REACTION OF 2,5-SUBSTITUTED 3,3,4,4-TETRACYANOPYRROLIDINES WITH ANILINES

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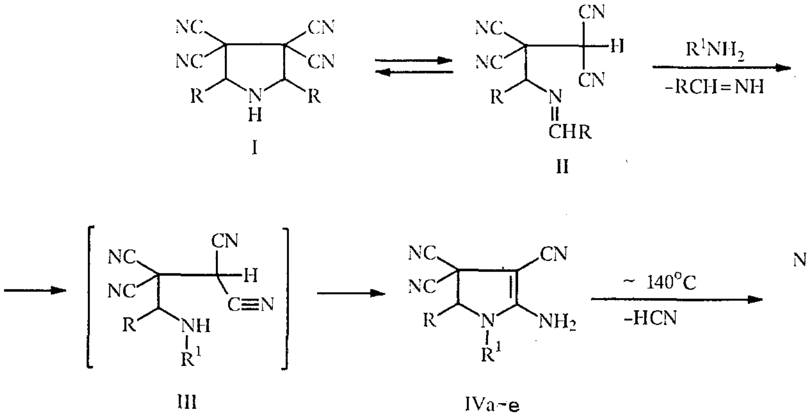
The ambiguity of the reaction of primary aromatic amines with 2,5-substituted 3,3,4,4-tetracyanopyrrolidines depending on conditions was shown: At room temperature 2-amino-1-R^1-5-R-3,4,4-tricyano-2-pyrrolines are formed, while on heating-2-aryl-amino-1,1,-dicyanoethylenes are obtained.

The presence of a ring–chain tautomerism of 3,3,4,4-tetra-cyanopyrrolidines I has been reported in [1], which caused their unusual interaction with primary amines and aliphatic amines [2].

In the present article we discuss the reaction of compounds I with anilines. Aniline and its derivatives react at room temperature with pyrrolidines I with the formation of 2-amino-1-R^1-5-R-3,4,4-tricyano-2-pyrrolines IVa-e (Table 1).

The subsequent heating of the reaction mixture to 140°C leads to the elimination by pyrrolines IV of hydrogen cyanide and the formation of 2-amino-3,4-dicyanopyrroles V.



In the IR spectra (Table 2) of both pyrrolines IV and of pyrroles V absorption bands are observed of the stretching vibrations in the 3400-3200 (NH$_2$) and 2270-2220 cm^{-1} (C ≡ N) regions, characteristic for the enaminonitrile fragment. The ^{13}C NMR spectrum of compound Va also supports the proposed structure (C$_{(2)}$ 149.3; C$_{(3)}$ 70.8; C$_{(4)}$ 90.9; C$_{(5)}$ 136.6; C(C ≡ N) 115.4 ppm and the C atoms of the two phenyl substituents in the range of 128-137 ppm). For an unequivocal determination of the structure of the synthesized compounds, an x-ray diffraction investigation of 2-amino-3,4-dicyano-1,5-diphenyl-pyrrole (Va) was carried out. Its molecule without hydrogen atoms is illustrated in Fig. 1, and the atom coordinates are given in Table 3.

According to the proposed scheme (in analogy to [2]), tetracyanopyrrolidine I in the presence of a base completely transforms into the open form II, in which the nucleophilic substitution of the aldimine fragment by the reacting amine becomes possible, followed by cyclization of aminic center of III formed at the nitrile group carbon atom.

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TABLE 1. Properties of Compounds IIVa-e, Va, b and IXa, b

Compound	Empirical formula	R	R^1	mp, °C	Yield, %
IVa	$C_{19}H_{13}N_5$	C_6H_5	C_6H_5	220...230 (разл.)	82
IVb	$C_{20}H_{15}N_5$	C_6H_5	3-$H_3CC_6H_4$	163...164 (разл.)	43
IVc	$C_{20}H_{15}N_5O$	2-$H_3COC_6H_4$	C_6H_5	270...271 (разл.)	12
IVd	$C_{16}H_{15}N_5$	*i*-C_3H_7	C_6H_5	201...202	18
IVe	$C_{16}H_{15}N_5$	*n*-C_3H_7	C_6H_5	148...150	25
Va	$C_{18}H_{12}N_4$	C_6H_5	C_6H_5	229...230	53
Vb	$C_{19}H_{14}N_4$	C_6H_5	3-$H_3CC_6H_4$	210...211	27
IXa	$C_{10}H_7N_3$	C_6H_5	—	254...256	25
IXb	$C_{11}H_9N_3$	3-$H_3CC_6H_4$	—	183...185	11

