NEGATIVE-ION MASS SPECTRA OF THE SYNTHETIC ALKALOID DIPTOCARPILIDINE AND ITS DEOXY PRECURSOR

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UDC 543.51:547.495.2

The existence of the molecules of the synthetic alkaloid diptocarpilidine in a folded conformation as a consequence of the intramolecular interaction of the sulfoxide and cyano groups through space has been established by negative-ion mass spectrometry.

The molecules of the synthetic alkaloids diptocarpiline, $CH_3SOC_6H_{12}NHCONHC_6H_{12}SCH_3$, diptocarpidine, $(CH_3SOC_6H_{12}NH)_2CO$; and diptocarpamine, $CH_3SOC_6H_{12}NHCONHCH(CH_3)_2$ have previously been investigated by negative-ion (NI) mass spectrometry in the resonance electron capture (REC) regime. It was shown that a folded conformation is a characteristic feature of these compounds because of the spatial propinquity of the urea and sulfur-containing groups [1, 2]. In the present communication we give the REC mass spectra of the synthetic alkaloid diptocarpilidine $CH_3SOC_6H_{12}CN$ (I) and of its sulfide precursor $CH_3SC_6H_{12}CN$ (II) and the model compound DMSO, CH_3SOCH_3 (III).

The simplest is the mass spectrum of (II). Ions formed on the dissociation of M^- both by simple bond cleavage and as a result of the migration of a hydrogen atom were recorded: $(M-H)^-$, $(M-CH_3)^-$, $(M-CH_3SH)^-$, $(CH_3S)^-$, $(CH_2S)^-$, $(CHS)^-$, $(HS)^-$, $(S)^-$, $(NC)^-$.

In the mass spectra of compounds (I) and (III), a number of monotypical peaks were recorded of the ions $(M-H)^-$, $(CH_3SO)^-$, HSO^-, SO^-, CH_3S^-, CH_2S^-, HS^-, S^-, HO^-, O^-, CH_3^-. In addition, in the mass spectrum of (I) the peaks of the ions with m/z 158 $(M-CH_3)^-[NCC_6H_{12}SO]^-$, m/z 142 $(M-OCH_3)^-[NCC_6H_{12}S]^-$, m/z 110$(M-CH_3SO)^-[NCC_6H_{12}]^-$ were formal analogues of the peaks with m/z 63 $(M-CH_3)^-[CH_3SO]^-$, m/z 47 $(M-OCH_3)^-[CH_3S]^-$, m/z 15 CH_3^- $[M-CH_3SO]^-$ for compound (III), respectively. Attention was attracted by the fact that, for practically all the ions mentioned above, the peaks of the resonance maxima of compound (I) in the 5 eV region had been shifted towards higher energies in comparison with (III); m/z 16 (5.1 and 5.0), m/z 17 (5.5 and 5.2), m/z 32 (5.25 and 5.2), m/z 33 (5.2 and 5.05), m/z 48 (5.6 and 5.2), m/z 49 (5.5 and 5.25). A similar pattern was observed for the NI peaks of (I) that were analogues of the peaks of (III): CH_3^- 5.2, $(C_6H_{12}CN)^-$ $[M-CH_3SO]^-$ 5.1 (I) and CH_3^- $(M-CH_3SO)^-$ 4.9 (III); CH_3S^- 5.5, $NCC_6H_{12}S^-[M-OCH_3]^-$ 5.7 (I) and $CH_3S^-[M-OH_3^-]$ 5.35 (III); CH_3SO^- 5.3, $NCC_6H_{12}SO^-[M-CH_3^-]$ 5.1 (T) and CH_3SO^- 4.9 (III). We may also note that the peak of the NI $(M - H)^-$ was recorded at an energy of 3 eV in (I), as compared with 2.75 eV in (III) (Fig. 1a).

It has been established previously that resonances at electron-capture energies of ~5 eV are electronically excited states of the molecular NI and correspond to the excitation of electrons from an occupied into a vacant molecular orbital [3]. The increase in the resonance energy in (I) as compared with (III) therefore corresponds to a higher-energy electronic transition in the molecular NI. A possible explanation of this may be an interaction of the CH_3SO- and cyano groups in (I). According to the results of photoelectron spectroscopy, the ionization energy of the π-orbital of the CN group of acetonitrile, taken as a model compound, is 12.18 eV, and that of the unshared electron pair of oxygen, n_0, in (III) is 12.57 eV [4, 5]. On interaction, these orbitals in (I) must split, which leads, in particular, to the stabilization of the n_0 of (I) as compared with (III) and may be responsible for the increase in the energy of the electronic transition in the molecular NI of (I). This was the first evidence in favor of an interaction of the sulfoxide and cyano groups in (I).

