Resonance capture of electrons by substituted pyrazoline molecules

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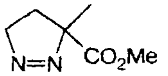
The negative ion mass spectra and photoelectron spectra of substituted pyrazolines were studied. A correlation between the ionization energy of the highest occupied molecular orbital and the yield of $[MeNHNH_2^-]$ ions was found. Isomerization of molecular negative ions was studied by resonance electron capture mass spectrometry.

Key words: negative ions, resonance electron capture, mass spectrometry, photoelectron spectroscopy, triplet-excited state, substituted pyrazolines.

Nondissociative resonance capture of thermal and above-thermal electrons (REC) by molecules of azobenzene and its derivatives has been studied previously.[1] The properties of azo compounds ($R^1N{=}NR^2$) depend appreciably on both the geometry of the molecules and the nature of the R groups.[2] In this work, we employed REC mass spectrometry to study the formation and dissociation of negative molecular ions (NI) of cyclic analogs of azo compounds in the *cis*-form, substituted pyrazolines, namely, 3-methoxycarbonyl-3-methyl-4,5-dihydro-3*H*-pyrazole (**1**), 3-vinyl-4,5-dihydro-3*H*-pyrazole (**2**), 3,4-dimethyl-3-vinyl-4,5-dihydro-3*H*-pyrazole (**3**), 3,4-diazatricyclo[$5.2.1^{1,7}.0^{2,6}$]dec-3-ene (**4**), and 3,4-diazatricyclo[$5.2.1^{1,7}.0^{2,6}$]deca-3,8-diene (**5**).



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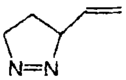

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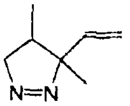

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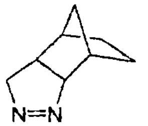

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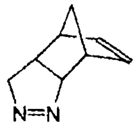

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Experimental

The REC mass spectra were recorded on an MI-1201 mass spectrometer adapted for detecting NI.[3] The energy scale of electrons was calibrated against the maxima of the curves of the effective yield from SF_6 (0 eV) and of NH_2^- from NH_3 (5.65 eV).

Photoelectron spectra were measured on a spectrometer designed at St. Petersburg State University and manufactured at the Institute of Organic Chemistry of the Ufa Scientific Center of the Russian Academy of Sciences. The scale of kinetic energy of photoelectrons was calibrated against xenon lines (the ionization energies are 12.13 and 13.43 eV).

Pyrazolines **1**—**5** were synthesized by known procedures.[4—6] The REC mass spectra are presented in Table 1.

Results and Discussion

Compounds **1**—**5** tend to form the following NI: $[MeNHNH_2]^-$, $[M - H - N_2]^-$, $[M - 49]^-$ ($[M - 2\ NH_3 - Me]^-$ and/or $[M - H - MeNH_2 - NH_3]^-$), $[C_4H_7N_2]^-$, $[C_3H_5N_2]^-$, $[C_3H_5]^-$, $[C_3H_3]^-$, $[N_2H_3]^-$, and $[NC]^-$ (Table 2). The ionization energies of the n^- HOMO (E) and the relative intensities of 100% NI peaks (I_{max}) are presented below.

	1	**2**	**3**	**4**	**5**
E/eV	9.09	8.90	—	8.90	8.80
I_{max} (%)	57.8	30.9	8.4	19.9	1

A distinctive feature of the behavior of pyrazolines **1**—**5** under REC conditions is the formation of unusual rearranged ions due to migration of several hydrogen atoms to the $—CH_2—N{=}N$ fragment. They include the pseudomolecular NI of methylhydrazine $[MeNHNH_2]^-$ (compounds **1**—**4**), the $[NH—NH_2]^-$ ions (compounds **1** and **3**—**5**), and the $[M - 49]^-$ NI ($[M - 2\ NH_3 - Me]^-$ and/or $[M - H - MeNH_2 - NH_3]^-$) (compounds **1**, **3**, and **4**). The REC mass spectra of compounds **1** and **3**, in which the peaks of the $[MeNHNH_2]^-$ and $[C_3H_3]^-$ NI are the most intense, also exhibit peaks of the $[M - MeNHNH_2]^-$ and $[M - C_3H_3]^-$ ions, respectively.

Apart from the REC mass spectra, we also studied the photoelectron spectra of compounds **1**, **2**, **4**, and **5** and performed MNDO quantum-chemical calculations in the sp basis set. The following ionization energies

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 4, pp. 701—704, April, 2000.

