3-(α-Methylamino-4-nitrobenzyl)indole (If). A mixture of 2.3 g (0.2 mole) of indole and 3.3 g (0.2 mole) of 4-nitrobenzalmethylamine in 3 ml of benzene was heated at 70° for 30 h, after which it was allowed to stand at room temperature until crystallization was complete. The yellow crystalline product was recrystallized from benzene to give 4 g (72%) of If with mp 139-141°.

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INDOLE DERIVATIVES.

CXI.* INTRODUCTION OF A 3-INDOLYL GROUP IN CH ACIDS

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A method for the introduction of a 3-indolyl group in compounds with an active methylene group was developed. The corresponding 3-indolyl diketones were obtained by condensation of 1-acetyl-3-indolinone with dimedone, 4-hydroxycoumarin, 1,2-diphenyl-3,5-pyrazolinedione, and barbituric and thiobarbituric acids and subsequent alkaline hydrolysis of the condensation products. The existence of cyclic six-membered 3-indolyl diketones in the enol form and of cyclic five-membered 3-indoly diketones in the keto form was shown by IR and UV spectroscopy. Depending on the conditions, (1-acetyl-3-indolyl)cyanoacetamide, 1,3-bis(1-acetyl-3-indolyl)-1,3,3-tricyano-2-amino-1-propene, and 1-acetyl-3-indolylmalononitrile are obtained in the condensation of 1-acetyl-3-indolinone with malononitrile. 1-Acetyl-3-indolylmalononitrile exists in equilibrium with the keteneimine form and in protic solvents is converted to 3-cyano-8-acetylpyrrolo[2,3-b]indole by intramolecular cyclization.

No methods have been developed for the introduction of a 3-indolyl group in compounds with an active methylene group. The basis of the method used in the present research was condensation of 1-acetyl-3-indolinone (acetylindoxyl) (I) with a number of CH acids that differ with respect to their acidity constants (pK_a). 1-Acetylindoxyl rather than indoxyl was selected as the carbonyl component because of its high accessibility and stability.

The condensation of 1-acetylindoxyl (I) with cyanoacetic acid was first used for the preparation of 3-indolylacetonitrile [2]. The reaction was carried out under severe con-

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*See [1] for communication CX.

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TABLE 1. 3-Indolyl Diketones VIII-XVII and XIX

Compound	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	N		C	H	N	
VIII	224—225[a]	72,1	6,1	4,7	$C_{18}H_{19}NO_3$	72,1	6,4	4,7	76
IX	274—276[a]	71,5	4,1	4,4	$C_{19}H_{13}NO_4$	71,5	4,1	4,4	64
X	138—140[a]	71,3	5,7	9,2	$C_{25}H_{19}N_3O_3 \cdot C_2H_5OH$	71,2	5,5	9,2	72
XI	210[a,b]	58,6	4,1	14,6	$C_{14}H_{11}N_3O_4$	58,9	3,9	14,7	84
XII	339—340[c]	55,5	3,6	13,8	$C_{14}H_{11}N_3O_3S$[d]	55,8	3,7	13,9	99
XIII	186—188[e]	75,1	6,8	5,0	$C_{16}H_{17}NO_2$	75,3	6,7	5,5	87
XIV	216—217[a]	73,1	4,1	4,8	$C_{17}H_{11}NO_3$	73,6	4,0	5,1	89
XV	215—217[a]	75,2	4,8	11,5	$C_{23}H_{17}N_3O_2$	75,2	4,7	11,4	80
XVI	350[b,f]	58,7	4,0	16,9	$C_{12}H_9N_3O_3$	59,2	3,7	17,3	88
XVII	360[b,f]	52,3	3,9	15,1	$C_{12}H_9N_3O_2S \cdot H_2O$[g]	52,1	4,1	15,2	77
XIX	205—207[a]	64,3	4,9	18,1	$C_{13}H_{11}N_3O_2$	64,7	4,6	17,7	79

