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HIGHLY POLARIZED ENAMINES. 3.* STUDY OF THE SPATIAL STRUCTURE OF α,α-DIAMINO-β-CYANO-β-NITROETHYLENE† DERIVATIVES

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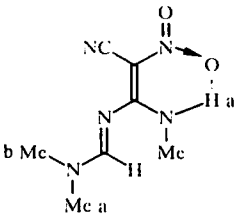
The spatial structure of various derivatives of α,α-diamino-β-cyano-β-nitroethylene has been investigated using ^1H and ^{13}C NMR spectroscopy. It was shown that the configuration of the investigated push–pull enamines is determined by the possibility of creating an intramolecular hydrogen bond between NH and NO_2 groups or by steric interactions. A series of 3,5-diamino-5-nitropyrazole derivatives has been synthesized by reacting these amines with hydrazine hydrate.

In the previous communications of this series, the synthesis and some properties of push–pull enamines, derivatives of α,α-diamino-β-cyano-β-nitroethylene, were described [1]. The latter are extremely interesting starting materials for the synthesis of various substituted heterocycles. However, the presence in their structure of a completely substituted ethylene fragment creates significant difficulties when investigating their configuration [2]. We note the indications in the literature that the configuration of compounds of this type has not been successfully determined previously [3]. The aim of the present work was to study the fine structure of the indicated enamines by NMR spectroscopy. The primary subject selected for investigation was α-methylamino-(N,N-dimethylaminomethylene)amino-β-cyano-β-nitroethylene (I).



I

Signals were observed in the ^1H NMR spectrum of this compound in DMSO-D_6 and DMF-D_7 (see Table 1) for the NH group proton as quartets at 9.82 ($^3J_{NH,Me}$ = 3.9 Hz) and 9.96 ppm ($^3J_{NH,Me}$ = 3.8 Hz) respectively. Taking the spectrum at reduced temperature in DMF-D_7 showed that the position of the signal remained practically unchanged δ_{NH} = 10.08 at −30°C and 10.10 ppm at −40°C. This indicates that a fairly stable intramolecular hydrogen bond (IMB) between the NO_2 and NH groups is a characteristic of compound (I) and determines its configuration unequivocally. Clarification of the conformational features of enamine (I) was carried out using the nuclear Overhauser effect (NOE). On irradiating the proton signal of the NMe group (of the NHMe fragment) at 2.92 ppm (DMSO-D_6), an increase was observed in the intensity of the signals of the NH group protons (at 9.82 ppm) of 15% and of the =CH proton (8.11 ppm) of 5% which indicates the spatial proximity of the meso proton of the amidine fragment and the methyl group of the NHMe substituent. Assignment of the methyl

*For Part 2, see [1].

†These compounds may also be considered as derivatives of acrylonitrile.

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TABLE 1. Data of ^1H NMR Spectra of Compounds (I)-(VIII) (δ, ppm, coupling constant J, Hz)

