely protonated by trifluoroacetic acid. This is confirmed by the UV spectroscopic data and visual observations. Thus the color of IIIa changes from dark red to pale yellow in solution in CF_3COOH; this change is accompanied by a strong hypsochromic shift of the long-wave absorption band as compared with a solution in dimethyl sulfoxide (DMSO) (Fig. 3) and by disappearance of the long-wave absorption band. It has been previously shown by means of the PMR spectra that pyrrolo[1,2-a]-benzimidazoles that do not contain substituents in the 1 and 3 positions are protonated exclusively in the 1 position by trifluoroacetic acid, i.e., their cations have the X structure [9].

The UV spectra of IIIa-c in acetic acid are extremely similar to the spectra of solutions in CF_3COOH; however, the long-wave band at 350 nm is less intense, and a solution of IIIa in acetic acid is red brown. On the basis of this it may be concluded that III and V are also primarily protonated in acetic acid; however, in addition, some of the molecules (probably ~1%) exist in neutral form. Since dimerization takes place in acetic acid but does not occur in trifluoroacetic acid, it may be assumed that a necessary condition for its occurrence is the simultaneous presence in the reaction mixture of protonated and unprotonated molecules of IIIa-c and V. At first glance, this corresponds to an electrophilic mechanism for dimerization in which the π-surplus position of the neutral molecule is attacked by the electron-deficient center of the cation. It is readily noted that unsymmetrical dimers should be obtained in this case, as, for example, in the indole series [12]. It is apparent that joining of the molecules of III and V at the 1 positions to give the same completely aromatized dimers is impossible via this mechanism.

One must assume a radical mechanism for dimerization that takes into account partial protonation of the starting compound. The following scheme, which is in agreement with the results of oxidative polarography and the solvent and substituent effects, seems extremely likely to us.

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*The participation of anion radicals in the dimerization seems unlikely, inasmuch as it is hard to imagine that there could be significant spin density in the 1 positions in the anion radicals of IIIc and V.

The key step in this scheme is electron transfer from a molecule of the starting compound to cation X, as a result of which cation radical XI and neutral radical XII are formed.* The results of oxidative polarography provide evidence for the instability of cation radicals XI. It may therefore be assumed that they are readily dimerized and, after splitting out of two protons, give dimer IV or VI. The most likely fate of neutral radical XII is disproportionation to the starting compound and its dihydro derivative XIV. The latter should be unstable and should readily undergo polymerization. In fact, a certain amount of resin is always isolated from the reaction mixture. It is apparent from the scheme that no more than two thirds of the starting compound should theoretically participate in the formation of dimers, and the other third should accept two hydrogen atoms. In conformity with this, the yields of dimers do not exceed 65-70% even in the most successful experiments. An external oxidizing agent such as air oxygen could, of course, also participate in the reaction. However, we found that dimerization proceeds in absolutely the same way in an inert atmosphere.
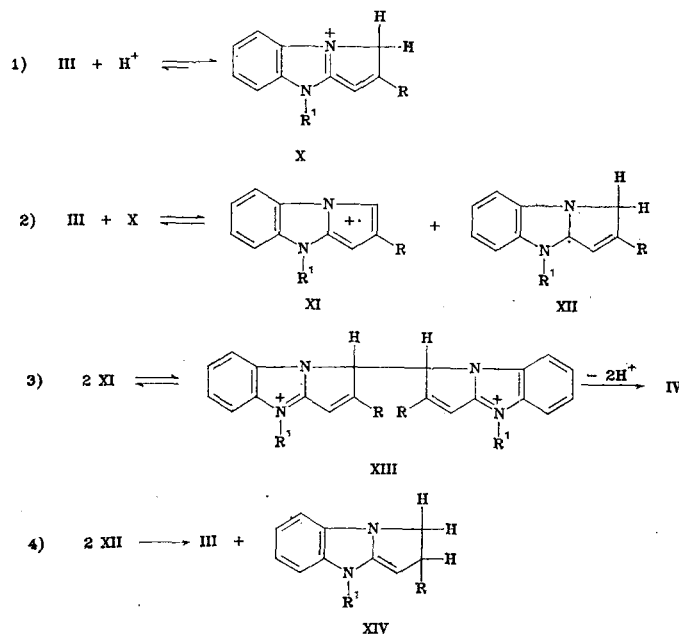
It is understandable why IIId and IIIe do not undergo dimerization. The results of oxidative polarography show that IIId forms a relatively stable cation radical that evidently is not inclined to undergo dimerization. The second compound (IIIe) is protonated primarily at the diethylamino group, and the resulting cation does not undergo subsequent protonation by acetic acid at the $C_{(1)}$ atom.