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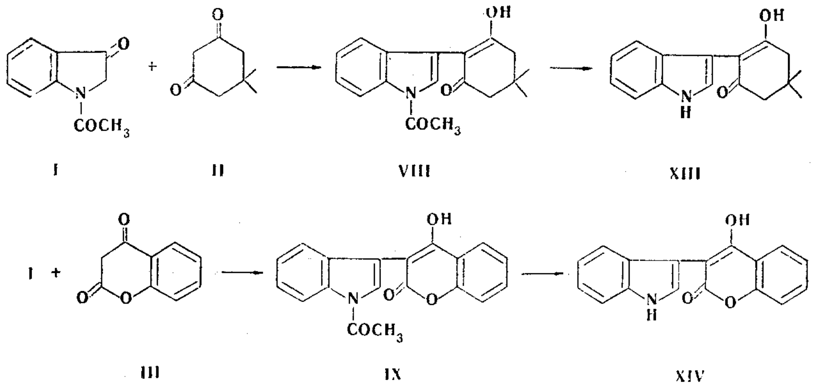
[a] From ethanol. [b] With decomposition. [c] From acetic acid. [d] Found: S 10.4%. Calculated: S 10.6%. [e] From methanol. [f] From aqueous ethanol. [g] Found: S 11.5%. Calculated S 11.6%.

ditions and was accompanied by decarboxylation; it subsequently has no found application as a method for the introduction of a 3-indolyl group.

We used dimedone (II), 4-hydroxycoumarin (III), 1,2-diphenyl-3,5-pyrazolidinedione (IV), barbituric and thiobarbituric acids (V, VI), acetylacetone, malononitrile (VII), and cyanoacetic and malonic esters as substrates for condensation with acetylindoxyl.

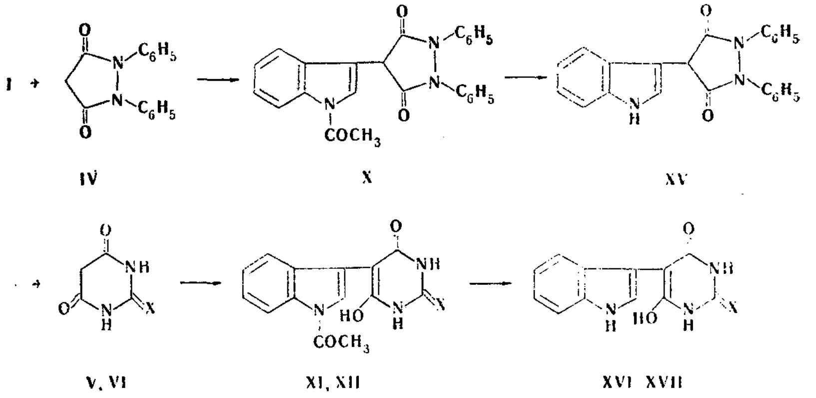
It was established that the ease of condensation depends on the pK_a value of the CH acid. Thus the reaction proceeds readily with "strongly acidic" II-IV (pK_a 4-6) when the components are heated in acetic acid in the presence of triethylamine; under these conditions, 1-acetyl-3-indolyl diketones VIII-XII, rather than indoline compounds — products of the possible Knoevenagel reaction — were obtained in 70-90% yields (Table 1). The acetyl protective group is removed when VIII-XII are dissolved in 5% NaOH or 5% Na_2CO_3, and XIII-XVII are obtained in 80-90% yields (Table 1). An increase in the time during which 3-indolydimedone XIII exists in an alkaline medium leads to a sharp decrease in the yield of this compound. Moreover, one observes the formation of a series of acids, which we did not isolate in pure form; this is probably associated with the ease of cleavage of the cyclohexanedione ring in an alkaline medium. A decrease in the yields as the hydrolysis time is extended is less characteristic for XIV-XVII.