Compound	Plotting temperature, °C	Solvent	NH, NH_2	α-NCH_3 / α-NCH_2	Amidine fragment	
					$N(CH_3)_2$, s	=CH, s
I	+23	DMSO-D_6	9,82 (1H, q, a*-H)	2,92 (3H, d, $^3J_{Me,a-H}$ = 3,9)	3,01 (3H, b†-CH_3) and 3,13 (3H, a-CH_3)	8,11 (1H)
	-40	DMF-D_7	10,10 (1H, q, a-H)	3,04 (3H, d, $^3J_{Me,a-H}$ = 3,8)	3,10 (3H, b-CH_3) and 3,24 (3H, a-CH_3)	8,20 (1H)
II	+23	DMSO-D_6	8,13 (2H, br s) and 8,76 (1H, q, a-H)	2,85 (3H, d, $^3J_{Me,a-H}$ = 5,0)		
	-40	DMF-D_7	8,56 (2H, s) and 9,10 (1H, s)	3,07 (3H, d, $^3J_{Me,a-H}$ = 4,7)		
III	+23	DMSO-D_6	7,60 (4H, s)			
	-40	DMF-D_7	8,29 (2H, s) and 8,42 (2H, s)			
IV	+23	DMSO-D_6	8,22 (1H, br s, b-H) and 8,63 (1H, s, a-H)		2,86 (6H)	
	-40	DMF-D_7	8,60 (1H, s, b-H) and 9,01 (1H, s, a-H)		3,12 (6H, br s)	
V	+23	DMSO-D_6	9,05 (1H, br s, b-H) and 9,32 (1H, s, a-H)		3,08 (3H, b-CH_3) and 3,14 (3H, a-CH_3)	8,25 (1H)
	-40	DMF-D_7	9,40 (1H, br s, b-H) and 9,60 (1H, s, a-H)		3,01 (3H,‡ b-CH_3, $^4J_{b\text{-}CH_3,CH}$ = 0,7) and 3,26 (3H,‡ a-CH_3, $^4J_{a\text{-}CH_3,CH}$ = 0,7)	8,47 (1H)
VI	+23	DMSO-D_6	–	3,11 (3H, br s) and 3,17 (3H, br s)	3,14 (3H, b-CH_3) and 3,24 (3H, a-CH_3)	8,22 (1H)
	-40	DMF-D_7		3,18 (3H, br s) and 3,25 (3H, br s)	3,23 (3H,‡ b-CH_3, $^4J_{b\text{-}CH_3,CH}$ = 0,8) and 3,37 (3H,‡ a-CH_3, $^4J_{a\ CH_3,CH}$ = 0,7)	8,26 (1H)
VII	+23	DMSO-D_6	–		3,10 (6H, b-CH_3) and 3,19 (6H, a-CH_3)	8,24 (2H)
	-40	DMF-D_7			3,18 (6H, b-CH_3) and 3,31 (6H, a-CH_3)	8,40 (2H, br s)
VIIIa	+23	DMSO-D_6	8,77 (2H, s)	3,62 [4H, s, 2-(α'-CH_2)]		
	-40	DMF-D_7	9,13 (2H, br s)	3,88 [4H, br s, 2-(α'-CH_2)]		
VIIIb	+23	DMSO-D_6	8,76 (2H, br s)	3,33 [4H, t, 2-(α'-CH_2)], $^3J_{\alpha'\text{-}CH_2,\alpha''\text{-}CH_2}$ = 5,8; 1,83 (2H, quintet, α''-CH_2)		

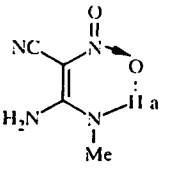
*Here and subsequently the spatial disposition of the proton is shown (see formula in text).

†Here and subsequently the spatial disposition of the CH_3 group is shown.

‡Partially split singlet.

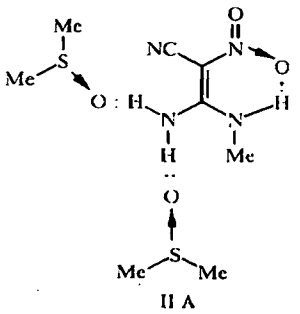
group signals of the NMe_2 substituent was made analogously. Saturation of the low field signal at 3.13 ppm led to a significant (30%) increase in the intensity of the CH fragment signal. However it was almost unchanged on saturating the second signal at 3.00 ppm. Hence it follows that the low field signal belongs to the CH_3 group *a*-located relative to this proton and the high field signal to the b-CH_3 group. Regrettably, it was not possible to obtain further information on the configuration of compound (I) from ^{13}C NMR spectra (in DMSO-D_6) of a labelled sample of it containing a $^{15}NHMe$ fragment, which was synthesized specially according to [1] using $Me^{15}NH_2$. In this case the heteroconstant $^3J_{15_N13_C}$ proved to be close to zero. Parameters of this spectrum were δ_{NH} = 9.82 (d.q), $^1J_{15_{NH}}$ = 94.8 Hz, $J_{NMe,NH}$ = 3.9 Hz, δ_{NMe} = 2.92 (d.d), $^2J_{15_{N,Me}}$ = 2 Hz.

The configuration of α-methylamino-α-amino-β-cyano-β-nitromethylene (II) was determined in a similar manner.



