3. O. E. Nasakin, V. V. Alekseev, A. Kh. Bulai, and S. Yu. Sil'vestrova, Khim. Geterotsikl. Soedin., No. 8, 1137 (1980).
4. G. C. Levy and G. L. Nelson, Carbon-13 Nuclear Magnetic Resonance for Organic Chemists, Wiley, New York (1972).
5. F. de Roy Johnson and W. C. Jankowski, Carbon-13 NMR Spectra, Wiley-Interscience, New York (1972).
6. F. Wehri and T. Wirthlin, Interpretation of ^{13}C NMR spectra, London (1976).

MASS-SPECTROMETRIC BEHAVIOR OF 5-SUBSTITUTED 1-ALKYLIDENEIMINO-2-AMINOPYRROLES AND THEIR 2,5- AND 4,5-DIHYDRO DERIVATIVES*

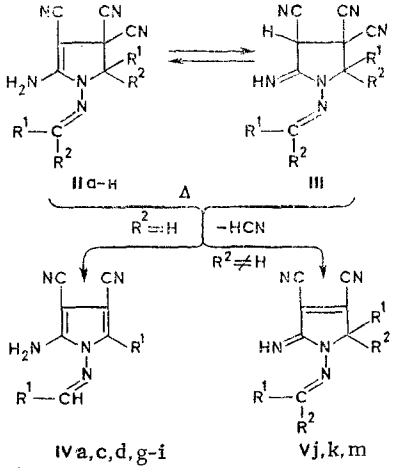
P. B. Terent'ev, O. E. Nasakin, V. V. Alekseev, A. G. Kalandarishvili, and M. Sh. Kaviladze

UDC 543.51:547.741'743

A comparative analysis of the mass spectra of 5-substituted 1-alkylideneimino-2-amino-3,4-dicyanopyrroles and their 2,5-dihydro and 4,5-dihydro derivatives makes it possible to find the typical fragmentation pathways that characterize each group of compounds and to detect the presence of tautomeric amino-imino forms in the gas phase.

In our previous communications we demonstrated that the reaction of sym-tetracyanoethane (I) with azomethines leads to the formation of 1,5-disubstituted 2-amino-3,4,4-tricyano-4,5-dihydropyrroles [1, 2], while the reaction of the same cyanide I with azines makes it possible to obtain 5-substituted 1-alkylideneimino-2-amino-3,4,4-tricyano-4,5-dihydropyrroles (II) in high yields [3]; it was established by NMR spectroscopic methods that the presence of tautomeric imino form III (Scheme 1) cannot be detected in solutions by spectral methods. The Δ^2-pyrrolines obtained undergo dehydrocyanation even in the case of slight heating; the 5-mono-

Scheme 1



II—Va-i R^2=H; a R^1=CH_3; b R^1=C_2H_5; c R^1=*n*-C_3H_7; d R^1=*iso*-C_3H_7; e R^1=*iso*-C_4H_9; f R^1=*n*-C_6H_{13}; g R^1=C_6H_5; h R^1= 2-furyl, i R^1= 3-pyridyl; j R^1=R^2=CH_3; k R^1=CH_3, R^2=C_2H_5; *l* R^1=R^2=C_2H_5; m R^1+R^2=—$(CH_2)_5$—

*Communication 5 from the series "sym-Tetracyanoethane in the synthesis of heterocycles." See [1] for communication 4.

M. V. Lomonosov Moscow State University, Moscow 117234. I. N. Ul'yanov Chuvash State University, Cheboksary 428015. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1071-1075, August, 1983. Original article submitted October 28, 1982.

 0009-3122/83/1908-0858$07.50

TABLE 1. Intensities of the Peaks of the Characteristic Ions in the Mass Spectra of Pyrroles IV (%, Σ_{39})

Compound	W_M	F_1	F_2	F_3	F_4	F_5
IVa	25,9	4,1	9,9	8,0	1,9	—
IVc	6,0	3,6	1,1	14,8	2,5	1,6
IVd	8,8	3,1	1,0	25,0	1,2	3,8
IVg	18,3	—	—	25,4	8,8	8,2
IVh	14,8	—	—	37,0	6,4	7,8
IVi	19,1	—	—	8,1	6,3	9,3