According to the IR spectral data, solid β-diketones VIII-XVII exist, depending on the ring size, either in the keto or enol form. The enol form is characteristic for six-membered diketones VIII, IX, XI-XIV, XVI, and XVII, whereas the diketone form is characteristic for five-membered X and XV. The IR spectra of mineral oil suspensions of VIII, IX, XII, and XIV contain absorption bands of an associated hydroxyl group at 3100-3390 cm^{-1} and absorption bands of conjugated C=C and C=O bands of the enol form (Table 2). In the IR spectra of barbituric and thiobarbituric acids XI, XII, XVI, and XVII the absorption bands of an associated hydroxyl group are observed at 2600-2800 cm^{-1}; this was also characteristic for the spectra of the previously obtained 5-skatylbarbituric acids [3].



I II VIII XIII

III IX XIV



V, XI, XVI X = O. VI, XII, XVII X = S

3-Indolylpyrazolidinedione X was obtained in the form of a complex with an alcohol molecule. In addition to the multiplet of aromatic protons at 7.1-8.0 ppm, the PMR spectrum of this compound in d_6-DMSO contains signals of an ethyl group in the form of a triplet and a quartet at 1.1 and 3.5 ppm and of a hydroxyl group in the form of a singlet at 8.55 ppm.

The IR spectrum of 3-indolylpyrazolidinedione XV contains absorption bands of two carbonyl groups of the diketo form at 1720 and 1760 cm^{-1}.

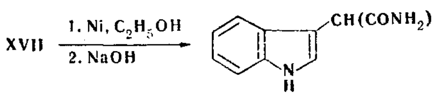
The UV spectrum of 3-indolyldimedone XIII in alcohol (Fig. 1), like the spectrum of indole [4], contains three absorption maxima. The bathochromic shift of 8 nm of the K band is evidently associated with the development of a new conjugated system involving the indole ring and the double bond of the enol form of dimedone [5]. The bathochromic shift is not observed in the spectrum of a solution of this compound in alcoholic NaOH (Fig. 1). This is apparently associated with the practically complete dissociation of XIII both in alcohol and in alcoholic NaOH [5, 6]. The spectrum of XIII in alcoholic HCl is characteristic for the undissociated form of an enol [5, 6].

The UV spectra of 3-indolylbarbituric and 3-indolylthiobarbituric acids XVI and XVII in alcohol are similar to the spectrum of XIII, and the bathochromic shift of the K band of indole in this case is 10 nm. The character of the changes in the spectra on passing to alcoholic NaOH and HCl solutions is analogous to that in the case examined above (Fig. 2).

A characteristic feature of the UV spectrum of XIV is the presence of a weak long-wave maximum [λ_{max} 346 nm (log ε 3.95)], which evidently corresponds to a p—π transition of the unshared pair of electrons of the oxygen atom of the pyran ring; as in the case of dimedone, the shift of the K band of indole is 8 nm. According to the data from the UV spectra in alcohol and alcoholic NaOH solution (Fig. 1), XIV is completely dissociated under these conditions.

The band of benzene absorption at 230-260 nm and the absorption band of indole at 280 nm are overlapped in the UV spectrum of 3-indolylpyrazolidinedione XV. The UV spectra in alcohol and in alcoholic NaOH solution are identical (Fig. 2). The UV spectrum in alcoholic HCl solutions is evidently characteristic for the undissociated form of the diketone.

An attempt to obtain 5-(3-indolyl)-4,6-diketohexahydropyrimidine by desulfuration over Raney nickel of thioacid XVII led to amide XVIII. The UV spectrum of XVIII is similar to the spectrum of acid XVI (Fig. 3).



XVIII

In contrast to II-VI, "weak" CH acids with pK_a 9-14 (malonic and acetoacetic esters and acetylacetone) do not react with 1-acetyl-3-indolinone in acetic acid in the presence of triethylamine. The use of stronger catalysts with basic character such as sodium hydride or lithium ethoxide in tetrahydrofuran (THF) also does not give positive results. Thus the