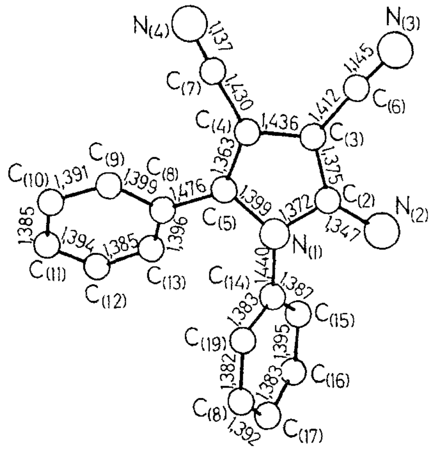

Fig. 1. Molecule of 2-Amino-1,5-diphenyl-3,4 dicyanopyrrole (Va) without hydrogen atoms.

A reaction has been described of 1,1,2,2-tetracyanoethane with the azomethine compounds proceeding through the formation of intermediate III [3, 4]. Thus, pyrrolines IV or pyrroles V have been synthesized, depending on the temperature regime. Comparison of the spectral data with those given in [3, 4] showed their complete identity and the mixed samples do not give a depression of the melting points. On this basis, we believe that the only possible direction of the reaction is the substitution of the aldimine in the acyclic form II.

Another path of the reaction of pyrrolidines with anilines has also been discovered. It was found that on heating their mixture to 140°C without preliminary holding of it at room temperature with the same amine, one and the same compound is formed irrespectively of the substitution in the initial pyrrolidine I. This led to the conclusion that a more extensive splitting of the pyrrolidine ring occurs. As a result of this reaction 2-arylamino-1,1-dicyanoethylenes IX were isolated in a yield of up to 25%.

Since in this case the heating of the reaction mixture is carried out immediately, then possibly in the beginning the elimination of hydrogen cyanide takes place (and not the substitution of the aldimine fragment) leading to an intermediate VI, similarly as has been observed during the thermal rearrangement of pyrrolidines I [1]. In contrast to the scheme in [1], here, besides the intramolecular migration of the aldimine fragment, an addition at the activated double bond may take place [5], which is possibly also realized in the present case. The stabilization of the intermediate anion VII is possible both by the elimination of the cyanide anion and the formation of a new anion VIII by a Claisen-type rearrangement, as has been proposed in reactions with alcohols [2]. In anion VIII a substitution of the aldimine by the amino group is possible. The thus-formed intermediate product can fairly easily split off the corresponding Schiff base with a proton transfer from the amine center to the anionic center. The elimination of CN^- from the anion obtained leads to the end product IX.

TABLE 2. IR and Mass Spectra of Compounds IV, V, and IX

Compound	IR spectrum, cm^{-1}				Mass spectrum,* m/z (relative intensity, %)
	ν_{N-H}	$\nu_{C\equiv N}$	$\nu_{C=C}$	δ_{NH}	
IVa	3435, 3410, 3250, 3200	2265, 2200	1590	1640	311 (0,6), 284 (100), 207 (10), 181 (4), 180 (15), 129 (6), 104 (12), 78 (9), 77 (24), 65 (14), 51 (9)
IVb	3440, 3330, 3240, 3195	2265, 2200	1600	1640	325 (0,6), 298 (100), 297 (17), 207 (7), 194 (6), 180 (13), 104 (9), 92 (8), 91 (21), 77 (8), 65 (17)
IVc	3370, 3325, 3240, 3210	2265, 2225	1595	1645	341 (1,5), 315 (36), 314 (100), 271 (11), 254 (7), 237 (3), 210 (3), 207 (12), 119 (11), 77 (15), 72 (7)
IVd	3400, 3335, 3260, 3200	2260, 2195	1595	1645	277 (0,5), 250 (27), 236 (21), 235 (100), 157 (3), 147 (4), 146 (5), 130 (3), 104 (7), 77 (25), 51 (12)
IVe	3435, 3320, 3230, 3190	2250, 2195	1585	1645	277 (0,5), 250 (52), 222 (45), 221 (100), 207 (11), 194 (12), 140 (25), 117 (7), 78 (9), 77 (48), 51 (25)
Va	3395, 3330, 3250, 3210	2225	1600	1645	284 (100), 169 (13), 207 (8), 181 (4), 180 (12), 169 (17), 104 (25), 78 (16), 77 (43), 69 (13), 51 (36)
Vb	3400, 3330, 3245, 3220	2225	1600	1645	298 (100), 283 (9), 207 (9), 194 (5), 180 (13), 142 (16), 104 (29), 92 (18), 91 (29), 77 (17), 65 (39)
IXa	3310, 3215	2235, 2225	1590	1655	—
IXb	3300, 3210	2235, 2225	1595	1650	—

