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INTERACTION OF 2-ARYL-6-HYDROXY-5,6-TETRA-METHYLENEPIPERIDINE-3,3,4,4-TETRACARBONITRILES AND 2-ARYL-5,6-TETRAMETHYLENE-3,3,4-TRICYANO-2,3,4,5-TETRAHYDROPYRIDINE-4-CARBOXAMIDES WITH AMMONIA

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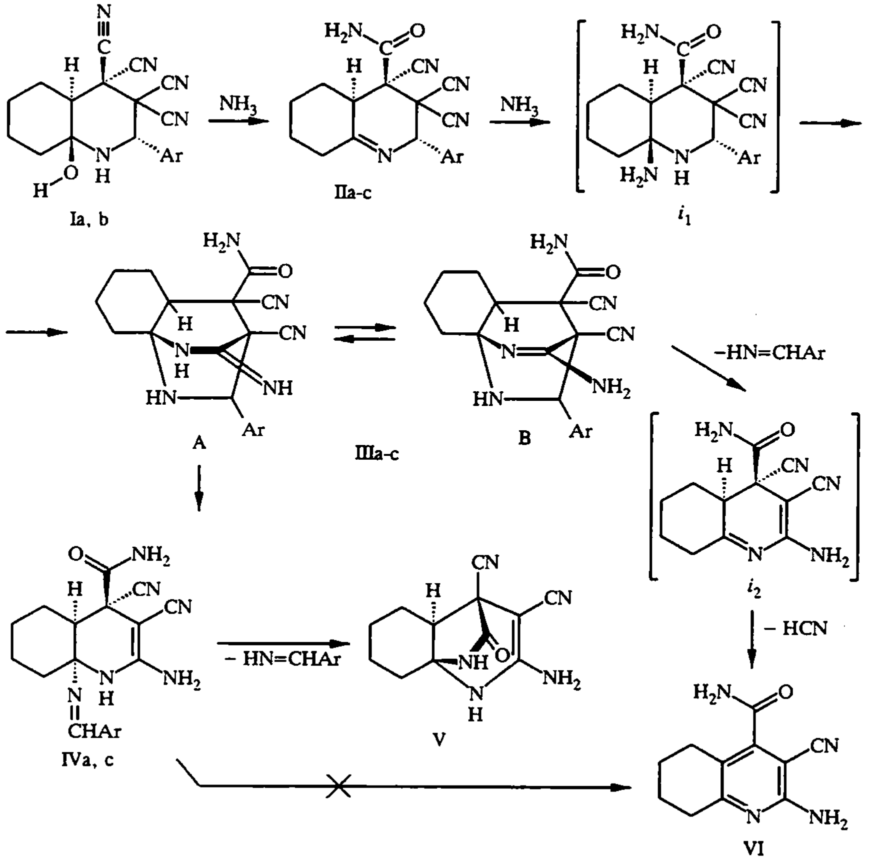
The interaction of 2-aryl-6-hydroxy-5,6-tetramethylenepiperidine-3,3,4,4-tetracarbonitriles and 2-aryl-5,6-tetramethylene-3,3,4-tricyano-2,3,4,5-tetrahydropyridine-4-carboxamides with ammonia results in the formation of 5-aryl-1,7-tetramethylene-3-imino-4,8-dicyano-2,6-diazabicyclo[2.2.2]octane-8-carboxamides. In solvents, these latter compounds are converted to 3-amino-6-oxo-1,8-tetramethylene-2,7-diazabicyclo-[3.2.1]octa-3-ene-4,5-dicarbonitrile and 2-amino-3-cyano-5,6-tetramethylenepyridine-4-carboxamide.

As described in a recent paper [1], in the interaction of (2-oxocyclohexyl)ethane-1,1,2,2-tetracarbonitriles with 1,3,5-triaryl-2,4-diaza-1,4-pentadienes, we isolated as intermediates 2-aryl-6-hydroxy-5,6-tetramethylenepiperidine-3,3,4,4-tetracar-



I-IVa) Ar = Ph; I-IVb) Ar = 2-furyl; I-IVc) Ar = p-MeOC$_6$H$_4$

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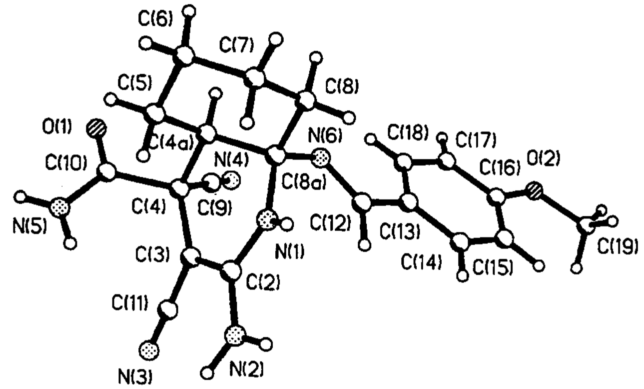

Fig. 1. Molecular structure of compound IVc.