TABLE 2. Principal Bands (cm^{-1}) in the IR spectra of 3-Indolyl Diketones

Compound	$CH_3-C=O$	Dimeric enol C=C and C=O	Enol C=C and C=O	Bonded (free) OH	NH	
					amide	indole
VIII	1705 s	1570 m 1590 w 1605 w 1635 s 1660 s		3260—3360 br m		
IX	1710 s	1610 s 1630 s 1650 s		3050—3150 br m		
X	1710 w					
XI	1730 s		1650 w 1700 s 1630 s 1640 s 1685 s 1710 s	3630, 3150—3300 br m 2600—2800 br m	3100—3180 br m	
XII[a]	1710s		1600 s 1620 m	2650—2750 br m	3100—3250 m	
XIII[a]		1610 s 1630 s 1650 s 1650 s		3275 c		3450s
XIV		1610 s 1690 s		3200—3390 br m		3400—3450 br m
XV[b]			1720 s			3340s
XVI			1690 s 1710 s 1730 s 1760 s	2650—2750 br s	3150—3250 br s	3420s
XVII[a]			1600 s 1635 s 1685 sh, m	3550 s, 3650 s 2600—2800 m	3200—3380 s	3420—3480 m
XVIII			1570 s 1655 s	2600—2800 br m	3060 s 3140 s	3340
XIX[c]	1725		1695 s 1705 m		3230 m 3310 m 3350 m	3425s

[a] $\nu_{C=S}$ 1540 cm^{-1} (s). [b] Diketone $\nu_{C=O}$ cm^{-1} (s). [c] $\nu_{C\equiv N}$ 2265 cm^{-1} (w).

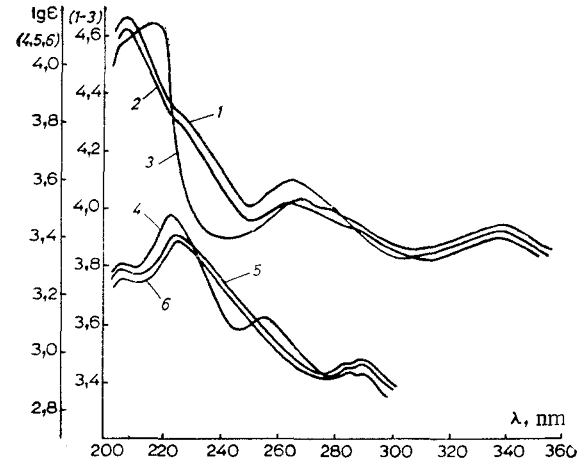


Fig. 1. UV spectra ($3 \cdot 10^{-5}$ M): 1, 2, and 3) XIV in C_2H_5OH, C_2H_5OH + NaOH, and C_2H_5OH + HCl; 4, 5, and 6) XIII in C_2H_5OH + HCl, C_2H_5OH, and C_2H_5OH + NaOH.

lithium and sodium salts of 1-acetyl-3-oxindole were obtained in 80-85% yields in the case of lithio- and sodiomalonic ester. This is explained by the higher acidity of 1-acetylindoxyl (the pK_a value of acetylindoxyl determined by potentiometric titration is 11) as compared with malonic ester (pK_a 13).

Malononitrile occupies a special position in the case of condensation reactions with acetylindoxyl. Although it is a weak acid with pK_a 11, it readily reacts with I, and various products are formed, depending on the conditions. The product in acetic acid in the presence of triethylamine is (1-acetyl-3-indolyl)cyanoacetamide (XIX). The PMR spectrum of XIX in d_6-DMSO contains a $COCH_3$ singlet at 2.6 ppm, the singlet of a methyldyne proton at 5.3 ppm, and signals of aromatic protons at 7.2-8.4 ppm; an indole ring 2-H signal is observed as a singlet at 7.9 ppm.