TABLE 2. Intensities of the Peaks of the Characteristic Ions in the Mass Spectra of Δ^3-Pyrrolines V ($\%\Sigma_{39}$)

Compound	W_M	F_3	F_4	F_6	F_7	F_8	F_9
Vj	13,4	16,0	5,3	11,2	11,2	2,7	2,7
Vk	12,3	4,3	1,8	11,3	1,6	7,0	2,1
Vm	24,7	2,8	3,6	*	*	1,7	—

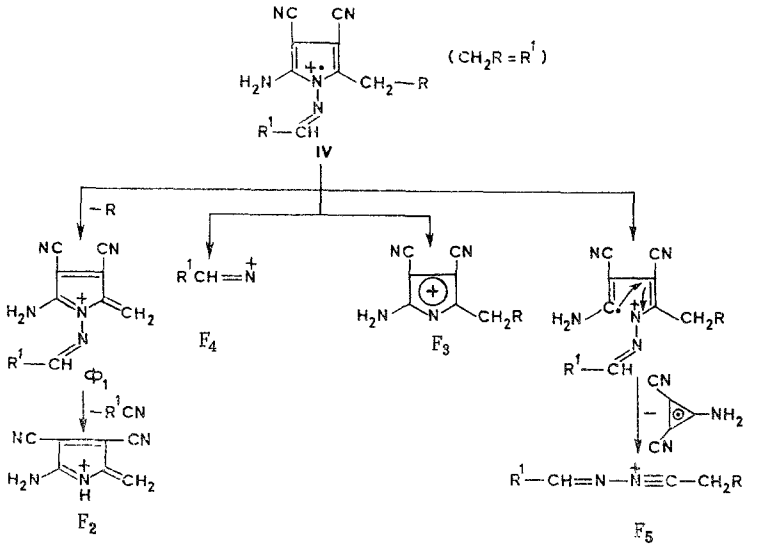
*Note: $[M-C_4H_9]^+$ (3.4%) and $[M-C_3H_6]^+$ (2.8%).

substituted compounds give pyrroles IV, while Δ^3-pyrrolines V were obtained in the dehydrocyanation of the 5,5-disubstituted Δ^2-pyrrolines. The formation of V can only be conceived of as being products of tautomeric form III.

It has been recently shown in a number of studies that the existence in the gas phase of certain organic compounds of their tautomeric forms, which are absent in solutions, can be detected by mass-spectrometric methods [4-6]. In this connection, we made a detailed study of the mass-spectrometric behavior of II, IV, and V in which we directed our attention to the possibility of the existence of some Δ^2-pyrrolines in the gas phase in tautomeric imino form III.

The processes involved in the dissociative ionization of pyrroles IV (Scheme 2) are characterized by "benzyl" cleavage of the side C–C bond (when R = alkyl) to give stable F_1 ions that subsequently lose a nitrile molecule (to give the F_2 ion).

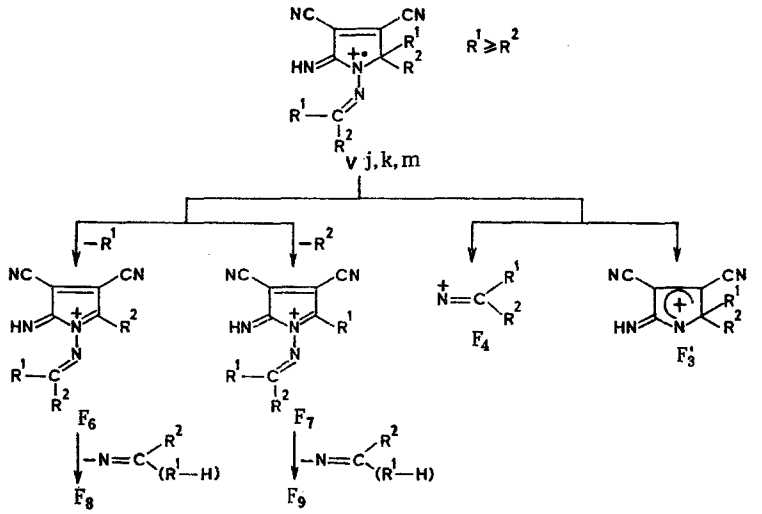
Scheme 2



This pathway is typical for the fragmentation of the molecular ions of most alkylpyrroles [7, 8]. A second important process in the fragmentation of the molecular ions of pyrroles IV is cleavage of the N–N bond, which leads to F_3 and F_4 ions. This type of frag-