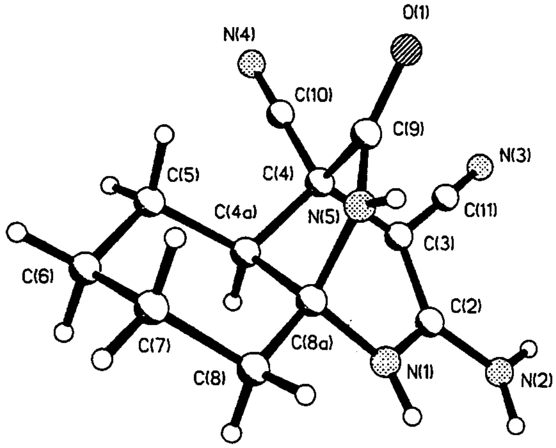

Fig. 2. Molecular structure of compound V.

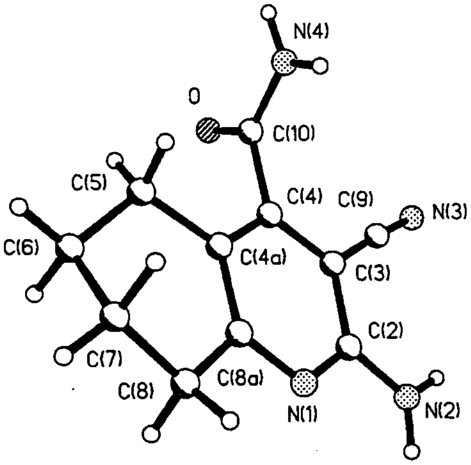

Fig. 3. Molecular structure of compound VI.

bonitriles (I) and 2-aryl-5,6-tetramethylene-3,3,4-tricyano-2,3,4,5-tetrahydropyridine-4-carboxamides (II), which are readily isomerized to 3-amino-4-aryl-6,7-tetramethylene-1-oxo-3a,4,5,7a-tetrahydro-1H-pyrrolo[3,4-c]pyridine-3a,7a-dicarbonitriles upon heating in alcohols. This process is accelerated by the presence of a tertiary amine.

TABLE 1. Characteristics of Compounds IIIa-c and IVa, c

Compound	Empirical formula	Found, % / Calculated, %			mp (decomp.), °C	Yield, %
		C	H	N		
IIIa	$C_{19}H_{20}N_6O$	65,37 65,50	5,65 5,78	24,04 24,12	119...121	50
IIIb	$C_{17}H_{18}N_6O$	60,12 60,29	5,42 5,36	24,67 24,83	>110	30
IIIc	$C_{20}H_{22}N_6O_2$	63,32 63,47	5,76 5,86	22,03 22,21	95...96	15
IVa	$C_{19}H_{20}N_6O$	65,38 65,50	5,65 5,78	24,12 24,12	>110	80
IVc	$C_{20}H_{22}N_6O_2$	63,35 63,47	5,78 5,86	22,14 22,21	>130	75

TABLE 2. IR Spectra of Compounds IIIa-c and IVa, c

Compound	ν, cm^{-1}		
	$\nu_{C=O}$, $\nu_{C=C}$, $\nu_{C=N}$, δ_{NH2}	$\nu_{C\equiv N}$	ν_{NH2}, ν_{N-H}
IIIa	1695, 1640, 1590	2260	3575, 3490, 3370, 3260, 3150
IIIb	1695, 1645, 1580	2255	3525, 3405, 3340, 3270, 3150
IIIc	1695, 1635, 1600, 1590	2255	3590, 3495, 3380, 3280, 3160
IVa	1730, 1670, 1620, 1600	2265, 2190	3590, 3510, 3390, 3270, 3100
IVc	1730, 1670, 1630, 1600	2240, 2180	3490, 3340, 3260

Continuing these studies, we found that in contrast to substituted amines, aqueous ammonia with compounds Ia, b and IIa-c forms 5-aryl-1,7-tetramethylene-3-imino-4,8-dicyano-2,6-diazabicyclo[2.2.2]octane-8-carboxamides (IIIa-c). These compounds, which are stable in the crystalline state, undergo further conversions in solution, the degree of which depends on the nature of the solvent and the reaction conditions. Compounds IIIa, c in acetone are isomerized to 2-amino-6-arylidenamino-5,6-tetramethylene-3,4-dicyano-1,4,5,6-tetrahydropyridine-4-carboxamides (IVa, c). When the bicyclo compounds IIIa-c are heated or held for an extended period in isopropyl alcohol, they are converted to 3-amino-6-oxo-1,8-tetramethylene-2,7-diazabicyclo[3.2.1]octa-3-ene-4,5-dicarbonitrile (V). When the bicyclo compounds IIIa-c are held in acetonitrile at room temperature, the products include, along with V, a small amount of 2-amino-3-cyano-5,6-tetramethylenepyridine-4-carboxamide (VI). The structures of compounds IVc, V, and VI were established by x-ray diffraction measurements on single crystals (Figs. 1-3). The structure of compound IVa was determined by comparing its IR spectrum with that of compound IVc. The structures of the bicyclo compounds IIIa-c were established on the basis of elemental analyses and IR spectra (Tables 1 and 2), and also by the fact that they are converted quantitatively to the bicyclo compounds V through the intermediates IVa-c.