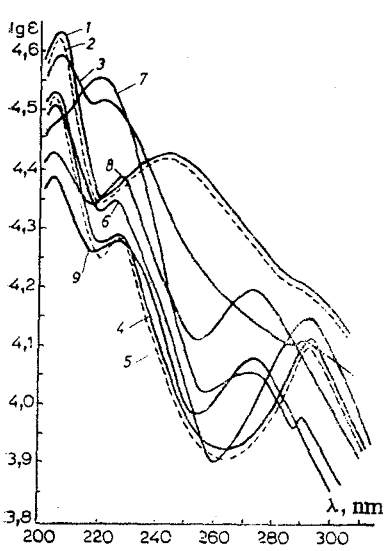


Fig. 2

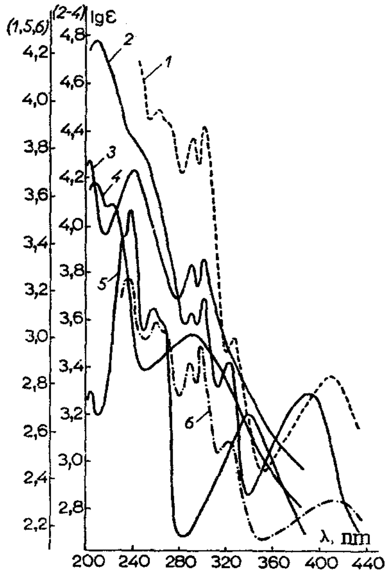


Fig. 3

Fig. 2. UV spectra ($3 \cdot 10^{-5}$ M): 1, 2, and 3) XV in C_2H_5OH + NaOH, C_2H_5OH, and C_2H_5OH + HCl; 4, 5, and 6) XVII in C_2H_5OH + NaOH, C_2H_5OH, and C_2H_5OH + HCl; 7, 8, and 9) XVI in C_2H_5OH + HCl, C_2H_5OH + NaOH, C_2H_5OH.

Fig. 3. UV spectra (10^{-5} M): 1, 2, and 6) XXV in $CHCl_3$, C_2H_5OH, and THF; 3) XIX; 4) XVIII; 5) I (all in C_2H_5OH).

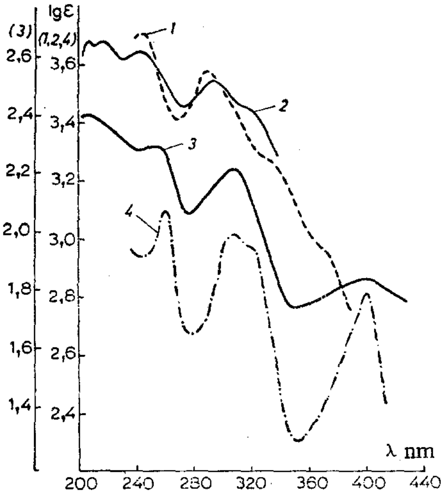
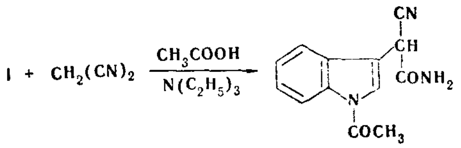
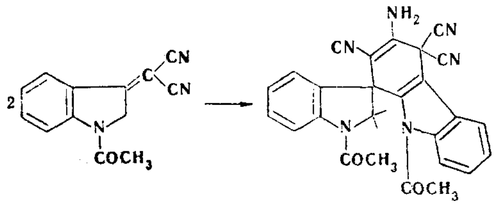


Fig. 4. UV spectra (10^{-5} M): 1 and 2) XXIV in THF and C_2H_5OH; 3 and 4) XXVII in C_2H_5OH and THF.



XIX

In an attempt to prepare the corresponding dinitrile in benzene in the presence of acetic acid and piperidine we isolated a substance having, according to the mass-spectral data, a dimeric rather than a dinitrile composition. The dimer could have structure XX, which is formed as a result of nucleophilic addition of the methylene group of one molecule of the normal product of the Knoevenagel reaction (XXI) to the double bond of another such molecule.



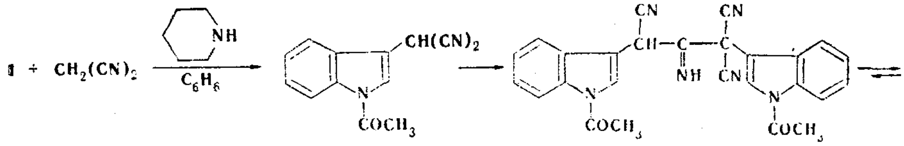
XXI XX

Examples of reactions of this sort are widely known [7]. However, the PMR spectrum of the dimer does not contain the signals of aliphatic protons that should be observed in the case of structure XX. Its IR spectrum contains characteristic absorption bands of NH, C=C, and C=N groups, and three groups of bands are observed in the UV spectra of solutions in alcohol and THF (Fig. 4).