It is apparent that the proposed mechanism does not take into account the biradicaloid nature of IIIa-c and V in explicit form, although it does specify the indispensable presence of a high π-donor component and an electron acceptor in the molecule. The role of the latter consists in decreasing the basicity of the compound to optimal limits and, possibly, in assisting electron transfer from the neutral molecule to the cation. Moreover, one still cannot completely exclude the purely biradicaloid character of the dimerization presented at the beginning of this paper. An extremely important problem is therefore the search for other media in which dimerization may occur and particularly the search for new types of dimerized biradicaloid compounds. We attempted to realize the dimerization in acetic acid of 2-(p-nitrophenyl)indolizine, which, however, was unsuccessful. This fact can be explained within the framework of both mechanisms. First, indolizine is a considerably weaker π-donor system than pyrrolo[1,2-a]benzimidazole. Thus 2-phenylindolizine is oxidized electrochemically at 0.97 V (Table 1), and the charge-transfer band in the spectrum of the complex of 2-phenylindolizine with 1,3,5-trinitrobenzene is located at 480 nm, as compared with 585 nm for 2-phenyl-4-methylpyrrolo[1,2-a]benzimidazole. In addition, a crystalline sample of 2-(p-nitrophenyl)indolizine does not display an EPR signal. Hence, it follows that this

*In fact, in the case of the cation of IIIa we found that salts X are reduced more readily than the corresponding bases (Table 1).

compound is not a biradicaloid compound and cannot undergo dimerization. In addition, indolizines are less basic by approximately three orders of magnitude than pyrrolo[1,2-a]-benzimidazoles [9]. They therefore remain primarily in the unprotonated form in acetic acid, and this also does not favor the formation of cation-radical particles.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The UV spectra were obtained with a Specord UV-vis spectrophotometer. The EPR spectra were recorded with a Zeiss ER-9 spectrometer. The PMR spectra were obtained with a Brucker HX-90 spectrometer with tetramethylsilane as the internal standard. The mass spectra were recorded with a Varian MAT-311A spectrometer at an accelerating voltage of 3 kV, a cathode emission current of 300 µA, and an ionizing voltage of 70 eV. The cyclical voltammetric curves were recorded with a P 5827 M potentiostat with a triangular pulse source [13] at a frequency of 0.1 Hz on a platinum working electrode with an area of $3 \cdot 10^{-4}$ cm^2 (in DMF); the inert electrolyte was tetrabutylammonium perchlorate, and the reference electrode was an aqueous silver chloride electrode with an asbestos—aluminum hydroxide diaphragm [14]. The UV spectra of the charge transfer complexes (CTC) of IIIf and 2-phenyl-indolizine with 1,3,5-trinitrobenzene (TNB) in chloroform were measured with an SF-4 spectrophotometer. The IIIf, 2-phenylindolizine, and TNB concentrations were, respectively, $1.01 \cdot 10^{-1}$, $4.42 \cdot 10^{-2}$, and $1.63 \cdot 10^{-3}$ mole/liter. A solution of the donor with a concentration equal to the concentration of the donor in the investigated solution was used as the reference solution. The CTC were not isolated in individual form.

