

## COMPOUNDS OF AZIADAMANTANE TYPE: MASS SPECTROMETRIC STUDY

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Azi and hydrazi derivatives of adamantane, adamantanone and diamantane were studied by mass spectrometry. The EI spectra of azi derivatives lack completely molecular ions; the presence of abundant dehydroadamantane or dehydrodiamantane ions corresponds to elimination of nitrogen molecule from the molecular ion. Comparison of the EI ionization with photolysis or pyrolysis allowed to deduce some analogies and to suggest the mechanism of decomposition of the molecular ion.

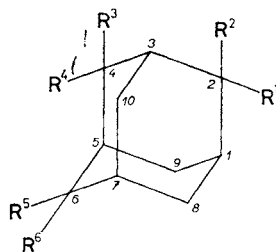
Within the framework of investigation of diamantoid polycyclic hydrocarbons and their derivatives we studied by mass spectrometry a group of adamantane and diamantane derivatives with hydrazi (NH—NH) or azi (N=N) substituents, and some related compounds.\* Electron impact (EI) spectra were determined for all the compounds and in some cases also chemically induced ionization (CI) spectra were taken.

Electron impact mass spectra of hydraziadamantane (I) and aziadamantane (II) markedly differ at the first glance. The spectrum of aziadamantane has no molecular ion (vide infra) whereas in the spectrum of hydraziadamantane the molecular ion is quite abundant (about 60 rel. int. %). The fission of the hydrazi derivative proceeds along two independent pathways, the loss of NH<sub>2</sub> and NH being more intense than that of the whole substituent N<sub>2</sub>H<sub>2</sub> or N<sub>2</sub>H.

As already mentioned, no molecular ion has been found in the EI spectra of aziadamantane even at low ionization energies (below 20 eV). The highest discernible ion at *m/z* 134 corresponds to molecular ion of dehydroadamantane. Thus, the presence

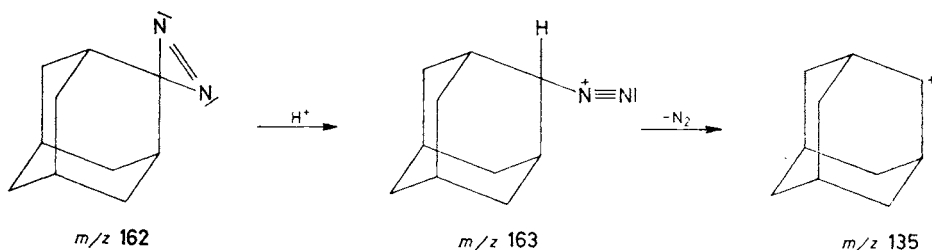
\* The nomenclature of those compounds coming from the diaziridine or diazirine cycle (adamantanespirodiaziridine, adamantanespirodiazirine) in some previous papers was used, but that is not corresponding to the IUPAC's nomenclature rules.

of aziadamantane molecule could not be proven from the EI spectra. It could not be decided whether the aziadamantane is first ionized and then decomposed (loss of  $N_2$ ) or first loses nitrogen at the ion source temperature, giving rise to dehydro-



- I,  $R^1, R^2 = \text{NHNH}$ ;  $R^3 = R^4 = R^5 = R^6 = \text{H}$   
 II,  $R^1, R^2 = \text{N}=\text{N}$ ;  $R^3 = R^4 = R^5 = R^6 = \text{H}$   
 VII,  $R^1, R^2 = \text{O}$ ;  $R^3, R^4 = \text{N}=\text{N}$ ;  $R^5 = R^6 = \text{H}$   
 VIII,  $R^1, R^2 = \text{O}$ ;  $R^3 = R^4 = \text{H}$ ;  $R^5, R^6 = \text{N}=\text{N}$   
 X,  $R^1, R^2 = \text{N}=\text{N}$ ;  $R^3, R^4 = \text{N}=\text{N}$ ;  $R^5 = R^6 = \text{H}$   
 XI,  $R^1, R^2 = \text{N}=\text{N}$ ;  $R^3 = R^4 = \text{H}$ ;  $R^5, R^6 = \text{N}=\text{N}$