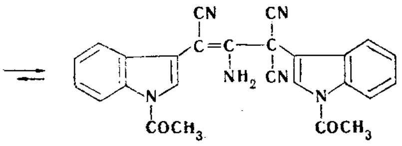
Dimerization of nitrile XXII gives XXIII, which is in equilibrium with enamine form XXIV or exists primarily in form XXIV, as attested to by the presence of three bands of NH stretching vibrations at 3160-3300 and 3450 cm^{-1} and two bands at 3200 and 3330 cm^{-1} in the spectrum of a mineral oil suspension and in the spectrum of a 0.5% solution in THF, respectively, and also by the presence of a C=C absorption band at 1625 cm^{-1}.

The reaction of 1-acetyl-3-indolinone with sodiomalononitrile in DMSO gives a substance that gives a molecular ion (M^+) in its mass spectrum with m/e 223, which corresponds either to the normal product of Knoevenagel condensation (XXI) or to dinitrile XXII with an aromatic indole structure. The maximum peak is the peak of a fragment ion with m/e 181, which corresponds to detachment of a carbomethylene particle from the 1 position with migration of a hydrogen atom to nitrogen. The second step in the process is elimination of CN and HCN particles to give fragment ions with mass of 155 and 154. The peaks of fragment ions with masses of 127, 126 and 101 confirm the presence of another two CN groups. The peak with mass 101 evidently corresponds to ejection of a neutral HCN particle from the indole ring. The ejection of carbomethylene and HCN particles is confirmed by metastable transitions with apparent masses of 146.9 ($COCH_2$), 132.2, 104.1, and 80.3.

The XXI structure is excluded by comparison of the UV spectra of the reaction product and the starting 1-acetyl-3-indolinone (Fig. 3). In addition, the IR spectrum of a KBr pellet of the product does not contain absorption bands of an exocyclic double bond. The PMR spectrum does not contain signals of the aliphatic 2-H protons of the indoline ring.



XXII XXIII

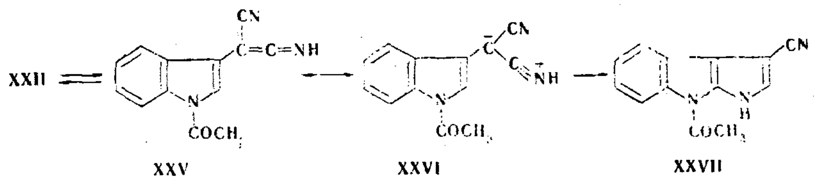


XXIV

The UV spectra of XXII in $CHCl_3$, THF, and alcohol contain long-wave absorption maxima at 325 (log ε 2.99) and 410 nm (log ε 2.87); 322 (log ε 2.55) and 415 nm (log ε 2.30); 322 (log ε 3.42) and 390 nm (log ε 3.28), respectively; the extinction coefficients vary as a function of the solvent (Fig. 3). According to the data in [8], this is characteristic for dicyano and tricyano compounds that display nitrile–ketimine tautomerism. The presence of ketimine structure XXV, which is tautomeric with respect to dinitrile structure XXII, is confirmed by the presence of an NH absorption band at 3400 cm^{-1} in the IR spectrum of a mineral oil suspension of the compound. Signals of protons of both tautomeric structure XXII and XXV at 6.7 and 5.4 ppm, with an intensity ratio of 3:1, are observed in the PMR spectrum of the compound in d_6-DMSO; the chemical shift at 5.4 ppm is extremely close to the signal of the methylidyne proton (5.3 ppm) of amidonitrile XIX.

In addition, a characteristic feature of this compound is the absence in the IR spectra of a mineral oil suspension and solution in THF of the absorption bands of nitrile and ketimine groups (the presence of C≡N groups was established by mass spectrometry); the IR spectrum of a KBr pellet contains two weak-intensity bands at 2245 and 2270 cm^{-1}.