The data suggest that the alcohols Ia, b are first converted to the amides IIa, b. What takes place next in the compounds IIa-c is the nucleophilic addition of ammonia at the C=N double bond, followed by intramolecular cyclization to form the bicyclo compounds IIIa-c. The stereochemical conditions of this process are such that during the addition, a new C-N bond is formed in the cis-position relative to the carbamoyl group. Only in this case can the stereochemical features of compounds IV and V be observed (Figs. 1 and 2). In the formation of compounds IV and V, the determining stage is apparently heterolytic cleavage of the $C_{(4)}$–$C_{(5)}$ bond of compound III. Compound VI is not obtained from compounds IVa,c even when the reaction is carried out in a strongly basic medium, probably because the potentially leaving groups (H and N=CHAr, or H and C≡N) cannot be split out via an E2 mechanism, since they are in a gauche-position relative to each other, and since any occurrence of the process through an anionic mechanism is prevented by the faster process of intramolecular nucleophilic substitution with the formation of compound V. The source of formation of the pyridine VI may be a reaction that competes with the heterolytic splitting, namely a retro-Diels-Alder reaction from the tautomeric form B of compound III, with the formation of the intermediate i_2. In the intermediate i_2, there is apparently a syn-elimination of hydrogen cyanide. In favor of this hypothesis is the lower yield of compound VI when the reaction is performed in toluene rather than in acetonitrile. Thus, two directly opposite conditions are necessary for the formation of

TABLE 3. Coordinates of Nonhydrogen Atoms ($\times 10^4$) and Coefficients of Equivalent Isotropic Displacement (Å^2 $\times$ 10^3) of Compound IVc

Atom	*x*	y	*z*	$U_{(eq)}$
$O_{(1)}$	5064(3)	9699(2)	1042(2)	35(1)
$O_{(2)}$	2134(3)	7391(2)	5932(2)	47(1)
$O_{(3)}$	3409(4)	2630(3)	6540(3)	94(2)
$O_{(4)}$	765(5)	9740(4)	6989(3)	74(3)
$N_{(1)}$	2270(3)	11594(3)	2311(2)	27(1)
$N_{(2)}$	643(4)	11400(3)	1311(2)	32(2)
$N_{(3)}$	1070(3)	9206(3)	226(2)	42(2)
$N_{(4)}$	3776(3)	8406(3)	2243(2)	42(2)
$N_{(5)}$	3661(4)	10510(3)	182(2)	33(2)
$N_{(6)}$	3277(3)	10389(2)	3317(2)	28(1)
$C_{(2)}$	1710(4)	11120(3)	1634(2)	25(2)
$C_{(3)}$	2247(4)	10380(3)	1289(2)	24(2)
$C_{(4)}$	3487(4)	10172(3)	1585(2)	24(2)
$C_{(4a)}$	4092(4)	10979(3)	2205(2)	26(2)
$C_{(5)}$	4413(4)	11886(3)	1772(3)	31(2)
$C_{(6)}$	4980(5)	12656(4)	2388(3)	39(2)
$C_{(7)}$	4223(5)	12965(3)	2943(3)	40(2)
$C_{(8)}$	3891(4)	12066(3)	3385(3)	33(2)
$C_{(8a)}$	3342(4)	11251(3)	2796(2)	26(2)
$C_{(9)}$	3657(4)	9187(4)	1983(3)	29(2)
$C_{(10)}$	4141(4)	10098(3)	891(3)	26(2)
$C_{(11)}$	1591(4)	9747(3)	706(3)	30(2)
$C_{(12)}$	2354(5)	10187(3)	3500(2)	29(2)
$C_{(13)}$	2267(4)	9406(3)	4092(2)	29(2)
$C_{(14)}$	1323(4)	9374(3)	4421(3)	34(2)
$C_{(15)}$	1243(4)	8716(3)	5036(3)	36(2)
$C_{(16)}$	2112(4)	8066(3)	5319(3)	34(2)
$C_{(17)}$	3048(5)	8062(4)	4976(3)	39(2)
$C_{(18)}$	3116(4)	8727(4)	4375(3)	38(2)
$C_{(19)}$	1195(6)	7396(4)	6315(4)	59(3)
$C_{(20)}$	3035(6)	2105(6)	5962(4)	76(3)
$C_{(21)}$	3692(7)	1297(8)	5757(5)	80(4)
$C_{(22)}$	1913(9)	2342(8)	5385(8)	80(6)
$C_{(23)}$	1613(5)	9834(4)	7499(4)	59(3)
$C_{(24)}$	2732(10)	9616(8)	7320(6)	82(6)
$C_{(25)}$	1578(6)	10127(4)	8335(4)	62(3)

compound VI—a nonpolar solvent for the first stage, and a polar solvent for the second stage—since elimination of hydrogen cyanide most likely takes place through an anionic mechanism (ElcB mechanism). The comparatively low yield of compound VI when the reaction is performed in acetonitrile is explained by the possibility of a competing process: Acetonitrile, as a polar solvent, promotes heterolytic cleavage of the $C_{(4)}-C_{(5)}$ bond of compounds IIIa-c. The even lower yield of VI when the reaction is performed in toluene may be explained on the basis that the second stage of the reaction, the elimination of hydrogen cyanide, proceeds at a very low rate.