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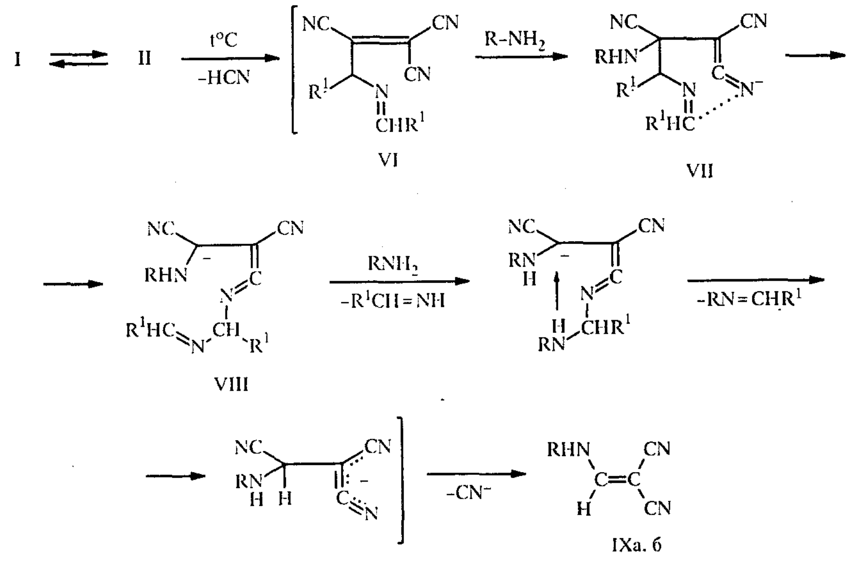
*The peak of the molecular ion and 10 most intensive peaks of the fragmentary ions are given.



The correctness of the proposed scheme is indicated by the fact that practically twice the amount of the corresponding Schiff base was isolated in this reaction.

The structure of compound IX can be verified by the data of x-ray diffraction analysis (Fig. 2, the atom coordinates are given in Table 4).

It should be noted that the melting points of compounds IXa, b do not give depression of the mixed melting points with samples synthesized from ethoxymethylenemalononitrile and amines by the method described in [6].

TABLE 3. Atom Coordinates in the Molecule of Va, $\times 10^4$ (for H, $\times 10^3$)