1-Benzyl-2-methyl-3-(p-nitrophenacyl)benzimidazolium Bromide. A solution of 2.22 g (0.01 mole) of 1-benzyl-2-methylbenzimidazole and 2.44 g (0.01 mole) of p-nitrophenacyl bromide in 100 ml of acetone was refluxed for 1.5 h, after which it was cooled, and the precipitate was removed by filtration and washed with acetone to give 3.9 g (83%) of colorless crystals with mp 247-249°C (from alcohol). Found: C 59.6; H 4.0; Br 16.9; N 8.7%. $C_{23}H_{20}BrN_3O_3$. Calculated: C 59.3; H 4.3; Br 17.2; N 9.0%.

1-(β-Diethylaminoethyl)-2-methyl-3-(p-nitrophenacyl)benzimidazolium Bromide. This compound was obtained in 72% yield by a procedure similar to that used to obtain the preceding compound. The colorless crystals had mp 197-198°C (from alcohol). Found: C 55.4; H 5.8; Br 17.1; N 11.6%. $C_{22}H_{27}BrN_4O_3$. Calculated: C 55.6; H 5.7; Br 16.8; N 11.8%.

1-Phenyl-2-methyl-3-(p-nitrophenacyl)benzimidazolium Bromide. This compound was similarly obtained in 87% yield. The colorless crystals had mp 226-227°C (from water). Found: C 58.6; H 3.8; Br 18.0; N 9.1%. $C_{22}H_{18}BrN_3O_3$. Calculated: C 58.4; H 4.0; Br 17.7; N 9.3%.

1,2-Dimethyl-5-nitro-3-phenacylbenzimidazolium Bromide. A 1.81-g (0.01 mole) sample of 1,2-dimethyl-5-nitrobenzimidazole was fused with 1.99 g (0.01 mole) of phenacyl bromide at 120°C for 10 min, after which the mixture was cooled and triturated with ether. The solid was removed by filtration and washed with acetone to give 3.55 g (88%) of colorless crystals with mp 264-265°C (from alcohol). Found: C 52.5; H 4.0; Br 20.3; N 10.9%. $C_{17}H_{16}BrN_3O_3$. Calculated: C 52.3; H 4.1; Br 20.5; N 10.8%.

2-(p-Nitrophenyl)-4-benzylpyrrolo[1,2-a]benzimidazole (IIIb). A suspension of 4.66 g (0.01 mole) of 1-benzyl-2-methyl-3-(p-nitrophenacyl)benzimidazolium bromide in 150 ml of a 1% solution of NaHCO$_3$ was refluxed for 1 h, after which it was cooled, and the precipitate was removed by filtration, washed with water, and purified by chromatography with a column packed with Al$_2$O$_3$ (elution with chloroform) to give 2.45 g (67%) of red crystals with mp 185-186°C (from DMF). UV spectrum (in DMSO), λ_{max} (log ε): 263 (4.18) and 380 nm (4.3). PMR spectrum (d$_6$-DMSO): 5.25 (2H, s, CH$_2$C$_6$H$_5$), 6.03 (1H, s, 3-H), 7.28 (8H, m, aromatic protons), and 7.6-8.2 ppm (6H, m, aromatic protons). Found: C 75.2; H 4.8; N 11.2%. $C_{23}H_{17}N_3O_2$. Calculated: C 75.2; H 4.6; N 11.4%.

Compounds IIIe, f and V were similarly obtained.

2-(p-Nitrophenyl)-4-methylpyrrolo[1,2-a]benzimidazole (IIIa) [15]. UV spectrum (in DMSO), λ_{max} (log ε): 260 (4.22) and 380 nm (4.3). PMR spectrum (d$_6$-DMSO): 3.65 (3H, s, N—CH$_3$), 6.07 (1H, d, J = 1.2 Hz, 3-H), 7.09-7.44 (3H, m, aromatic protons), 7.75 (1H, m, aromatic protons), 7.85 (2H, d, J = 9.0 Hz, 2',6'-H), 7.95 (1H, d, J = 1.2 Hz, 1-H), and 8.20 ppm (2H, d, J = 9.0 Hz, 3',5'-H).