II

In the low field region of the ^1H NMR spectrum of compound (II) taken in DMSO-D_6 at 20°C, there was a signal for the NH group proton as a quartet at 8.76 ($^3J_{NH,Me}$ = 5 Hz) and a broad signal for the protons of the NH_2 group at 8.13 ppm. In the spectrum taken in DMF-D_7 at 20°C, the values of δ_{NH} and δ_{NH_2} were close to those given above (8.88 and 8.38 ppm respectively), but at −40°C a small shift towards low field was observed and δ_{NH} = 9.10 and δ_{NH_2} = 8.56 ppm. The fairly low field position of the NH group signal suggests that in this case an IMB exists between the NHMe and NO_2 substituents although the data given may indicate a certain weakening of this bond in enediamine (II) compared with the bond in amidine (I). It seems probable that the large bulk of the second α-substituent in compound (I) assists the coming together of the NH and NO_2 groups and as a result strengthens the hydrogen bond. An experiment using NOE showed that irradiation of the signal of the NMe fragment (2.86 ppm) of compound (II) leads to an increase in the intensity of the signals of the NH group (by 8%) and the NH_2 group (by 3.5%). In this case also no additional information was obtained on analyzing the ^{13}C NMR spectrum (DMSO-D_6) of a labelled sample containing a $^{15}NHMe$ fragment: $^3J_{15_N13_C}$ = 0 Hz, δ_{NH} = 8.76 (d.q), δ_{NMe} = 2.85 ppm (d.d), $^1J_{15_{NH}}$ = 96 Hz, $^2J_{15_{NMe}}$ = 1.5 Hz, $^3J_{NH,Me}$ = 4.7 Hz. However a problem arises which requires special consideration when considering the structure of enediamine (II). In reality, it is not clear why the IMB arises from the NHMe group and not from NH_2. We suggest that the presence of the methyl substituent sterically hinders the formation of intermolecular hydrogen bonds with the solvent and the situation most favorable energetically is that in which one of the reactive groupings participates in an intramolecular and the other in an intermolecular hydrogen bond [see (IIA)].

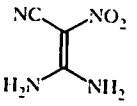


II A

Experiments were carried out plotting the ^1H NMR spectra in saturated and dilute solution to obtain support for the proposed interpretation. In the latter case, fission of intermolecular and retention of the IMB might be expected. Acetonitrile-D_3 was selected as solvent for these experiments with a small addition of DMSO-D_6 to increase the solubility of compound (II). The ^1H NMR spectrum was taken for saturated and dilute (1:10, 1:100, and 1:250) solutions. Analysis of the results obtained showed that on 10-fold dilution the signal for the NH group proton was shifted towards high field by 0.3 ppm (from 8.48 to 8.22 ppm). On further dilution the chemical shift was practically unchanged (8.18 ppm). At the same time, the NH_2 group signal was shifted from 7.76 to 7.19 (10-fold dilution) then to 7.05 ppm (100-fold dilution), and only after 250-fold dilution was its position unchanged. For the NHMe group $\Delta\delta$ was 0.3 and for the NH_2 group 0.71 ppm which supports the probable

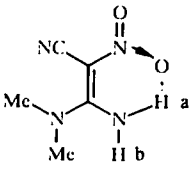
structure (IIA) in which the proton of the NH group is included in an intramolecular and the NH_2 group protons in intermolecular hydrogen bonds.

A similar picture was observed on diluting solutions of α,α-diamino-β-cyano-β-nitroethylene (III).

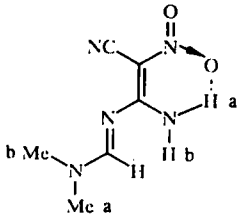


III

In the spectrum of this compound taken in acetonitrile-D_3 with several drops of DMSO-D_6 added, all four protons were displayed as a general signal at 7.60 ppm which on dilution 10, 100, and 250 times was shifted towards high field to 7.22, 7.05, and 7.05 ppm respectively, i.e., $\Delta\delta$ was 0.55 ppm. The results suggest that the spatial interaction referred to above between the α substituents in enediamines prove to have a significant influence on the strength of the IMB between the NH and NO_2 groups. The spectra of α-dimethylamino-α-amino-β-nitroethylene (IV) and α-dimethylaminomethyleneamino-α-amino-β-cyano-β-nitroethylene (V) were studied to test this hypothesis. In these compounds the α-amino group is adjacent to a dimethylamino group and an amidine fragment.



IV

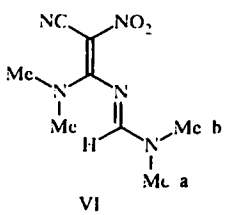


V

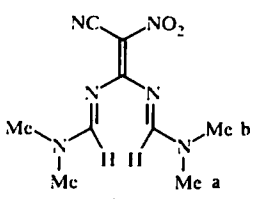
In the low field region of the spectrum of compound (IV) (DMSO-D_6) there were two strongly broadened signals at 8.22 and 8.63 for the NH group protons and also a narrow signal for the six protons of the methyl substituents of the NMe_2 group at 2.86 ppm. Similarly, for the spectrum taken in DMF-D_7 at 20°C the chemical shifts of the NH_2 group protons were 8.40 and 8.84, and at −40°C they were 8.60 and 9.01 ppm, the low field signal being broadened to a significantly lesser extent. In other words the situation of the primary amino group is totally different from that considered above for compounds (II) and (III). It is possible that the increase in volume of the second α substituent contributes to an increase in the energy of the IMB between the NH and NO_2 groups (the NH group proton participating in the IMB corresponds to the low field signal).