EXPERIMENTAL

IR spectra were taken in a UR-20 instrument on samples in white mineral oil. The elementary cell constants and the intensities of reflections for x-ray structure analysis of compounds V and VI were measured in a Siemens P3/PC automatic four-circle diffractometer (λMoKα, graphite monochromator, $\theta/2\theta$ scanning), and those of compound IV in a Syntex $P2_1$ automatic four-circle diffractometer (λMoKα, graphite monochromator, $\theta/2\theta$ scanning) The structures of the compounds were deciphered by the direct method and refined by full-matrix LSM in the anisotropic approximation for the nonhydrogen atoms. The hydrogen atoms, localized objectively in a Fourier difference synthesis, were refined in the isotropic approximation. All calculations were performed by means of the SHELXTL PLUS program (PC version). The coordinates of the atoms, bond lengths, bond angles, and the thermal parameters were entered into the files of the Cam-

TABLE 4. Bond Lengths and Bond Angles in Molecule of Compound IVc

Bond	Length, Å	Angle	ω, deg	Angle	ω, deg
$O_{(1)}$—$C_{(10)}$	1,226(6)	$C_{(16)}$—$O_{(2)}$—$C_{(19)}$	116,8(4)	$N_{(1)}$—$C_{(8a)}$—$C_{(8)}$	109,3(3)
$O_{(2)}$—$C_{(16)}$	1,374(5)	$C_{(2)}$—$N_{(1)}$—$C_{(8a)}$	122,3(4)	$N_{(6)}$—$C_{(8a)}$—$C_{(8)}$	105,8(3)
$O_{(2)}$—$C_{(19)}$	1,439(9)	$C_{(8a)}$—$N_{(6)}$—$C_{(12)}$	119,3(4)	$C_{(4a)}$—$C_{(8a)}$—$C_{(8)}$	110,5(4)
$O_{(3)}$—$C_{(20)}$	1,206(8)	$N_{(1)}$—$C_{(2)}$—$N_{(2)}$	117,3(4)	$N_{(4)}$—$C_{(9)}$—$C_{(4)}$	176,0(4)
$O_{(4)}$—$C_{(23)}$	1,187(7)	$N_{(1)}$—$C_{(2)}$—$C_{(3)}$	119,9(4)	$O_{(1)}$—$C_{(10)}$—$N_{(5)}$	124,8(5)
$N_{(1)}$—$C_{(2)}$	1,346(5)	$N_{(2)}$—$C_{(2)}$—$C_{(3)}$	122,8(4)	$O_{(1)}$—$C_{(10)}$—$C_{(4)}$	118,7(3)
$N_{(1)}$—$C_{(8a)}$	1,450(5)	$C_{(2)}$—$C_{(3)}$—$C_{(4)}$	122,1(3)	$N_{(5)}$—$C_{(10)}$—$C_{(4)}$	116,4(4)
$N_{(2)}$—$C_{(2)}$	1,347(6)	$C_{(2)}$—$C_{(3)}$—$C_{(11)}$	118,9(4)	$N_{(3)}$—$C_{(11)}$—$C_{(3)}$	178,2(5)
$N_{(3)}$—$C_{(11)}$	1,166(6)	$C_{(4)}$—$C_{(3)}$—$C_{(11)}$	118,7(4)	$N_{(6)}$—$C_{(12)}$—$C_{(13)}$	121,8(4)
$N_{(4)}$—$C_{(9)}$	1,147(6)	$C_{(3)}$—$C_{(4)}$—$C_{(4a)}$	111,6(3)	$C_{(12)}$—$C_{(13)}$—$C_{(14)}$	119,0(4)
$N_{(5)}$—$C_{(10)}$	1,321(5)	$C_{(3)}$—$C_{(4)}$—$C_{(9)}$	109,9(3)	$C_{(12)}$—$C_{(13)}$—$C_{(18)}$	123,0(5)
$N_{(6)}$—$C_{(8a)}$	1,478(5)	$C_{(4a)}$—$C_{(4)}$—$C_{(9)}$	109,8(3)	$C_{(14)}$—$C_{(13)}$—$C_{(18)}$	117,9(4)
$N_{(6)}$—$C_{(12)}$	1,267(7)	$C_{(3)}$—$C_{(4)}$—$C_{(10)}$	114,6(3)	$C_{(13)}$—$C_{(14)}$—$C_{(15)}$	121,5(4)