mentation characterizes hydrazine derivatives [9]. Finally, F_5 ions, the formation of which is associated with characteristic opening of the pyrrole ring [10] is also observed (see Table 1). The ion peaks of this type are particularly intense in the mass spectra of aryl- and hetarylpyrroles IVg-i, in the fragmentation of which F_1 and F_2 ions are not formed. The overall intensity of the peaks of the M^+ and F_1-F_5 ions generally exceed 40% of the total ion current, which indicates the high selectivity of the fragmentation. On the other hand, the loss of the R^1 or R^2 substituent entirely (to give F_6 and F_7 ions, Scheme 3 and Table 2), which is typical for 2-alkylpyrrolines and pyrrolidines [10, 11], is more characteristic for the fragmentation of the molecular ions of Δ^3-pyrrolines V.

Scheme 3



The subsequent fragmentation of the F_6 and F_7 ions is associated with elimination of the azomethine fragment with the transfer from it of one hydrogen atom to the heteroring nitrogen atom; this is typical for N-alkylpyrroles [10, 12]. The overal percentage of the M^+ and F_3-F_9 ions also constitutes 40% of the total ion current.

An analysis of the mass spectra of Δ^2-pyrrolines II shows that, on the one hand, their molecular ions undergo the typical (for pyrrolines [11]) fragmentation with the loss of substituent R (to give the F_{11} ion, Scheme 4 and Table 3) or undergo the characteristic (for hydrazines [9]) cleavage of the N–N bond (to give the F_{10} ion). However, the principal pathway of fragmentation of such compounds under electron impact (as in the case of thermal action) is elimination of a molecule of hydrocyanic acid; the formation of M' and M'' ions with both pyrrole and Δ^3-pyrroline structures is possible in this case if some of the molecules of II existed in the tautomeric 2-iminopyrrolidine form in the gas phase.

Scheme 4

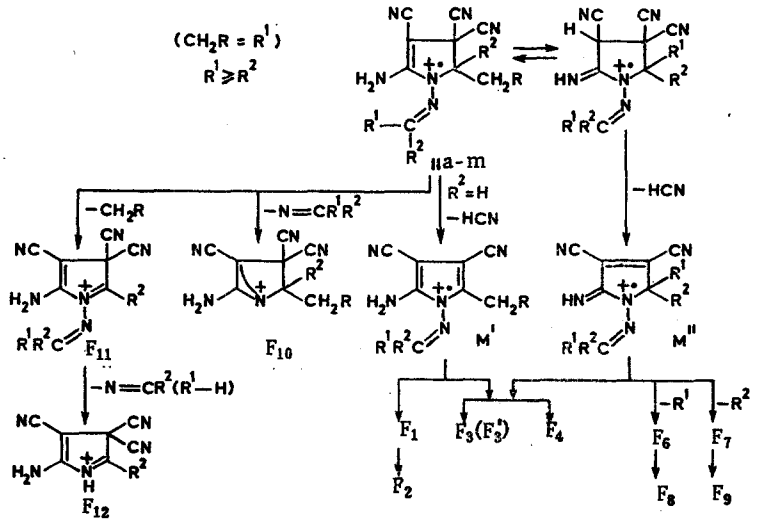


TABLE 3. Intensities of the Peaks of the Characteristic Ions in the Mass Spectra of Δ^2-Pyrrolines II ($\%\Sigma_{39}$)