The broadened signals of equal intensity at 9.05 and 9.32 ppm were observed in the spectrum of compound (V) taken in DMSO-D_6, as in the case of (III), which also points in favor of the existence of an IMB. An experiment using NOE confirmed this proposal and enabled the mutual orientation of the NH_2 group and the amidine fragment to be determined. On irradiating the high field signal of the NH group proton at 9.05 ppm, a clear increase (10%) was observed in the intensity of the proton signal of the −CH fragment at 8.25 ppm, which was changed very insignificantly on irradiating the low field signal at 9.32 ppm. The NMe_2 group in the spectrum of compound (V) was represented as two singlets at 3.08 and 3.14 ppm (DMSO-D_6): Irradiation of the low field signal led to a significant (17%) increase in the intensity of the =CH fragment proton (α-orientation) but only an insignificant change was seen on irradiating the high field signal. Consequently the favored configuration for the majority of the unsaturated diamines studies is that in which the molecule is stabilized by an IMB between a proton on a nitrogen atom and the β nitro group. The presence of such a bond enables the configuration of these compounds to be determined unequivocally.

In contrast to the diamines considered above, the determination of the configuration of compounds (VI) and (VII) containing in their structures no protons capable of forming hydrogen bonds was hampered significantly.



VI



VII

TABLE 2. Data of ^{13}C NMR Spectra (DMSO-D_6) of Compounds (I)-(VII) (δ, ppm, coupling constant J, Hz)

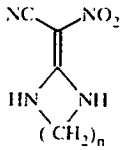
Compound	C(α)	C(β), s	CN, s	α-NHCH$_3$, α-N(CH$_3$)$_2$	Amidine fragment	
					N(CH$_3$)$_2$ q m	CH, d m
I	164,0 (d), $^3J_{C(\alpha),H}$ = 6,1	96,7	116,4	29,4 (q), $^1J_{C,H}$ = 126,7	34,6, $^1J_{C,H}$ = 140,0 (a*) and 40,8, $^1J_{C,H}$ = 141,0 (b)	157,6, $^1J_{C,H}$ = 184,0
II	157,0 (s)	92,3	115,0	29,1 (q d), $^1J_{C,H}$ = 141,1		
III	158,5 (s)	92,4	114,8			
IV	158,6 (s)	89,9	116,9	40,3 (q q), $^1J_{C,H}$ = 140,4		
V	164,8 (d), $^3J_{C(\alpha),H}$ = 6,9	99,0	115,6		35,0, $^1J_{C,H}$ = 138,7 (a) and 41,2, $^1J_{C,H}$ = 139,6 (b)	158,8, $^1J_{C,H}$ = 181,6
VI	165,2 (m)	91,3	117,3	39,2 (br s)), 42,1 (br s)	35,9, $^1J_{C,H}$ = 140,3 (a) and 41,6, $^1J_{C,H}$ = 140,4 (b)	162,3, $^1J_{C,H}$ = 183,6
VII	172,0 (t), $^3J_{C(\alpha),H}$ = 11,5	103,2	117,0		35,5, $^1J_{C,H}$ = 141,0 (a) and 41,3, $^1J_{C,H}$ = 139,7 (b)	160,2, $^1J_{C,H}$ = 185,4

*Here and subsequently the spatial disposition of the CH_3 group is given.