$C_{(2)}$—$C_{(3)}$	1,399(6)	$C_{(4a)}$—$C_{(4)}$—$C_{(10)}$	107,1(3)	$C_{(14)}$—$C_{(15)}$—$C_{(16)}$	119,4(5)
$C_{(3)}$—$C_{(4)}$	1,509(6)	$C_{(9)}$—$C_{(4)}$—$C_{(10)}$	103,5(3)	$O_{(2)}$—$C_{(16)}$—$C_{(15)}$	124,5(5)
$C_{(3)}$—$C_{(11)}$	1,406(6)	$C_{(4)}$—$C_{(4a)}$—$C_{(5)}$	112,7(3)	$O_{(2)}$—$C_{(16)}$—$C_{(17)}$	115,5(4)
$C_{(4)}$—$C_{(4a)}$	1,576(5)	$C_{(4)}$—$C_{(4a)}$—$C_{(8a)}$	109,4(4)	$C_{(15)}$—$C_{(16)}$—$C_{(17)}$	120,0(4)
$C_{(4)}$—$C_{(9)}$	1,493(6)	$C_{(5)}$—$C_{(4a)}$—$C_{(8a)}$	111,5(3)	$C_{(16)}$—$C_{(17)}$—$C_{(18)}$	119,7(5)
$C_{(4)}$—$C_{(10)}$	1,560(7)	$C_{(4a)}$—$C_{(5)}$—$C_{(6)}$	111,3(4)	$C_{(13)}$—$C_{(18)}$—$C_{(17)}$	121,5(5)
$C_{(4a)}$—$C_{(5)}$	1,530(6)	$C_{(5)}$—$C_{(6)}$—$C_{(7)}$	111,1(4)	$O_{(3)}$—$C_{(20)}$—$C_{(21)}$	120,9(6)
$C_{(4a)}$—$C_{(8a)}$	1,542(7)	$C_{(6)}$—$C_{(7)}$—$C_{(8)}$	109,9(4)	$O_{(3)}$—$C_{(20)}$—$C_{(22)}$	120,2(7)
$C_{(5)}$—$C_{(6)}$	1,522(6)	$C_{(7)}$—$C_{(8)}$—$C_{(8a)}$	113,2(4)	$C_{(21)}$—$C_{(20)}$—$C_{(22)}$	118,7(7)
$C_{(6)}$—$C_{(7)}$	1,516(8)	$N_{(1)}$—$C_{(8a)}$—$N_{(6)}$	115,0(4)	$O_{(4)}$—$C_{(23)}$—$C_{(24)}$	121,4(7)
$C_{(7)}$—$C_{(8)}$	1,535(7)	$N_{(1)}$—$C_{(8a)}$—$C_{(4a)}$	108,2(3)	$O_{(4)}$—$C_{(23)}$—$C_{(25)}$	120,1(6)
$C_{(8)}$—$C_{(8a)}$	1,534(6)	$N_{(6)}$—$C_{(8a)}$—$C_{(4a)}$	108,0(3)	$C_{(24)}$—$C_{(23)}$—$C_{(25)}$	118,4(6)
$C_{(12)}$—$C_{(13)}$	1,476(6)				
$C_{(13)}$—$C_{(14)}$	1,391(7)				
$C_{(13)}$—$C_{(18)}$	1,390(6)				
$C_{(14)}$—$C_{(15)}$	1,387(7)				
$C_{(15)}$—$C_{(16)}$	1,381(7)				
$C_{(16)}$—$C_{(17)}$	1,395(8)				
$C_{(17)}$—$C_{(18)}$	1,373(7)				
$C_{(20)}$—$C_{(21)}$	1,45(1)				
$C_{(20)}$—$C_{(22)}$	1,52(1)				
$C_{(23)}$—$C_{(24)}$	1,50(2)				
$C_{(23)}$—$C_{(25)}$	1,467(9)				

bridge Crystallographic Data Center. The purity of the synthesized compounds and the degree of completion of the reaction were established by TLC on Silufol UV-254 plates.

5-Aryl-1,7-tetramethylene-3-imino-4,8-dicyano-2,6-diazabicyclo[2.2.2]octane-8-carboxamides (IIIa-c). *A.* To 10 ml of a concentrated aqueous ammonia solution, 3 mmoles of the alcohol Ia, c was added, and the mixture was stirred until the reaction was completed (5-10 min). The precipitate was filtered off, washed with ethyl acetate, and vacuum-dried.

B. Compounds IIIa-c were obtained analogously from the amides IIa-c.

6-Amino-2-arylidenamino-2,3-tetramethylene-4,5-dicyano-1,2,3,4-tetrahydropyridine-4-carboxamides (IVa, c). A 3-mmole quantity of the bicyclo compound IIIa, c was dissolved in 10 ml of acetone and held for 2 h. The resulting precipitate was separated, washed, and vacuum-dried to constant weight.