2-(m-Nitrophenyl)-4-methylpyrrolo[1,2-a]benzimidazole (IIIc) [15]. UV spectrum (in DMSO), λ_{max} (log ε): 274 (4.4), 306 (4.5), and 340 nm (3.8).

2-(p-Nitrophenyl)-4-phenylpyrrolo[1,2-a]benzimidazole (IIIf). This compound was obtained in 72% yield in the form of dark-red crystals with mp 205-206°C (from DMF). Found: C 74.7; H 4.2; N 11.7%. $C_{22}H_{15}N_3O_2$. Calculated: C 74.8; H 4.2; N 11.9%.

2-(p-Nitrophenyl)-4-β-diethylaminoethylpyrrolo[1,2-a]benzimidazole (IIIe). This compound was obtained in 63% yield in the form of orange crystals with mp 108-109°C (from alcohol). Found: C 70.5; H 6.2; N 15.2%. $C_{22}H_{24}N_4O_2$. Calculated: C 70.2; H 6.4; N 14.9%.

2-Phenyl-4-methyl-7-nitropyrrolo[1,2-a]benzimidazole (V). This compound was obtained in 87% yield in the form of dark-red crystals with mp 225-226°C (aqueous DMF). UV spectrum (in DMSO), λ_{max} (log ε): 260 (4.16), 290 (4.48), 333 (3.86), and 455 nm (3.95). Found: C 70.0; H 4.5; N 14.3%. $C_{17}H_{13}N_3O_2$. Calculated: C 70.1; H 4.5; N 14.4%.

4,4'-Dibenzyl-2,2'-bis(p-nitrophenyl)-1,1'-bispyrrolo[1,2-a]benzimidazole (IV). A solution of 0.74 g (2 mmole) of IIIb in 10 ml of glacial acetic acid was refluxed for 3 h. A precipitate began to separate from the hot solution after 1.5 h. The mixture was cooled, and the precipitate was removed by filtration and washed with acetic acid and water to give 0.34 g (47%) of red crystals with mp 261-262°C (from aqueous dioxane). UV spectrum (in DMSO), λ_{max} (log ε): 270 (4.92), 305 (4.89), and 368 nm (4.18). PMR spectrum (d$_6$-DMSO): 5.48 (2H, s, CH$_2$C$_6$H$_5$), 6.36 (1H, d, J = 7.2 Hz, 5-H), 6.51 (1H, s, 3-H), 6.74 (1H, t, 6-H), 7.1 (1H, t, 7-H), 7.39 (6H, m, 8-H + C$_6$H$_5$), 7.62 (2H, d, J = 9.0 Hz, 2'-H), and 8.0 ppm (2H, d, J = 9.0 Hz, 3'-H).

Dimers IVa, c and VI were similarly obtained.

4,4'-Dimethyl-2,2'-bis(p-nitrophenyl)-1,1'-bispyrrolo[1,2-a]benzimidazole (IVa). This compound was obtained in 70% yield. UV spectrum (in DMSO), λ_{max} (log ε): 260 (4.40) and 368 nm (4.58). PMR spectrum (d$_6$-DMSO): 3.79 (3H, s, N—CH$_3$), 6.45 (1H, d, J = 7.2 Hz, 5-H), 6.46 (1H, s, 3-H), 6.75 (1H, t, 6-H), 7.15 (1H, t, 7-H), 7.40 (1H, d, J = 7.2 Hz, 8-H), 7.62 (2H, d, J = 9.0 Hz, 2'-H), and 7.81 ppm (2H, d, J = 9.0 Hz, 3'-H).