In contrast to the similarly constructed amidonitrile XIX with pK_a 9.9, XXII is a strong acid with pK_a 5.3. Similar anomalous properties have been observed in the case of cyanoform [9] and were explained by the existence of an equilibrium between the ionized and nonionized forms of the dicyanoketimine, which, in turn, is in equilibrium with cyanoform. Thus the anomalous properties of XXII can be explained within the framework of the assumption of the existence of polar structure XXVI.



In fact, the amphoteric nature of this substance is confirmed by the existence of two ionization constants: acid pK_a 2.6 and basic pK_a 5.3. According to the data in [10], the ratio of the constants is characteristic for zwitterions. Evidence in favor of structure XXVI is also afforded by the considerable increase in the dielectric permeability (D) of a solution as compared with the dielectric permeability (D_0) of the solvent (benzene) [10]. The δ value found from the equation $D = D_0 + \delta c$ (for c = 0.0179 M) is 42.46.

In contrast to the unstable nitrogen-unsubstituted ketimines, XXI is extremely stable in solid form and in aprotic solvents (benzene, THF, and DMSO). At the same time, in protic solvents (alcohol and water) it is readily converted to isomeric XXVII, which, in contrast to the starting compound, gives an IR spectrum with an intense band of a C≡N group at 2235 cm^{-1} and a low-intensity NH absorption band at 3120 cm^{-1}, which constitutes evidence for the presence of a pyrrole ring. The UV spectrum of XXVII contains absorption maxima at 256 (log ε 2.29), 308 (log ε 2.21), and 400 nm (log ε 1.83) (Fig. 4).

Compound XXVII is evidently formed from dipolar from XXVI as a result of electrophilic attack on the 2 position of the indole ring.

EXPERIMENTAL

The IR spectra were recorded with a UR-10 spectrometer. The PMR spectra were recorded with a JNM-4H-100 spectrometer with tetramethylsilane as the internal standard. The mass spectra were recorded with an MKh-1303 spectrometer at an ionization chamber temperature of 110° and an ionizing voltage of 50 eV. The ionization constants of I, XIX, and XXIII were determined by potentiometric titration with a pH-262 pH-meter at 25° by means of solutions in 60% aqueous alcohol and 30% aqueous DMSO. The dielectric measurements were made with a Tangens apparatus.*

General Method for the Preparation of VIII-XII and XIX (Tables 1 and 2). A mixture of 0.87-g (5 mmole) of 1-acetyl-3-indoline (I), 5 mmole of the β-dicarbonyl compound II-VI or malononitrile VII, and 0.51 g (5 mmole) of triethylamine was refluxed in glacial acetic acid, after which the acetic acid was vacuum evaporated, and the residue was allowed to stand for crystallization. The crystals were removed by filtration, washed with alcohol, and recrystallized. Compound XII was obtained in the form of the salt with one molecule of triethylamine and was then converted to the acid by recrystallization of the salt from acetic acid.

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*The authors thank S. B. Khubetsov (D. I. Mendeleev Moscow Chemical Engineering Institute) for making the dielectric measurements and discussing the results.

General Method for the Preparation of XIII-XVII (Tables 1 and 2). A solution of 5 mmole of IX-XI in 10-15 ml of 5% NaOH or 5% Na_2CO_3 (in the case of VIII) (in 5% aqueous alcoholic NaOH in the case of XII) was acidified with 10% hydrochloric acid and extracted rapidly with ether. The ether extract was washed with water and dried with magnesium sulfate, the ether was removed by distillation, and the residue was recrystallized.