Compound	F_M	M'(M")	F_1	F_2	F_3	F_4	F_6	F_8	F_{10}	F_{11}	F_{12}	$F_6 : F_1$
IIa	15,6	18,2	15,9	21,7	4,3	8,7	—	—	8,0	—	—	0 : 1
IIb	2,9	6,5	0,8	6,2	20,8	3,7	—	—	8,1	1,5	1,9	0 : 1
IIc	3,4	9,4	8,1	11,4	13,8	8,6	8,2	7,1	8,2	3,5	5,7	1 : 1
IId	1,5	2,0	1,8	4,5	11,3	4,4	3,2	1,3	3,2	1,8	7,5	1,8 : 1
IIe	1,7	3,2	7,0	8,2	0,7	2,3	1,2	—	1,2	0,2	0,6	0,2 : 1
IIf	4,5	6,5	3,4	8,1	3,3	2,2	2,0	0,3	2,0	0,6	0,8	0,6 : 1
IIh	1,6	5,5	—	—	42,0	8,9	—	—	8,0	—	—	0 : 1
IIj	1,4	4,8	—	—	7,1	1,6	6,5	3,4	1,6	0,9	0,4	1 : 0
IIk*	0,9	5,1	—	—	10,2	2,1	7,4	3,6	1,9	0,8	1,2	1 : 0
IIl†	0,7	4,1	—	—	12,8	5,1	7,1	2,3	1,1	1,5	5,0	1 : 0
IIm†	0,3	8,3	—	—	1,4	4,5	2,2	1,9	0,8	—‡	1,2	1 : 0

*F_7 (1.0%), F_9 (2.9%).
†F_7 (3.0%).
‡$[M-C_4H_9]^+$ (1.6%), $[M-C_3H_7]^+$ (1.5%).

TABLE 4. Mass Spectra* of Δ^2-Pyrrolines II, Pyrroles IV, and Δ^3-Pyrrolines

Compound	m/z (relative intensities, %)
IIa	214 (88), 188 (18), 187 (11), 179 (100), 146 (24), 145 (11), 129 (15), 104 (11), 71 (11), 70 (13), 41 (18)
IIb	242 (13), 215 (38), 186 (46), 159 (100), 145 (30), 132 (32), 105 (16), 77 (10), 56 (16), 42 (23), 41 (24)
IIc	270 (38), 243 (67), 214 (58), 200 (58), 173 (100), 158 (40), 145 (83), 133 (52), 131 (60), 70 (62), 43 (77)
IId	270 (13), 243 (29), 200 (28), 173 (100), 159 (40), 158 (67), 71 (49), 70 (38), 57 (75), 55 (67), 43 (92)
IIe	298 (9), 271 (28), 228 (84), 214 (12), 187 (8), 158 (9), 145 (100), 84 (27), 57 (32), 43 (22), 41 (26)
IIf	354 (46), 327 (80), 326 (53), 256 (42), 242 (25), 215 (41), 145 (100), 112 (28), 83 (23), 56 (41), 53 (59)
IIh	318 (3), 291 (11), 224 (19), 197 (100), 169 (5), 142 (5), 115 (8), 96 (10), 95 (8), 94 (15), 69 (8)
IIj	242 (16), 215 (68), 200 (91), 183 (24), 173 (51), 159 (100), 146 (25), 145 (47), 135 (33), 121 (24), 56 (24)
IIk	270 (7), 243 (50), 214 (73), 197 (23), 187 (18), 173 (100), 159 (28), 146 (24), 145 (36), 70 (21), 42 (49)
IIl	298 (4), 271 (33), 269 (12), 242 (56), 188 (31), 187 (100), 171 (39), 159 (18), 158 (36), 84 (40), 56 (23)
IIm	322 (10), 295 (100), 252 (36), 240 (26), 238 (41), 213 (28), 145 (28), 96 (54), 95 (24), 55 (38), 41 (47)
IVa	187 (100), 161 (18), 146 (45), 145 (36), 118 (82), 104 (13), 91 (15), 77 (32), 76 (14), 43 (37), 41 (15)
IVc	243 (34), 214 (25), 173 (100), 159 (36), 158 (11), 145 (74), 133 (15), 132 (11), 131 (40), 77 (12), 70 (15)
IVd	243 (27), 228 (13), 173 (100), 159 (39), 158 (13), 157 (8), 133 (17), 132 (10), 131 (6), 105 (7), 77 (6)
IVg	311 (45), 208 (43), 207 (100), 180 (17), 153 (6), 129 (5), 104 (32), 103 (9), 79 (7), 77 (21), 52 (5)
IVh	231 (40), 197 (100), 169 (9), 142 (8), 115 (4), 95 (12), 94 (21), 77 (4), 69 (5), 66 (5), 39 (14)
IVi	313 (50), 208 (100), 181 (20), 155 (5), 154 (10), 145 (8), 106 (100), 104 (50), 103 (5), 54 (8), 52 (5)
Vj	215 (71), 200 (71), 183 (22), 174 (18), 173 (36), 159 (100), 145 (17), 144 (8), 132 (32), 56 (32), 42 (28)
Vk	243 (5), 214 (100), 111 (28), 109 (31), 97 (54), 95 (54), 85 (40), 83 (59), 81 (47), 71 (81), 55 (82)
Vm	295 (100), 294 (13), 279 (10), 253 (13), 247 (25), 240 (15), 238 (25), 213 (14), 96 (18), 55 (13), 41 (15)