Institute of Organic Chemistry, Urals Branch, Russian Academy of Sciences, Ufa. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 543-546, September-October, 1992. Original article submitted February 20, 1992.

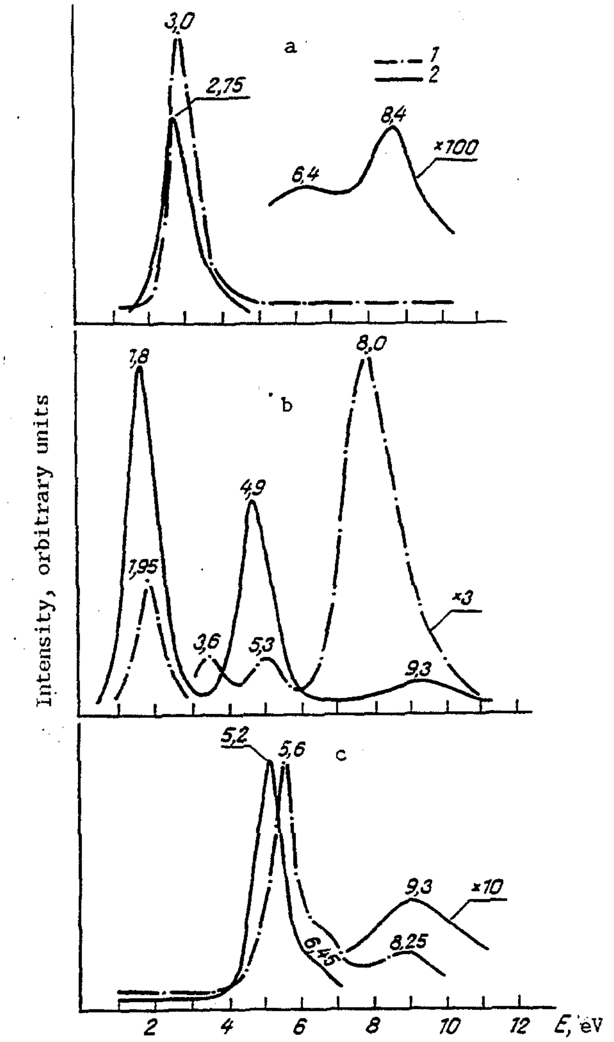

Fig. 1. Effective yield curves: a) the $(M - H)^-$ NI for diptocarpilidine (1) and DMSO (2); b) characteristic CH_3SO^- NIS for diptocarpilidine (1) and DMSO (2); c) the SO^- NIs for diptocarpilidine (1) and DMSO (2).

In the Ni mass spectrum of (I) we recorded the peaks of the rearrangement ions with m/z 42 $(OCN)^-$, 56 $(NCOCH_2)^-$, and 131 $(M - OCN)^-$, the formation of which can be explained only if a hydrogen atom migrates to the cyano group. Since the process of rearrangement in the formation of an NI competes with processes of dissociation and the autoejection of an electron, it must be assumed that such migration is possible only when the SO and CN groups are spatially close. This was a second fact in favor of the existence of an intramolecular interaction of the sulfoxide and cyano groups in (I).

A comparison of the NI mass spectra of (I) and (III) showed that for the characteristic peak of the ions of both compounds with m/z 63 [CH_3SO^- in (I)], a shift towards higher-energy resonance regions at 2 and 5 eV and also the presence of an additional resonance at 3.6 eV was observed (Fig. 1, b). In [6] it was reported that in bifunctional compounds separated by a polymethylene chain the presence of an additional resonance may serve as a confirmation of an intramolecular interaction of the functional groups in the molecule. This was the third point in favor of the existence of an intramolecular interaction of the functional groups in (I).

To answer the question of whether there were observable NI products of the breakdown of dimeric, trimeric, etc., forms of the molecular NI of (I) in the gas phase, we investigated the temperature dependence of the evaporation of compound (I) and established that in the range of temperatures of direct introduction of the sample up to 110°C the molecules of (I) were in the monomeric form. The NI mass spectrum of (I) was obtained with room-temperature direct introduction of the specimen (temperature of the ion source 60-70°C), and it may therefore be assumed that the molecular NIs of diptocarpilidine exist in the monomeric form.

Thus, it has been established that existence in a folded conformation is characteristic for the molecules of the synthetic alkaloid diptocarpilidine (I) as a consequence of an intramolecular interaction of the sulfoxide and cyano groups through space.

EXPERIMENTAL

REC mass spectra were obtained on an MI-1201 mass spectrometer reconstructed for recording NIs [7], using a direct sample-introduction system. The loading of the specimen through the direct introduction system was conducted at room temperature. The electron energy scale was calibrated from the maxima on the curves of effective yield of SF_6^- from SF_6 (0 eV) and of NH_2^- from NH_3 (5.65 eV).