Atom	x	y	z	B(A2)
N(1)	5051(6)	1513(3)	6155(2)	2,79(8)
N(2)	7613(7)	1726(3)	5451(2)	4,4(1)
N(3)	8395(8)	-1227(4)	5157(2)	5,0(1)
N(4)	3615(9)	-2186(4)	6426(2)	6,2(1)
C(2)	6369(8)	1101(4)	5761(2)	2,9(1)
C(3)	6161(8)	2(4)	5760(2)	2,8(1)
C(4)	4609(8)	-255(4)	6165(2)	2,8(1)
C(5)	3948(8)	677(4)	6405(2)	2,9(1)
C(6)	7369(9)	-692(4)	5429(2)	3,5(1)
C(7)	4038(9)	-1325(4)	6316(2)	3,8(1)
C(8)	2425(8)	866(4)	6852(2)	2,9(1)
C(9)	527(8)	267(4)	6825(2)	3,5(1)
C(10)	-934(8)	444(5)	7240(2)	4,2(1)
C(11)	-532(9)	1224(5)	7670(2)	4,4(1)
C(12)	137(1)	1817(4)	7703(2)	4,0(1)
C(13)	2851(9)	1625(4)	7300(2)	3,4(1)
C(14)	4872(8)	2642(4)	6279(2)	2,7(1)
C(15)	2964(8)	3165(4)	6098(2)	3,4(1)
C(16)	2828(9)	4252(5)	6237(3)	4,3(1)
C(17)	454(1)	4772(4)	6547(2)	4,3(1)
C(18)	6430(9)	4221(4)	6721(2)	4,0(1)
C(19)	6608(8)	3145(4)	6586(2)	3,1(1)
H(N2)	739(6)	223(3)	540(2)	1,0(8)
H(9)	9(7)	-34(3)	649(2)	1(1)
H(10)	-244(8)	3(4)	719(2)	2(1)
H(11)	-138(9)	138(5)	797(2)	4(1)
H(12)	175(8)	234(4)	807(2)	2(1)
H(13)	434(7)	205(4)	738(2)	2(1)
H(15)	193(8)	280(4)	581(2)	2(1)
H(16)	144(8)	464(4)	612(2)	2(1)
H(17)	468(9)	553(4)	668(2)	2(1)
H(18)	747(7)	456(4)	691(2)	1(1)
H(19)	791(7)	273(3)	667(2)	0,4(9)

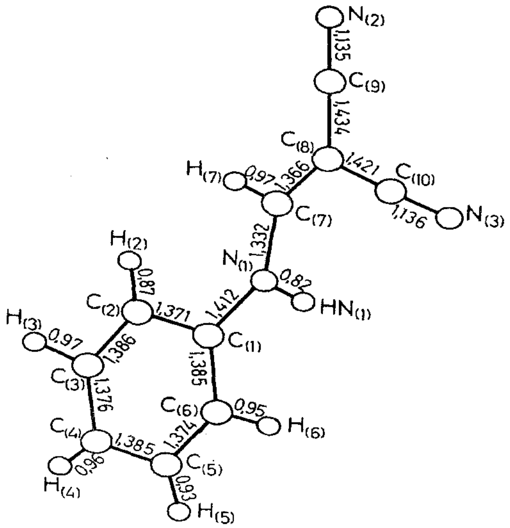


Fig. 2. Molecule of anilinomethylenemalononitrile (IXa).

TABLE 4. Atom Coordinates in the Molecule of IXa, × 10^4 (for H, × 10^3)

Atom	x	y	z	B(A2)
N(1)	8012(3)	3811(4)	5085(1)	3,84(5)
N(2)	8350(4)	2798(4)	7960(1)	5,35(6)
N(3)	10062(3)	-779(5)	5904(1)	5,91(6)
C(1)	7299(3)	5246(4)	4522(1)	3,55(5)
C(2)	6619(4)	7092(5)	4747(2)	4,92(7)
C(3)	5932(4)	8413(5)	4158(2)	5,73(8)
C(4)	5948(4)	7903(5)	3346(2)	5,07(7)
C(5)	6633(4)	6078(6)	3129(2)	5,67(8)
C(6)	7314(4)	4743(5)	3704(2)	5,20(7)
C(7)	7932(3)	3878(5)	5891(1)	3,74(5)
C(8)	8601(3)	2432(4)	6418(1)	3,56(5)
C(9)	8439(4)	2646(4)	7277(2)	3,99(6)
C(10)	9430(3)	642(5)	6148(1)	4,12(6)
HN(1)	855(3)	287(4)	490(1)	3,9(6)
H(2)	670(4)	751(5)	525(2)	7,3(8)
H(3)	555(3)	977(5)	431(2)	6,7(8)
H(4)	535(3)	881(5)	298(2)	6,4(8)
H(5)	660(4)	563(5)	259(2)	7,7(9)
H(6)	773(3)	340(5)	358(2)	6,1(8)
H(7)	728(3)	498(4)	611(2)	4,8(7)