4,4'-Dimethyl-2,2'-bis(m-nitrophenyl)-1,1'-bispyrrolo[1,2-a]benzimidazole (IVc). This compound was obtained in 25% yield in the form of dark-orange crystals with mp > 330°C (from DMF). UV spectrum (in DMSO), λ_{max} (log ε): 260 (4.28) and 368 nm (4.43). PMR spectrum (d$_6$-DMSO): 3.79 (3H, s, N—CH$_3$), 6.40 (1H, s, 3-H), 6.55 (1H, d, J = 7.5 Hz, 5-H), 6.75 (1H, t, 6-H), 7.13 (1H, t, 7-H), 7.39 (1H, d, J = 7.5 Hz, 8-H), 7.45 (1H, t, 5'-H), 7.72-7.92 (2H, m, 4',6'-H), and 8.14 ppm (1H, s, 2'-H).

4,4'-Dimethyl-2,2'-diphenyl-7,7'-dinitro-1,1'-bispyrrolo[1,2-a]benzimidazole (VI). This compound was obtained in 70% yield in the form of dark-violet crystals with mp 318-319°C (from DMF). UV spectrum (in DMSO), λ_{max} (log ε): 260 (4.35), 290 (4.50), 368 (4.09), and 480 nm (3.92).

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NUCLEOPHILIC RECYCLIZATION OF β-CARBOLINES — NEW VARIANT

OF THE SYNTHESIS OF THE CARBAZOLE RING

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The reaction of salts of 1,3-dimethyl-9H-pyrido[3,4-b]indole with hydroxide ions
was examined within the framework of the Pariser—Parr—Pople (PPP) method. It
is shown that the reaction may stop at the step involving the formation of an an-
hydro base (R = H) or lead to recyclization products (R = CH_3, C_2H_5), viz.,
carbazole derivatives. The calculated data are in good agreement with the experi-
mental data.

The isomerizational recyclization of nitrogen-containing heteroaromatic systems (the
Kost—Sagitullin reaction) has been well studied both experimentally [1, 2] and theoretically
(for example, see [3]). Let us note that chief attention in the investigation of this reac-
tion has been directed to the effects of chemical substitution in the pyridine fragment of
the molecule [1, 2], including aza substitution [3, 4], on the effect of annelation [5] and
the relationship between the aromatic character of the recyclized systems and the course of
the process [3, 6], on the structure of the N-alkyl group [7] and the nucleophilic fragment
in the molecule [1, 8], and on the dependence of the direction and rate of rearrangement
on the experimental conditions and the nucleophilic agent used [9, 10]. Steric effects [11]
and the structural aspects [12] of this recyclization have also been studied.

In the present research we studied the effect of a heterocyclic ring condensed with the
pyridine ring on the rearrangement of 1,2,3-trialkylpyridinium salts. Except for a few ex-
amples in which the nitrogen atom of the pyridine fragment was common to both rings, as in
the recyclization of indolizines to indoles [13], pyrimidoindoles to α-carbolines [14], and
pyrazolopyrimidines to pyrazolopyridines [5], this problem has not been dealt with in the
literature. As the subject of our investigation we selected the β-carboline system, in
which a pyridine ring is condensed with an indole ring. In addition to the relative accessi-
bility of this model, the selection of this system was dictated by the widely known bio-
logical activity of derivatives of isomeric carbolines. The β-carboline ring is included
in the composition of many natural and synthetic alkaloids, such as brevicolline, which dis-
plays high ganglion-blocking activity, and yohimbine and reserpine, which have hypotensive
activity [16, 17]. Derivatives of isomeric 1,2,3,4-tetrahydrocarbolines, which display
cytostatic and psychotropic activity [18, 19], have anti-inflammatory, analgesic, and anti-
pyretic effects [20]. The high biological activity of compounds of this class has stimu-
lated research on the synthesis or isolation of these compounds from natural substances and
their pharmacological screening in the last few decades. However, very little study has
been devoted to the reactivities of carboline systems and their transformations under the
influence of various reagents.

One of the possible pathways for the recyclization of the pyridine ring to a benzene
ring is prior formation of anhydro bases by the action of hydroxide ions on the correspond-
ing quaternary salts [1, 2]. This mechanism for rearrangement is confirmed indirectly by
recyclization of an isolated anhydro base (1-methyl-2-acetonylidene-5-nitropyridine) [21]