In the spectrum of α-dimethylaminomethyleneamino-α-dimethylamino-β-cyano-β-nitroethylene (VI) (DMSO-D_6) two sets of signals were present for the methyl protons of the NMe_2 groups as narrow singlets at 3.14 and 3.24 and strongly broadened signals at 3.11 and 3.17 ppm (each of 3 proton units in intensity) and also a signal for the =CH fragment proton at 8.22 ppm. An NOE experiment showed that the intensity of the latter increased by 215 on irradiating the singlet at 3.24 (the CH and the NMe_2 groups are spatially close) but was completely unchanged on irradiating the singlet at 3.14 ppm. The character of the spectrum was retained on plotting in a mixture (1:2) of DMSO-D_6–acetone-D_7, however, the narrow singlets of the methyl substituent protons were split little by long-range coupling of these protons with the CH group protons: chemical shift of NMe-b 3.20, $^4J_{NMe\text{-}b,CH}$ = 0.9 Hz, chemical shift of NMe-*a* 3.32 ppm, $^4J_{NMe\text{-}a,cH}$ = 0.5 Hz. The singlet of the CH group proton was also split weakly. Consequently the narrow signals were assigned to the NMe_2 group protons of the amidine fragment and broadened to the protons of the enamine NMe_2 group (as a result of partial inhibition of rotation relative to the single bond to CN). We noted that the signals of this NMe_2 group were significantly narrowed in the spectrum taken at −40°C (DMF-D_7), i.e., rotation relative to the C–NMe_2 bond is practically inhibited under these conditions. This suggests that the determining factor for the compound under consideration is steric, and the compound is most stable at a cis disposition of the small CN group and the more bulky NMe_2 group.

The spectrum of α,α-bisdimethylaminomethylenamino-β-cyano-β-nitroethylene (VII) (DMSO-D_6) contains one set of signals, two singlets of equal intensity at 3.10 and 3.19 and a singlet at 8.24 ppm (=CH), their relative intensities being 3:3:1 respectively. Application of NOE enabled assignment of the 3.10 ppm signal to the b methyl substituent and the 3.19 ppm signal to the b methyl substituent and the 3.19 ppm signal to the substituent. At −40°C (DMF-D_7) the signal of the CH group proton was broadened significantly due to inhibition of rotation of the amidine fragment. Construction of molecular models showed that the most favorable conformation for diamidine (VII) was that in which the protons of the =CH fragments were close together.

The information obtained on considering the spectra of the cyclic enediamines 2-(cyanonitromethylene)imidazolidine (VIIIa) and 2-(cyanonitromethylene)-1,2,3,4,5,6-hexahydropyrimidine (VIIIb) was sparse.



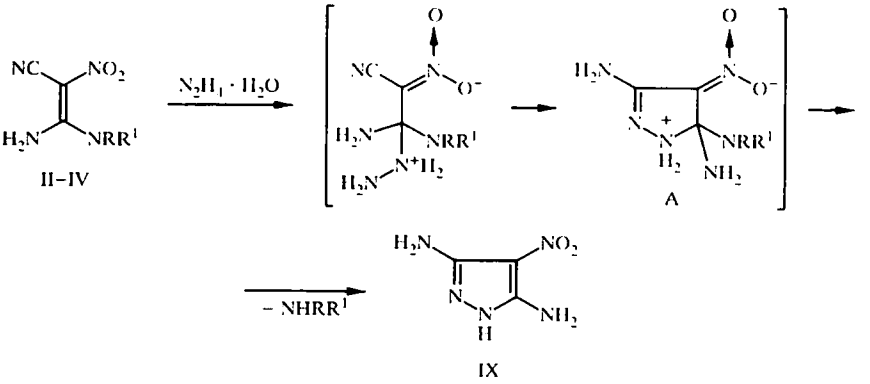
VIII a n = 2, b n = 3

A sharp singlet was observed in the spectrum compound (VIIIa) (DMSO-D_6) at 3.62 corresponding to the protons of two CH_2 groups and the broadened signal at 8.77 ppm was assigned to the NH group protons. A similar spectrum was characteristic for diamine (VIIIb) and differed in the presence of two signals at 1.83 (1H, quintet) and 3.32 (4H, t) for the protons of the pyrimidine ring. It also contained a signal at 8.76 ppm (2H, br.s, NH proton).