X-Ray Diffraction Study of Compound IVc. Transparent, colorless crystals obtained from acetone, monoclinic, solvated by acetone molecules in a 1:2 ratio, at $-80°C$: $a = 12.228(3)$, $b = 13.641(3)$, $c = 16.754(4)$ Å, $\beta = 103.42(1)°$, $V = 2718.8(2)$ Å^3, $d_{calc} = 1.214$ g/cm^3, space group $P2_1/n$, $Z = 4$. A total of 2716 reflections were measured, $\theta_{max} = 25°$. The final divergence factors were $R = 0.032$ based on 2365 independent reflections with $I > 2\sigma(I)$ and $R_w = 0.032$ based on all 2716 independent reflections.

TABLE 5. Coordinates of Nonhydrogen Atoms ($\times 10^4$) and Coefficients of Equivalent Isotropic Displacement (Å^2 × 10^3) of Compound V

Atom	*x*	*y*	*z*	$U_{(eq)}$
$O_{(1)}$	4048(2)	3339(1)	941(1)	40(1)
$N_{(1)}$	7058(2)	8605(1)	2944(1)	34(1)
$N_{(2)}$	9755(2)	8199(2)	4236(1)	43(1)
$N_{(3)}$	7374(2)	3394(2)	4509(1)	69(1)
$N_{(4)}$	1179(2)	2026(2)	3089(1)	59(1)
$N_{(5)}$	4785(2)	6437(1)	1174(1)	31(1)
$C_{(2)}$	7694(2)	7488(2)	3586(1)	31(1)
$C_{(3)}$	6212(2)	5692(2)	3532(1)	33(1)
$C_{(4)}$	3958(2)	5030(2)	2696(1)	30(1)
$C_{(4a)}$	3296(2)	6636(2)	2640(1)	31(1)
$C_{(5)}$	994(2)	6059(2)	1891(1)	40(1)
$C_{(6)}$	653(3)	7690(2)	1457(2)	49(1)
$C_{(7)}$	2224(2)	8688(2)	803(1)	45(1)
$C_{(8)}$	4518(2)	9386(2)	1577(1)	37(1)
$C_{(8a)}$	4962(2)	7848(2)	2076(1)	30(1)
$C_{(9)}$	4216(2)	4762(2)	1474(1)	30(1)
$C_{(10)}$	2397(2)	3340(2)	2923(1)	37(1)
$C_{(11)}$	6866(2)	4437(2)	4073(1)	41(1)

TABLE 6. Bond Lengths and Bond Angles in Molecule of Compound V

Bond	Length, Å	Angle	ω, deg	Angle	ω, deg
$O_{(1)}—C_{(9)}$	1,224(2)	$C_{(2)}—N_{(1)}—C_{(8a)}$	120,2(1)	$C_{(5)}—C_{(4a)}—C_{(8a)}$	112,6(1)
$N_{(1)}—C_{(2)}$	1,360(2)	$C_{(8a)}—N_{(5)}—C_{(9)}$	112,8(1)	$C_{(4a)}—C_{(5)}—C_{(6)}$	112,1(1)
$N_{(1)}—C_{(8a)}$	1,452(1)	$N_{(1)}—C_{(2)}—N_{(2)}$	117,1(1)	$C_{(5)}—C_{(6)}—C_{(7)}$	111,8(2)
$N_{(2)}—C_{(2)}$	1,340(2)	$N_{(1)}—C_{(2)}—C_{(3)}$	119,3(1)	$C_{(6)}—C_{(7)}—C_{(8)}$	110,5(1)
$N_{(3)}—C_{(11)}$	1,146(2)	$N_{(2)}—C_{(2)}—C_{(3)}$	123,6(1)	$C_{(7)}—C_{(8)}—C_{(8a)}$	112,0(1)
$N_{(4)}—C_{(10)}$	1,134(2)	$C_{(2)}—C_{(3)}—C_{(4)}$	117,9(1)	$N_{(1)}—C_{(8a)}—N_{(5)}$	110,6(1)
$N_{(5)}—C_{(8a)}$	1,469(2)	$C_{(2)}—C_{(3)}—C_{(11)}$	120,7(1)	$N_{(1)}—C_{(8a)}—C_{(4a)}$	107,9(1)
$N_{(5)}—C_{(9)}$	1,342(2)	$C_{(4)}—C_{(3)}—C_{(11)}$	120,6(1)	$N_{(5)}—C_{(8a)}—C_{(4a)}$	100,4(1)
$C_{(2)}—C_{(3)}$	1,390(2)	$C_{(3)}—C_{(4)}—C_{(4a)}$	110,1(1)	$N_{(1)}—C_{(8a)}—C_{(8)}$	110,4(1)
$C_{(3)}—C_{(4)}$	1,523(2)	$C_{(3)}—C_{(4)}—C_{(9)}$	104,6(1)	$N_{(5)}—C_{(8a)}—C_{(8)}$	112,4(1)
$C_{(3)}—C_{(11)}$	1,403(2)	$C_{(4a)}—C_{(4)}—C_{(9)}$	101,2(1)	$C_{(4a)}—C_{(8a)}—C_{(8)}$	114,8(1)
$C_{(4)}—C_{(4a)}$	1,543(2)	$C_{(3)}—C_{(4)}—C_{(10)}$	113,1(1)	$O_{(1)}—C_{(9)}—N_{(5)}$	128,4(1)
$C_{(4)}—C_{(9)}$	1,549(2)	$C_{(4a)}—C_{(4)}—C_{(10)}$	114,4(1)	$O_{(1)}—C_{(9)}—C_{(4)}$	126,5(1)
$C_{(4)}—C_{(10)}$	1,465(2)	$C_{(9)}—C_{(4)}—C_{(10)}$	112,4(1)	$N_{(5)}—C_{(9)}—C_{(4)}$	105,1(1)
$C_{(4a)}—C_{(5)}$	1,524(2)	$C_{(4)}—C_{(4a)}—C_{(5)}$	113,6(1)	$N_{(4)}—C_{(10)}—C_{(4)}$	179,4(1)
$C_{(4a)}—C_{(8a)}$	1,545(2)	$C_{(4)}—C_{(4a)}—C_{(8a)}$	97,3(1)	$N_{(3)}—C_{(11)}—C_{(3)}$	179,1(1)
$C_{(5)}—C_{(6)}$	1,525(3)				
$C_{(6)}—C_{(7)}$	1,527(3)				
$C_{(7)}—C_{(8)}$	1,516(2)				
$C_{(8)}—C_{(8a)}$	1,516(2)				