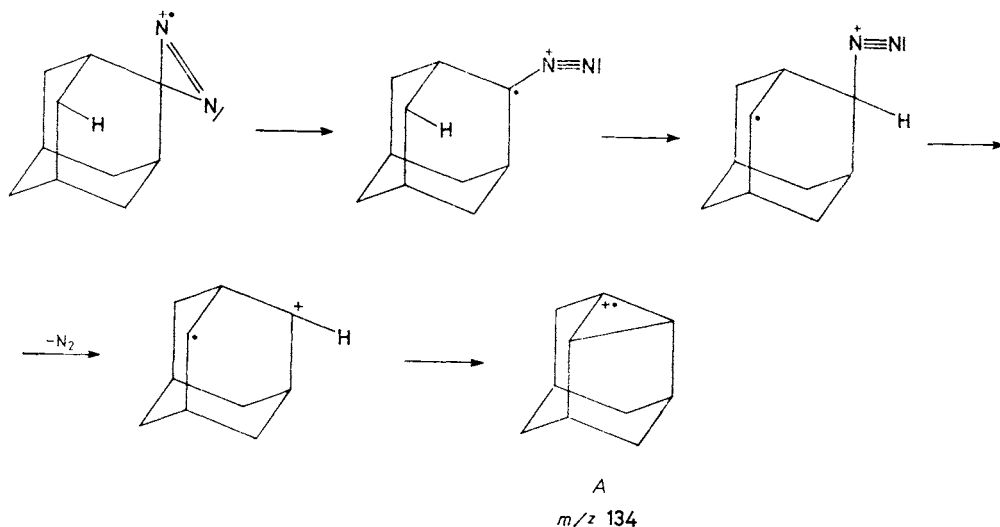
adamantane which is then ionized. However, the molecular ion of aziadamantane has been proven by the CI mass spectrum (with isobutane as reaction gas). The CI spectrum of II displayed ions at  $m/z$  219 and  $m/z$  163, corresponding to  $[\text{M} + \text{C}(\text{CH}_3)_3]^+$  and  $[\text{M} + \text{H}]^+$ , respectively. The ion  $[\text{M} + \text{H}]^+$  loses nitrogen molecule, probably according to Scheme 1, giving rise to the base ion at  $m/z$  135.



SCHEME 1

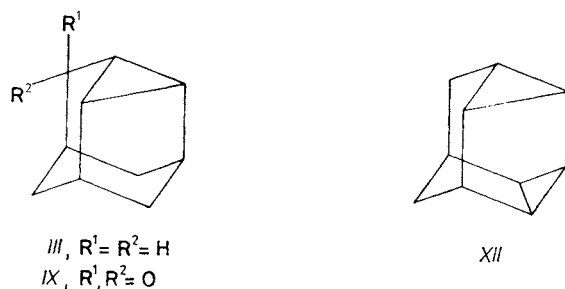
In our previous studies<sup>1</sup> on photolysis and pyrolysis of aziadamantane we also observed the loss of nitrogen. It has been shown<sup>2</sup> that in photolysis of diazirines the diazirine ring is first isomerized to form the linear diaza grouping. The isomerization is then followed by loss of nitrogen molecule leading to carbenes<sup>3,4</sup>. By way of analogy, we may assume that also in the electron impact ionization (EI) the diazirine

ring is cleaved first (as the bond of highest energy), the following step being migration of the radical center and elimination of  $N_2$ . The arising ion ( $m/z$  134) has the structure *A* (Scheme 2).