The investigation of the temperature dependence of the decomposition of the molecules of (I) in the gas phase was carried out on a Kratos MS 80 mass spectrometer in the interval of direct-introduction temperatures of 273-582 K [sic] at a rate of heating of 1 K/s.

REC mass spectra – m/z: assumed compositions of the ions – %; energy of the resonance maximum of the yield of the ions – eV.

8-Oxo-8-thianonanenitrile [(±)-diptocarpilidine] (I): 172–$(M - H)^-$ – 24 (3.0); 158 $(M - CH_3)^-$ –10(1.7), 5(51); 142 $(M - OCH_3)^-$ – 10(5.7); 131 $(M - OCN)^-$ – 6(7.6); 110 $(M - CH_3SO)^-$ – 15(5.1); 63 $(CH_3SO)^-$ – 100(1.95), 14(3.6), 13(5.3), 88(8.0); 56$(NCOCH_2)^-$ –15(0.5), 30(2.0); 49$(HSO)^-$ – 18(5.5), 14(8.3); 48$(SO)^-$ – 17(5.6), 8(8.3); 47 $(CH_3S)^-$ – 8(5.5), 4(8.5); 46 $(CH_2S)^-$ – 30(0.3); 42 $(OCN)^-$ – 4(2.0), 4(8.5); 40 $(NCCH_2)^-$ – 62(8.0); 33 $(HS)^-$ – 3(1.9), 4(5.2); 32$(S)^-$ – 5(1.6), 10(5.25), 4(6.5); 26$(NC)^-$ – 51(0), 12(2.7), 13(5.5), 42(8.2); 17$(HO)^-$ – 10(5.5), 6(8.5); 16$(O)^-$ – 18(5.1); 15$(CH_3)^-$ – 11(5.2), 2(8.5).

8-Thianonanenitrile (II): 156$(M - H)^-$ – 20(0.6); 143$(M - CH_3)^-$ – 6(0.6); 109$(M - CH_3SH)^-$ – 100(1.0); 47$(CH_3S)^-$ – 11(0.7), 10(8.0); 46$(CH_2S)^-$ – 81(0.3); 45(CHS) – 14(1.0); 33$(HS)^-$ – 12(1.0), 12(5.5); 32$(S)^-$ – 10(5.5); 26$(NC)^-$ – 72(0).

DMSO (III); 77$(M - H)^-$ – 7(2.75); 0.03(6.4), 0.06(8.4); 63$(CH_3SO)^-$ – 19(1.8), 11(4.9), 1(9.3); 62$(M - CH_4)^-$ – 0.5(5.4), 2(9.1); 61 $(M - CH_3 - H_2)^-$ – 2(5.35), 0.6(6.6), 7(9.75); 49$(HSO)^-$ – 2(5.35), 0.4(6.5), 2(8.8); 48$(SO)^-$ – 100(5.2), 11(6.45), 3(9.3); 47$(CH_3S)^-$ – 1(0.8), 17(5.35), 8(6.4), 3(8.7), 46$(CH_2S)^-$ – 7(5.35), 3(6.4); 45 $(CHS)^-$ – 24(5.2), 3(6.45); 33$(HS)^-$ – 1(2.1), 4(5.05), 1(6.5), 0.5(9.75); 32$(S)^-$ – 0.6(1.8), 2(3.0), 2(4.05), 4(5.2), 1(6.4), 1(9.6); 17$(HO)^-$ – 18(5.2), 4(6.4); 16$(O)^-$ – 21(5.0), 2(6.55), 10(8.4); 15$(CH_3)^-$ – 5(4.9), 0.5(6.45).

LITERATURE CITED

1. V. S. Shmakov, I. I. Furlei, E. G. Galkin, et al., Khim. Prir. Soedin., 390 (1988).
2. V. S. Shamkov, I. I. Furlei, E. G. Galkin, et al., Khim. Prir. Soedin., 80 (1989).
3. V. I. Khvostenko, O. G. Khvostenko, G. S. Lomakin, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 6, 1277 (1987).
4. D. C. Frost, F. G. Herring, and C. A. McDowell, Chem. Phys. Lett., 4, 533 (1970).
5. H. Bock and B. Solouki, Chem. Ber., 107, 2299 (1974).
6. I. I. Furlei, V. N. Odinokov, A. P. Zhavoronkov, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 10, 2238 (1984).
7. V. I. Khvostenko, V. A. Mazunov, V. S. Fal'ko, et al., Khim. Fiz., No. 7, 915 (1982).