The ^{13}C NMR spectra of all the noncyclic enamine and enediamines investigated in the present work have been studied (Table 2). It followed from analysis of the size of the chemical shifts that the signal of the $C_{(\alpha)}$ carbon atom was observed at significantly lower field than the signal of the $C_{(\beta)}$ carbon atom ($\Delta\delta C_{(\alpha)}C_{(\beta)}$ = 60 ppm) which is caused by the mesomeric effect of the electron-donating substituents in the α position and the electron-accepting action of the substituents in the β position. On going from enediamine (III) with two amino groups at the $C_{(\alpha)}$ carbon atom to the monoamidine derivative (V) and then to the diamidine (VII) a sequential displacement was observed for the signals of the $C_{(\alpha)}$ Δδ(V)-(III) = 6.3, Δδ(VII)-(V) = 7.2, and for $C_{(\beta)}$ Δδ(V)-(III) = 6.6 and Δδ(VII)-(V) = 4.2 ppm. The mesomeric effect of the substituent also showed on the carbon atom of the CN group but to a significantly lesser extent. Here Δδ(V)-(III) = 0.8 and Δδ(VII)-(V) = 1.4 ppm. Comparison of the chemical shifts of the $C_{(\alpha)}$ atom of the compounds investigated (Table 2) showed that their values were very close to one another in the enediamine series (II)-(III)-(IV) (156.0-158.6 ppm) and in the amidino-enediamine series (I)-(V)-(VI) (164.0-165.2 ppm), i.e., the change in the volume of the substituent on the amino group did not affect the chemical shift of $C_{(\alpha)}$. A different situation was observed for the $C_{(\beta)}$ atom. On replacing the α position substituent NH_2 by NHMe and then by NMe_2 the $C_{(\beta)}$ atom signal was displaced towards high field and Δδ(IV)-(III) = Δδ(II)-(III) + Δδ(IV)-(II) = −2.5, and Δδ(V)-(VI) = Δδ(VI)-(I) + Δδ(I)-(V) = −7.7 ppm.

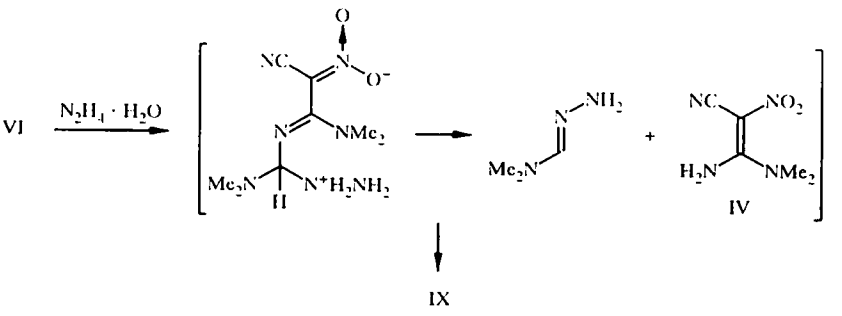
The sizes of the chemical shifts of the NHMe and N=C–NMe_2 groups remained practically unchanged in the enediamines investigated. In compound (IV) the NMe_2 group was represented by one narrow signal at 40.3 ppm and in compound (VI) by two strongly broadened signals at 39.2 and 42.1 ppm.

As already mentioned, the multifunctional push–pull enamines (I)-(VI) are promising starting materials for the synthesis of heterocyclic compounds. The problem considered in the present work was whether the structural changes in the enamine influence their interaction with hydrazine hydrate. It turned out that the noncyclic representatives (II)-(IV) interact with $N_2H_4 \cdot H_2O$ in one direction leading to 3,5-diamino-4-nitropyrazole (IX) in high yield. It is obvious that a true interpretation of these results requires further detailed investigation, however, the most probable mechanism for the processes occurring may be summarized in the following way:

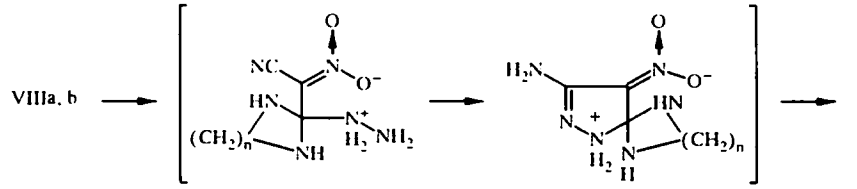


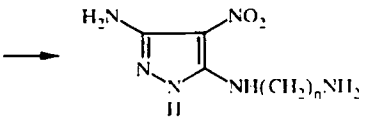
In other words, stabilization of intermediate (A) is effected preferably by elimination of the more bulky substituent, which in its turn is more favorable for reducing steric hindrance. We have observed such a phenomenon previously when closing a five-membered pyrrole ring in the synthesis of pyrrolo[1,2-*a*]indoles [4].