*The molecular-ion peak and the 10 most intense peaks are presented. The peaks of the isotope ions are excluded.

Since, as we have shown above, the molecular ions of these two groups of compounds dissociate via various pathways, one can estimate the probability of the formation in the gas phase of pseudomolecular M' and M" ions by comparing the relative percentages of the F_1 and F_6 (F_7) ions in the total current. It follows from the data in Table 3 that F_6 ions are observed in the mass spectra of Δ^2-pyrrolines that contain aliphatic $C_{(3)}$-$C_{(6)}$ radicals in the

5 position and are not observed for the first members of the series. At the same time, as one should have expected, F_1 ions are absent in the mass spectra of 5,5-disubstituted Δ^2-pyrrolines IIj-m.

Thus an analysis of the mass spectra of 2-amino-Δ^2-pyrroline derivatives II makes it possible to detect the presence in the gas phase of these compounds of tautomeric 2-imino forms that are not identifiable by spectral methods in solutions.

EXPERIMENTAL

The synthesis of II, IV, and V was described in [3]. The mass spectra were obtained with an MAT-212 spectrometer with direct introduction of the substances into the ion source at vaporization temperatures 20-25°C below the melting (decomposition) points of the preparations and at an ionization energy of 70 eV. The difference in the mass spectra recorded at different times did not exceed 10-15% (relative).

LITERATURE CITED

1. O. E. Nasakin, V. V. Alekseev, P. B. Terent'ev, A. Kh. Bulai, and M. Yu. Zablotskaya, Khim. Geterotsikl. Soedin., No. 8, 1067 (1983).
2. O. E. Nasakin, V. K. Promonenkov, Yu. P. Belov, A. Kh. Bulai, and S. Yu. Sil'vestrova, Khim. Geterotsikl. Soedin., No. 3, 402 (1981).
3. O. E. Nasakin, V. V. Alekseev, P. B. Terent'ev, A. Kh. Bulai, and M. Yu. Zablotskaya, Khim. Geterotsikl. Soedin., No. 8, 1062 (1983).
4. N. A. Klyuev, I. S. Shpileva, L. I. Medvedeva, G. N. Lyapunova, and N. P. Bednyagina, Khim. Geterotsikl. Soedin., No. 11, 1506 (1981).
5. I. L. Holmes and F. P. Lossing, Org. Mass Spectrom., 14, 512 (1979).
6. Ya. V. Rashkes, R. F. Ambartsumova, V. A. Saprykina, and N. K. Rozhkova, Zh. Org. Khim., 17, 614 (1981).
7. O. N. Porter and J. Baldas, Mass Spectrometry of Heterocyclic Compounds, Wiley-Interscience, New York (1971), p. 325.
8. H. Budzikiewicz, C. Djerassi, A. H. Jackson, and G. W. Kenner, J. Chem. Soc., No. 12, 1949 (1964).
9. M. I. Podgornaya, S. A. Nekhorosheva, I. G. Zenkevich, V. A. Isidorov, and B. V. Ioffe, Atlas of the Mass Spectra of Organic Compounds [in Russian], Vol. 1 (1977).
10. H. Budzikiewicz, C. Djerassi, and D. H. Williams, Mass Spectrometry of Organic Compounds, Holden-Day, New York (1967), p. 597.
11. D. J. Pedder, H. M. Falles, T. Jacnni, M. Blum, J. McConnel, and R. M. Grewe, Tetrahedron, 32, 2275 (1976).
12. R. G. Cooks, F. L. Warren, and D. H. Williams, J. Chem. Soc., C, No. 2, 286 (1967).