EXPERIMENTAL

The course of the reaction and the purity of the synthesized compounds were monitored by TLC on Silufol UV-254-type plates, using iodine vapor or UV irradiation for the development. The IR spectra were run on UR-20 spectrophotometer in a thin layer. The ^{13}C NMR spectra were recorded in deuterodimethylformamide on a Bruker WH-90 spectrometer with a working frequency of 22.63 MHz, using HMDS as an internal standard. The mass spectra were obtained on an MS 25PFA KRATOS spectrometer with a direct introduction of the substance into the ionic source and at an ionization energy of 50 eV. The x-ray diffraction investigations were carried out on an Enraph Nonius CAD-4 four-disc automatic diffractometer, using MoKα radiation and ω-scanning.

2-Amino-5-R-1-R^1-3,4,4,-tricyano-2-pyrrolines IVa-e. A 10 mmole portion of 3,3,4,4-tetracyanopyrrolidine I was added to 6 ml of the aromatic amine, and the mixture was stirred to complete dissolution of the starting compound. The solution obtained was held at room temperature for 1 h with periodic stirring. Then 15 ml of isopropanol was added, and the mixture was acidified with acetic acid. The precipitate that separated out was filtered off, washed with isopropanol, and recrystallized from isopropanol (see Table 1).

1,5-Substituted 2-Amino-3,4-dicyanopyrroles Va, b. The reaction was carried out in a similar way as the synthesis of compounds IV. After standing at room temperature, the reaction mixture was heated to 140°C and then was gradually cooled and diluted by an equal volume of isopropanol. The precipitate that separated out was filtered off, washed with isopropanol, and recrystallized from isopropanol.

X-Ray Diffraction Examination of Compound Va. The main crystallographic data are: a = 6.252(2), b = 12.455 (2), c = 22.712(3) Å; β = 95.51°, V = 1760.6 Å^3, Z = 4, space group P 21/C. In the region of $\Theta \leq 25°$ 2536 nonzero reflections were determined, of which 1786 reflections with $J > 3\sigma(J)$ were used for refining the position and thermal parameters of the molecule. Final R = 0.059.

Anilinomethylenemalononitriles IXa, b. A 10 mmole portion of 3,3,4,4-tetracyanopyrrolidine I was mixed with 8 ml of the corresponding aromatic amine and immediately after this the mixture was heated to 140°C. After cooling, it was diluted with an equal volume of isopropanol. The precipitate that separated out was filtered off, washed with isopropanol, and recrystallized from isopropanol (see Table 1).

X-Ray Diffraction Examination of Compound IXa. The main crystallographic data are: a = 8.224(2), b = 6.429(3), c = 16.459 Å; β = 93.20(2)°; V = 868.9 Å^3, Z = 4, space group P 21/n. The structure was resolved by the MULTAN method. The thermal and position parameters were refined in an anisotropic full-matrix variant. In the refinement 1246 reflections were used with $J > 3\sigma(J)$. Final R = 0.046.

REFERENCES

1. A. B. Zolotoi, A. N. Lyshchikov, P. M. Lukin, A. I. Prokhorov, O. E. Nasakin, A. Kh. Bulai, and L. O. Atovmyan, Dokl. Akad. Nauk SSSR, **313**, No. 1, 110, (1990).
2. O. E. Nasakin, A. N. Lyshchikov, P. M. Lukin, A. Kh. Bulai, V. A. Tafeenko, and P. A. Sharbatyan, Khim. Geterotsikl. Soedin., No. 11, 1502 (1991).
3. O. E. Nasakin, V. V. Alekseev, V. K. Promonenkov, Yu. P. Belowv, A. Kh. Bulai, and S. Yu. Sil'vestrova, Khim. Geterotsikl. Soedin., No. 3, 402 (1981).
4. O. E. Nasakin, V. V. Alekseev, P. B. Terent'ev, A. Kh. Bulai, and M. Yu. Zabolotskaya, Khim. Geterotsikl. Soedin, No. 8, 1062 (1983).
5. W. J. Middleton and V. A. Engelhardt, J. Amer. Chem. Soc., **80**, 2788 (1958).
6. J. W. Baker and R. K. Howe, US Patent 3,691,227 (CO7 c 121/78), Publ. 1972.