The situation is more complex for enamidines since it is known that transamination of the amidine fragment occurs at a more rapid rate than for an unsubstituted or substituted amino group [5]. On the other hand, the investigation carried out by us recently on the transamination of enamines and enamidines considered in the present work [1] suggests that attack at the *meso* carbon atom of the amidine grouping is a characteristic of this system. Consequently, for compound (VI), for example, the process may be described by the following scheme:



After the formation of the intermediate compound (IV) the reaction proceeds further by the former scheme and the analogous formation of pyrazole (IX) is also possible for other enamidines such as (I) and (VII). It is clear that similar mechanisms are not effected for the cyclic enamines (VIIIa,b). In reality the corresponding 3-amino-4-nitro-5-(R-amino)pyrazoles (Xa,b) are formed on heating the cyclic enamines with hydrazine hydrate, which confirms the considerations set out above to a certain extent.





X.a, b

a n = 2, b n = 3

EXPERIMENTAL

The IR spectra were taken on a Perkin-Elmer spectrophotometer in Nujol mulls. The NMR spectra were recorded on an Oxford Unity 400 spectrometer, internal standard being TMS. The mass spectra were obtained on a Varian SSQ 700 spectrometer with direct insertion of the sample into the ion source. A check on the purity of products and the progress of reactions was effected by TLC on Silufol UV 254 plates.

3,5-Diamino-4-nitropyrazole (IX). Hydrazine hydrate (3.2 ml: 64.1 mmole) was added with vigorous stirring to a suspension of compound (I)-(VII) (12.8 mmole) in methanol (20 ml) and the mixture boiled for 45 min. The reaction mxture was kept for 2 h at room temperature and then cooled to 5°C when a bright red crystalline precipitate of product (IX) separated. Yield was 85-95%, mp 261°C (methanol). M^+ 143. IR spectrum: 3300, 3210, 3125 (NH, NH_2), 1658, 1455, 980 cm^{-1}. Found, %: C 25.21; H 3.58; N 49.12. $C_3H_5N_5O_2$. Calculated, %: C 25.17; H 3.49; N 48.95.

3-Amino-5-aminoethylamino-4-nitropyrazole (Xa). Hydrazine hydrate (3.2 ml: 64.1 mmole) was added with vigorous stirring to a suspension of compound (VIIIa) (13.0 mmole) in methanol (20 ml) and the mixture boiled for 30 min. The reaction mixture was kept at room temperature for 2 h and then cooled to 5°C. A red crystalline precipitate of product (Xa) (1.9 g) was obtained. Yield was 79% of mp 172°C (isopropanol). M^+ 186. IR spectrum: 3350-3100 (NH, NH_2), 1665, 1410, 970 cm^{-1}. Found, %: C 32.37; H 5.22; N 44.98. $C_5H_{10}N_6O_2$. Calculated, %: C 32.25; H 5.37; N 45.16.

3-Amino-5-aminopropylamino-4-nitropyrazole (Xb). Hydrazine hydrate (3.2 ml: 64.1 mmole) was added with vigorous stirring to a suspension of compound (VIIIb) (11.9 mmole) in methanol (20 ml) and the mixture boiled for 30 min. The reaction mixture was kept at room temperature for 2 h and cooled to 5°C. A red crystalline precipitate of product (Xb) (1.7 g) was obtained. Yield was 71% of mp 148°C (isopropanol). M^+ 200. IR spectrum: 3320-3150 (NH, NH_2), 1648, 1476, 1004 cm^{-1}. Found, %: C 35.86; H 6.08; N 41.84. $C_6H_{12}N_6O_2$. Calculated, %: C 36.00; H 6.00; N 42.00.

REFERENCES

1. V. A. Makarov, A. L. Sedov, O. S. Anisimova, and V. G. Granik, Khim. Geterotsikl. Soedin., No. 6, 811 (1996).
2. V. A. Makarov, N. P. Solov'eva, O. S. Anisimova, and V. G. Granik, 211th American Chemical Society National meeting, 1996, Abstracts, ORGN78.
3. J. Clark, I. Gelling, I. W. Southon, and M. S. Morton, J. Chem. Soc., No. 3, 498 (1970).
4. S. Yu. Ryabova, Yu. I. Trofimkin, L. M. Alekseeva, I. F. Kerbnikova, G. Ya. Shvarts, and V. G. Granik, Khim.-farm. Zh., No. 9, 22 (1995).
5. V. G. Granik, E. N. Dozorova, N. B. Marchenko, L. I. Budanova, V. A. Kuzovkin, and R. G. Glushkov, Khim.-farm. Zh., No. 10, 1249 (1987).