Table 1. Mass numbers (m/z), compositions of NI, relative peak intensities (I_{rel}), and energies of the resonance maxima (E) in the mass spectra of compounds **1**—**5**

Compound	m/z	NI	I_{rel} (%)	E/eV
1	127	$[M - Me]^-$	0.1	4.5
	111	$[M - OMe]^-$	0.2	3.7
	106	$[M - 36]^-$	0.1	3.5
	98	$[M - 44]^-$	0.2, 0.2	3.85, 8.2
	96	$[M - MeNHNH_2]^-$	1.0	0.8
	89	$[M - 53]^-$	0.2	1.2
	73	$[MeCO_2CH_2]^-$	0.5	0.4
	45	$[CH_2NHNH_2]^-$	0.3	0.8
	29	$[N_2H^-$ and/or $OCH^-]$	0.7	0.3
	17	$[HO^-]$	0.3, 0.3	7.3, 8.5
	16	$[O^-]$	0.4	2.1
2	95	$[M - H]^-$	0.1, 0.2	1.2, 5.1
	81	$[M - Me]^-$	1.1	8.8
	79	$[M - 17]^-$	1.5	0.75
	67	$[M - H - N_2]^-$	1.1, 2.7	6.5, 8.0
	66	$[M - 30]^-$	4.2	7.0
	52	$[M - 44]^-$	8.0	6.8
	45	$[CH_2NHNH_2]^-$	1.2	1.4
	42	$[C_2H_4N]^-$	2.8, 3.8	2.7, 6.9
	40	$[M - 56]^-$	7.4	6.7
	28	$[CH_2N^-]$	7.4	7.0
	27	$[C_2H_3]^-$	7.1	7.0
	25	$[C_2H]^-$	3.1	8.4
3	109	$[M - Me]^-$	1.7	0.5
	99	$[M - C_2H]^-$	4.3, 14.1	2.6, 8.7
	98	$[M - 26]^-$	0.9, 1.1	3.7, 8.2
	97	$[M - C_2H_3]^-$	1.1, 3.5	1.0, 9.2
	85	$[M - C_3H_3]^-$	2.3, 3.0	3.7, 8.5
	84	$[M - 40]^-$	2.5, 2.8	1.5, 9.1
	82	$[M - 42]$	5.5	1.6
	81	$[M - C_3H_7]^-$	3.0, 2.7	4.7, 9.2
	77	$[M - 47]^-$	14.3	8.0
	57	—	29.7	9.1
	55	$[C_4H_7]^-$	2.2	9.5
	45	$[CH_2NHNH_2]^-$	1.9, 7.7	1.3, 9.2
3	43	—	4.3, 5.0, 16.6	4.0, 5.7, 9.2
	40	$[C_2H_2N]^-$	3.2	6.9
	27	$[C_2H_3]^-$	1.0	8.2
	25	$[C_2H]^-$	13.1	9.1
	16	$[NH_2]^-$	3.3	2.0
	15	$[Me]^-$	5.7, 84.8, 38.3, 43.5	4.3, 5.9, 8.4, 9.7
	14	$[CH_2]^-$	6.6	8.4
	13	$[CH]^-$	6.2	8.4
4	135	$[M - H]^-$	0.3, 0.5	4.6, 7.7
	133	$[M - H_2 - H]^-$	0.2	8.1
	109	$[M - C_2H_3]^{-\bullet}$	0.3	7.6
	108	$[M - 28]^-$	1.0	0.2
	107	$[M - H - N_2]^-$	10.4	0.2
	96	$[M - 40]^-$	9.1	0.6
	87	$[M - 2\ NH_3 - Me]^-$ and/or $[M - MeNH_2 -$ $- NH_3 - H]^-$	100, 1.1, 1.5, 1.9	0.2, 3.0, 7.7, 8.7
	80	$[M - 56]^-$	0.3	6.8
	67	$[C_5H_7]^-$	0.7	8.2
	56	$[C_3H_6N]^-$	0.9, 0.3	2.9, 4.6
	54	$[C_3H_4N]^-$	0.2	6.7
	52	$[C_3H_2N]^-$	0.2	7.2
	42	$[C_2H_4N]^-$	0.6	1.5
	40	$[C_2H_2N]^-$	0.5	6.9
	28	$[CH_2N]^-$	0.2, 0.3	3.1, 6.7
	16	$[NH_2]^-$	1.6	5.2
5	133	$[M - H]^-$	3.3	7.6
	107	$[M - C_2H_3]^-$	42.1	0.7
	96	$[M - C_3H_2]^-$	78.7, 12.1, 15.2	0.7, 3.8, 8.0
	73	$[M - 61]^-$	3.2, 2.5, 4.5	2.0, 5.6, 7.9
	67	$[C_5H_7]^-$	8.0	8.6
	45	$[CH_2NHNH_2]^-$	20.9	1.0
	42	$[C_2H_4N]^-$	32.2	2.1
	25	$[C_2H]^-$	37	7.3

corresponding to the removal of an electron from occupied molecular orbitals (OMO) were found, eV:

1 9.09 (n^-), 10.53 (n_{CO}), 11.31 (n^+), 11.85 (π), 12.48 (σ)
2 8.90 (n^-), 10.31 (π_{CC}), 11.30 (n^+), 11.70 (π), 12.56 (σ)
4 8.90 (n^-), 10.42 (n^+), 10.91 (π), 11.57 (σ), 12.31 (σ), 12.55 (σ)
5 8.80 (n^-), 9.53 (π_{CC}), 10.69 (n^+), 11.30 (π), 11.93 (σ), 12.49 (σ)

Previously,[2] a correlation between the quantum yield of elimination of an N_2 molecule in the photolysis of azaalkanes with the n^- HOMO ionization energy has been elucidated. For 2,3-diazabicyclo[2.2.1]hept-2-ene (**6**), 1,2-diaza-3,3,5,5-tetramethylcyclopentene (**7**), 2,3-diaza-1,4-dimethylbicyclo[2.2.2]oct-2-ene (**8**), and 1,2-diaza-3,3,6,6-tetramethylcyclohexene (**9**), the quantum yields for the elimination of an N_2 molecule in the photolysis ($n^- \rightarrow \pi^*$) are 1.0, 0.88, 0.14, and 0.02, and n^- ionization energies are 8.94, 8.63, 8.06, and 7.89 eV, respectively.

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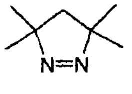

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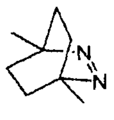

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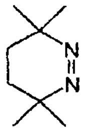

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Table 2. Relative intensities (I_{rel}) of the most intense peaks of characteristic NI in the REC mass spectra of **1**—**5**

m/z	Composition of the ion	I_{rel}* (%)				
		1	**2**	**3**	**4**	**5**
46	$MeNHNH_2^-$	100 (0.55)	17 (0), 100 (0.85)	18.6 (0.2), 48.1 (1.0)	5.8 (0.4)	—
83	$C_4H_7N_2^-$	0.2 (4.5), 0.5 (8.4)	0.4 (4.1), 0.6 (8.4)	24.7 (9.1)	0.5 (4.1), 1.3 (7.9)	17.0 (3.9), 6.5 (5.2) 52.6 (7.9)
[M − 29]	$[M - H - N_2]^-$	0.2 (0.6), 0.1 (2.2)	2.7 (6.5), 2.8 (8.0)	—	10.4 (0.2)	—
[M − 49]	$[M - 2\ NH_3 - Me]^-$ and/or $[M - MeNH_2 - NH_3 - H]^-$	0.2 (0.3)	—	1.8 (0.8), 1.0 (8.5)	100 (0.2)	—
69	$[C_3H_5N_2]^-$	0.2 (8.2)	1.6 (1.2), 1.8 (5.1), 5.0 (8.4)	—	0.9 (8.1)	9.1 (5.2), 8.5 (6.2), 27.4 (8.0)
65	$[C_5H_5]^-$	—	—	1.1 (5.7), 8.8 (9.0)	0.2 (7.5), 0.3 (8.7)	11.3 (1.9)
41	$[C_3H_5]^-$	0.2 (8.6)	1.3 (7.5)	44.0 (9.6)	1.0 (7.9)	2.5 (4.5)
39	$[C_3H_3]^-$	0.4 (0.8)	33.1 (1.2), 5.4 (8.4)	100 (1.4), 2.9 (9.2)	13.8 (0.2)	—
31	$[N_2H_3]^-$ $[OMe]^-$	1.2 (0.8), 0.6 (7.4)	—	0.7 (7.6)	0.5 (0.5), 2.2 (7.3)	27.8 (0.6), 27.8 (7.3)
26	$[NC]^-$	1.8 (1.1)	11.5 (1.9), 31.7 (6.8)	3.3 (1.8), 3.2 (7.6)	2.3 (1.6), 1.1 (6.8)	100 (2.0)

* The values in parentheses are the energies in the resonance maximum (eV).

We were unable to follow any correlation between the n⁻ HOMO ionization energy and the yield of fragmentation products from the molecular NI such as $[M - N_2]^-$ or $[M - H - N_2]^-$ in the mass spectra of **1**—**5**. However, the n⁻ HOMO ionization energy was found to correlate with the yield of the $[MeNHNH_2]^-$ NI. Destabilization of the n⁻ HOMO induces a decrease in the intensity of the $[MeNHNH_2]^-$ NI peaks down to their complete loss in the spectrum of **5**. This correlation becomes even more clearly defined if one takes into account the relative yields of the maximum ion peaks in the mass spectra of **1**—**5**; the yield of the maximum NI peak in **5** is taken to be unity (see Table 2). Thus, unlike the photolysis of azo compounds, which is accompanied by ejection of an N_2 molecule, dissociation of the molecular NI in the ground state gives fragments many of which still contain the N_2 atoms.