3-Indolylmalonic Acid Diamide (XVIII). A mixture of 0.3-g (0.75 mmole of thiobarbituric acid XVII and 1.5 g of Raney nickel was refluxed for 5 h in 60 ml of ethanol, after which the nickel was removed by filtration and washed with hot alcohol. The alcohol was evaporated to give 0.16 g (82%) of the N-acetyl derivative of 3-indolylmalonic acid diamide with mp 315°. This product was dissolved in a mixture of 8 ml of 10% NaOH and 1 ml of ethanol, and the solution was heated at 35-40° for 10-15 min. It was then cooled and extracted successively with ether and ethyl acetate. The alkaline solution was filtered, and the filtrate was acidified with 10% hydrochloric acid. The precipitated crystals were removed by filtration and washed with water to give 0.13 g (96%) of amide XVIII with mp 293-295° (from alcohol). Found: C 58.2; H 4.9; N 18.8; H_2O 4.0%; M 217 mass spectrometrically). $2C_{11}H_{11}N_3O_2 \cdot H_2O$. Calculated: C 58.3; H 5.3; N 18.6; H_2O 4.2%; M 452.

1,3-Bis(1-acetyl-3-indolyl)-1,3,3-tricyano-2-amino-1-propene (XXIV). A mixture of 2.30-g (12.5 mmole) of 1-acetyl-3-indolinone and 1.65 g (25 mmole) of malononitrile was refluxed for 1 h in 100 ml of absolute benzene in the presence of 5.2 g (87 mmole) of glacial acetic acid and 2.14 g (25 mmole) of piperidine, after which the solvent was evaporated, and the residue was treated with water. The product [2.25 g (40%)] was removed by filtration and purified by recrystallization to give a product with mp 255° (dec., from acetone). IR spectrum (mineral oil, ν, cm^{-1}): 1580 (C=C), 1700 s (C=O), 2210 s (C≡N), and 3160-3300, 3450 (N—H); (0.5% solution in THF): 3200, 3300 (N—H). PMR spectrum (in d_6-acetone): 2.60, 2.63 (s, $COCH_3$), 7.3-8.4 (m, aromatic protons). Found: C 69.8; H 4.0; N 18.7%; M 446 (mass spectrometrically). $C_{26}H_{18}N_6O_2$. Calculated: C 69.9; H 4.2; N 18.8%; M 446.

(1-Acetyl-3-indolyl)malononitrile (XXII). A 0.03-g sample of sodium hydride (an 80% suspension in mineral oil) and 0.16 g (2.5 mmole) of malononitrile were added with stirring to 10 ml of DMSO, after which a solution of 0.44 g (2.5 mmole) of 1-acetyl-3-indolinone in 10 ml of DMSO was added to the clear solution, and the mixture was stirred at room temperature for 10-15 min. It was then allowed to stand at 0-5° for 8-10 h, after which it was acidified to pH 4-5 with cold 10% hydrochloric acid. The precipitated nitrile [0.5 g (85%)] was removed by filtration and washed with water to give a product with mp 165-167° (from alcohol). IR spectrum (KBr), cm^{-1}: 1710 (C=O), 2245, 2270 (C≡N); (0.5% solution in THF): 1725 (C=O), 2250 (C≡N), 3600 (N—H). Found: C 69.3; H 4.2; N 18.9; M 223 (mass spectrometrically). $C_{13}H_9N_3O$. Calculated: C 69.9; H 4.2; N 18.8%; M 223.

3-Cyano-8-acetylpyrrolo[2,3-b]indole (XXVII). A solution of 0.22 g (1 mmole) of XII in 20 ml of ethanol was allowed to stand at room temperature for 40-48 h, after which the precipitated crystals (0.12 g) were removed by filtration and washed thoroughly with alcohol to give a product with mp 238° (dec., from methanol). Another 0.08 g of a more contaminated product was obtained by evaporation of the mother liquor. The overall yield was 91%. IR spectrum (mineral oil), cm^{-1}: 1590 (C=C), 1685 (C=O), 2235 (C≡N), 3120 (pyrrole N—H). PMR spectrum (in d_6-DMSO): 2.3 (s, $COCH_3$), 6.0 (d, pyrrole ring 2-H, J = 7 Hz); 7.0-7.9 (m, aromatic protons). Found: C 70.1; H 4.0; N 18.7%; M 223 (mass spectrometrically and by the Rast method). $C_{13}H_9N_3O$. Calculated: C 69.9; H 4.2; N 18.8%; M 223.

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