3-Amino-6-oxo-1,8-tetramethylene-2,7-diazabicyclo[3.2.1]octa-3-ene-4,5-dicarbonitrile (V). *A.* A suspension of 3 mmoles of compound IIIa-c in 10 ml of isopropyl alcohol was heated to boiling. The reaction mass was cooled, and the precipitate was filtered off, washed with isopropyl alcohol, and vacuum-dried. Yield 0.72 g (99%), white crystalline powder, mp > 240°C (decomp.). Found, %: C 59.12; H 5.27; N 28.65. $C_{12}H_{13}N_5O$. Calculated, %: C 59.25; H 5.38; N 28.79. IR spectrum, cm^{-1}: 3450, 3330, 3230, 3200 (ν_{NH2}, ν_{NH}); 2275, 2195 ($\nu_{C\equiv N}$); 1695, 1630; 1570 ($\nu_{C=N}$, ν_{NH2}, $\nu_{C=C}$).

X-Ray Diffraction Study of Compound V. Transparent, colorless crystals obtained from isopropyl alcohol, triclinic, at 20°C: a = 7.150(2), b = 8.035(3), c = 12.096(4) Å, α = 93.45(2)°, β = 104.71(2)°, γ = 113.74(2)°, V = 604.8(8) Å^3, d_{calc} = 1.342 g/cm^3, space group P$\bar{1}$, Z = 2. A total of 2337 reflections were measured, θ_{max} = 26°.

TABLE 7. Coordinates of Nonhydrogen Atoms ($\times 10^4$) and Coefficients of Equivalent Isotropic Displacement ($Å^2 \times 10^3$) of Compound VI

Atom	x	y	z	$U_{(eq)}$
O	6861(2)	7600(1)	6886(2)	49(1)
N$_{(1)}$	4470(2)	5489(1)	1875(2)	31(1)
N$_{(2)}$	6950(2)	5016(1)	2207(3)	43(1)
N$_{(3)}$	9691(2)	5850(1)	6341(3)	56(1)
N$_{(4)}$	6304(2)	6521(1)	8431(2)	44(1)
C$_{(2)}$	6036(2)	5473(1)	2879(2)	29(1)
C$_{(3)}$	6668(2)	5913(1)	4573(2)	29(1)
C$_{(4)}$	5642(2)	6374(1)	5173(2)	29(1)
C$_{(4a)}$	4016(2)	6399(1)	4113(2)	31(1)
C$_{(5)}$	2875(3)	6907(2)	4708(3)	46(1)
C$_{(6)}$	1289(3)	7059(2)	3162(4)	55(1)
C$_{(7)}$	645(3)	6276(2)	2075(4)	60(1)
C$_{(8)}$	1762(2)	5909(2)	1223(3)	41(1)
C$_{(8a)}$	3494(2)	5937(1)	2472(2)	30(1)
C$_{(9)}$	8349(2)	5895(1)	5586(3)	36(1)
C$_{(10)}$	6329(2)	6888(1)	6928(2)	31(1)