Judging by the results of quantum-chemical calculations, the lowest unoccupied molecular orbital (LUMO) in azo compounds is the $\pi^*_{N=N}$ MO. This is confirmed by the data of electron transmission spectroscopy (ETS), according to which short-lived NI states were found at energies of 1.96 eV (ester group), 1.73 eV (ethylene), 1.70 eV (norbornene), and 0.65 eV (azo group)[7—9] and were identified as the π^*_{CO}, $\pi^*_{C=C}$, π^*_{norb}, and $\pi^*_{N=N}$ MO, respectively. Therefore, for energies of up to 1 eV, the double peaks of the $[MeNHNH_2]^-$ NI in the mass spectra of compounds **2** and **3** can be interpreted as being due to the products of dissociation of molecular NI resulting upon the capture of an electron by the $\pi^*_{N=N}$ and $\pi^*_{C=C}$ orbitals.

In addition, comparison of the photoelectron spectra with the REC mass spectra allowed us to identify the series of resonance states (RS) of the NI which correlate in energy ranges with the ionization energies (IE) of compounds **1**, **2**, **4**, and **5**. The corresponding RS/eV and IE/eV are presented below.

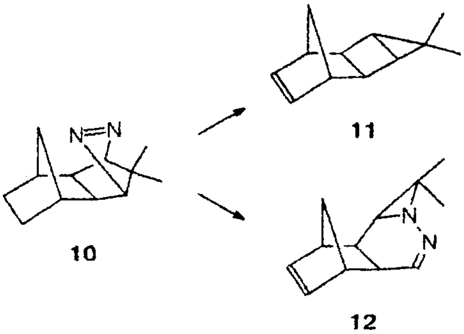
Compound	RS	IE
1	2.2, 3.7, 4.5	9.09, 10.53, 11.31
2	2.7, 4.1, 5.1, —, 6.5; 5.1, 6.5, 7.5, 8.0, 8.8	8.90, 10.31, 11.30, 11.70, 12.56
4	3.0, 4.6, 5.2, —, 6.7; 5.2, 6.7, 7.2, 7.7, 8.3, 8.7	8.9, 10.42, 10.91, 11.57, 12.31, 12.54
5	2.0, —, 3.8, 4.5, 5.2, 5.6	8.80, 9.53, 10.69, 11.30, 11.93, 12.49

The presence of such a series coinciding in energy ranges means that the formation of NI from the compounds under study occurs by successive excitation from several occupied MO to vacant MO (a dash means that no RS corresponding in energy to a particular IE was detected). The beginning of the low-energy series of compounds (2.2 eV for **1**, 2.7 eV for **2**, 3.0 eV for **4**, and 2.0 eV for **5**) correlates with the energy of the first triplet electron transition for azo compounds.[10] This permits the mechanism of formation of the NI to be classified as the electronically excited Feschbach resonance with two coupled electrons on the vacant $\pi^*_{N=N}$ MO.

In addition, the series of RS starting with energies of the captured electron of about 5 eV were found for compounds **2** and **4**. The formation of the NI from **2** and **4** at this energy is, apparently, due to the capture of electrons into one of the σ*-MO. Note as well that an $n^+ \rightarrow \sigma^*$ electron transition in 3-methyl-4,5-dihydro-3*H*-pyrazole has been identified at 7.3 eV.[10] According to our interpretation of electronically excited states in molecular NI, the energy of the $n^+ \rightarrow \sigma^*$ electron transition is 7.5 eV for **2** and 7.2 eV for **4**.

The REC mass spectrum of azo compound **5** differs markedly from the spectra of **1—4**. The mass spectrum of **5** exhibits no peak for the $[MeNHNH_2]^-$ ion, whereas the peak for the $[N{\equiv}C]^-$ NI is the most intense. This points to the possibility of isomerization of molecule **5** during the formation and dissociation of molecular NI giving a C=N bond instead of the N=N bond. This assumption is confirmed by the data[11] on the photolysis (excitation energy 3.53 eV) of the triplet-excited 12,12-dimethyl-4,5-diazatetracyclo$[6.2.1^{3,6}.0^{2,7}]$dodec-4-ene (**10**) molecule (Scheme 1).

Scheme 1



Judging by the photolysis products identified,[11] compound **11** is formed upon the ejection of an N_2 molecule and compound **12** results from migration of the double bond in the initial excited molecule **10**.

Thus, REC mass spectrometry makes it possible not only to distinguish structural isomers but also to study isomerization processes that accompany the formation and dissociation of molecular NI.

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Received August 4, 1999;
in revised form November 4, 1999