TABLE 8. Bond Lengths and Bond Angles in Molecule of Compound VI

Bond	Length, Å	Angle	ω, deg	Angle	ω, deg
O—C$_{(10)}$	1,223(2)	C$_{(2)}$—N$_{(1)}$—C$_{(8a)}$	119,7(2)	C$_{(5)}$—C$_{(4a)}$—C$_{(8a)}$	121,6(2)
N$_{(1)}$—C$_{(2)}$	1,342(2)	N$_{(1)}$—C$_{(2)}$—N$_{(2)}$	116,9(2)	C$_{(4a)}$—C$_{(5)}$—C$_{(6)}$	113,0(2)
N$_{(1)}$—C$_{(8a)}$	1,347(3)	N$_{(1)}$—C$_{(2)}$—C$_{(3)}$	120,6(2)	C$_{(5)}$—C$_{(6)}$—C$_{(7)}$	112,3(2)
N$_{(2)}$—C$_{(2)}$	1,346(3)	N$_{(2)}$—C$_{(2)}$—C$_{(3)}$	122,4(2)	C$_{(6)}$—C$_{(7)}$—C$_{(8)}$	112,5(2)
N$_{(3)}$—C$_{(9)}$	1,140(3)	C$_{(2)}$—C$_{(3)}$—C$_{(4)}$	119,0(2)	C$_{(7)}$—C$_{(8)}$—C$_{(8a)}$	114,0(2)
N$_{(4)}$—C$_{(10)}$	1,322(3)	C$_{(2)}$—C$_{(3)}$—C$_{(9)}$	118,9(2)	N$_{(1)}$—C$_{(8a)}$—C$_{(4a)}$	123,6(2)
C$_{(2)}$—C$_{(3)}$	1,415(2)	C$_{(4)}$—C$_{(3)}$—C$_{(9)}$	122,1(2)	N$_{(1)}$—C$_{(8a)}$—C$_{(8)}$	114,9(2)
C$_{(3)}$—C$_{(4)}$	1,395(3)	C$_{(3)}$—C$_{(4)}$—C$_{(4a)}$	120,3(2)	C$_{(4a)}$—C$_{(8a)}$—C$_{(8)}$	121,6(2)
C$_{(3)}$—C$_{(9)}$	1,432(3)	C$_{(3)}$—C$_{(4)}$—C$_{(10)}$	119,0(2)	N$_{(3)}$—C$_{(9)}$—C$_{(3)}$	176,8(2)
C$_{(4)}$—C$_{(4a)}$	1,396(2)	C$_{(4a)}$—C$_{(4)}$—C$_{(10)}$	120,6(2)	O—C$_{(10)}$—N$_{(4)}$	124,2(2)
C$_{(4)}$—C$_{(10)}$	1,515(2)	C$_{(4)}$—C$_{(4a)}$—C$_{(5)}$	121,6(2)	O—C$_{(10)}$—C$_{(4)}$	119,7(2)
C$_{(4a)}$—C$_{(5)}$	1,514(4)	C$_{(4)}$—C$_{(4a)}$—C$_{(8a)}$	116,8(2)	N$_{(4)}$—C$_{(10)}$—C$_{(4)}$	116,1(2)
C$_{(4a)}$—C$_{(8a)}$	1,397(3)				
C$_{(5)}$—C$_{(6)}$	1,514(3)				
C$_{(6)}$—C$_{(7)}$	1,486(4)				
C$_{(7)}$—C$_{(8)}$	1,522(4)				
C$_{(8)}$—C$_{(8a)}$	1,509(2)				

The final divergence factors were $R = 0.032$ based on 1983 reflections with $I > 2\sigma(I)$ and $R_w = 0.032$ based on all 2337 independent reflections.

2-Amino-3-cyano-5,6-tetramethylenepyridine-4-carboxamide (VI). *A.* A 0.35-g quantity (1 mmole) of compound IIIa was dissolved in 10 ml of acetonitrile and held for 5 days. The resulting precipitate was filtered off, washed with chilled acetonitrile, and vacuum-dried. Obtained 20 mg (10%) of rose-colored crystals, mp > 230°C (decomp.). Found, %: C 60.95; H 5.46; N 25.82. $C_{11}H_{12}N_4O$. Calculated, %: C 61.1; H 5.59; N 25.91. IR spectrum, cm^{-1}: 3420, 3375, 3320, 3240 (ν_{NH2}); 2230 ($\nu_{C\equiv N}$); 1680, 1650, 1635 ($\nu_{C=O}$, δ_{NH2}, $\nu_{C=N}$, $\nu_{C=C}$).

After concentrating the filtrate, obtained 0.08 g (40%) of compound V.

B. In 50 ml of absolute toluene, 5 mmoles of compound IIIa, c was dissolved with heating, and the solution was refluxed for 10 h. After cooling the reaction mass, the precipitate was filtered off, washed with ethyl acetate, and purified by reprecipitation from a dimethyl sulfoxide solution. Obtained 25 mg (2%) rose-colored crystals.

X-Ray Diffraction Study of Compound VI. Crystals of compound VI obtained from acetonitrile, monoclinic, at 20°C: $a = 9.084(2)$, $b = 15.698(3)$, $c = 7.856(4)$ Å, $\beta = 112.11(2)°$, $V = 1038(1)$ Å^3, $d_{calc} = 1.390$ g/cm^3, space group $P2_1/c$, $Z = 2$. A total of 2070 reflections were measured, $\theta_{max} = 26°$. The final divergence factors were $R = 0.040$ based on 1503 reflections with $I > 2\sigma(I)$ and $R_w = 0.040$ based on all 2070 independent reflections.

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