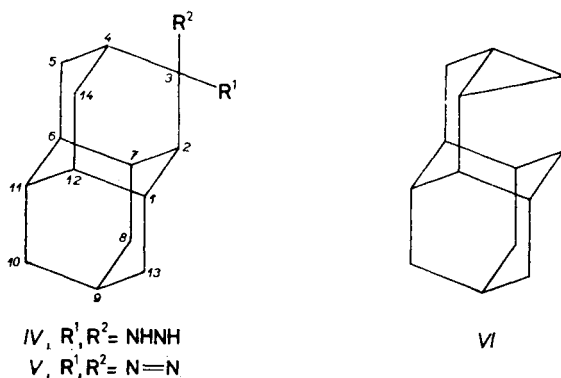
SCHEME 2

The same ion *A* also arises as the molecular ion in the EI ionization of dehydroadamantane (*III*). However, comparison of spectra of aziadamantane and dehydroadamantane reveals a considerable difference in intensities of the ion *A* as well as of the fragment ions. This difference is probably due to a different energy content of the arising ion *A*. Apparently, the leaving nitrogen molecule does not take away all the energy liberated in the fission of the diazirine ring and the excess energy causes more intense vibrations of the hydrocarbon skeleton and thus easier fragmentation of the ion *A* in the spectrum of aziadamantane.

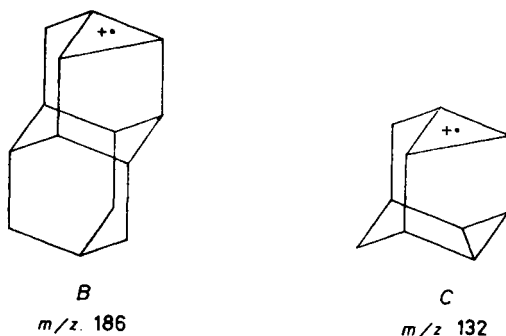


On the contrary, in the spectra of 2-substituted adamantane derivatives (2-chloro-adamantane, 2-hydroxyadamantane, 2-methoxyadamantane etc.) the  $[M - HX]^+$  ion *A* represents the base ion (100 rel. int. %, 20–30% of  $\sum_i$ ; see refs<sup>5,6</sup>) indicating that its energy content is still lower than that of dehydroadamantane itself (and consequently it is still more resistant to fragmentation).

Similar character and fragmentation mechanisms as discussed for the adamantane derivatives *I*, *II* and *III* have been found with the analogous diamantane derivatives: hydrazidiamantane (*IV*), azidiamantane (*V*), 3,5-dehydrodiamantane (*VI*). Spectra of all these three diamantane derivatives (*IV–VI*) exhibit more abundant dehydrodiaman-



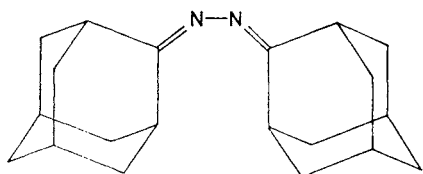
tane ion (*B*) than is dehydroadamantane ion (*A*) in the spectra of corresponding adamantane derivatives (*I–III*) – see spectral data and value in Table I. The higher intensity (and stability) of the ion *B* comparing with that of the ion *A* may be result of equipartition excess energy among the larger member of internal modes of freedom in the ion *B* than in the ion *A*.



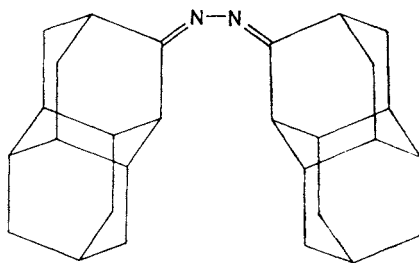
Introduction of a carbonyl group (as another possible fragmentation site) into the molecule of the adamantane derivatives *II* and *III* reduces the intensity of the de-

hydroadamantanone ions, ( $m/z$  148 in *VII*, *VIII* and *IX*) as compared with intensity of dehydroadamantane ions,  $m/z$  134, in *II* and *III*). The ions at  $m/z$  148 in the spectra of derivatives *VII* and *VIII* are less abundant than in the spectrum of dehydroadamantanone *IX*, and so is the ion at  $m/z$  134 when spectra of derivative *II* and dehydroadamantane (*III*) are compared.

When the adamantane system bears two azi groups (compounds *X* and *XI*), both these azo groups are easily cleaved off and the base peak in the spectra of *X* and *XI* is the ion at  $m/z$  132, corresponding to ionized didehydroadamantane (*C*).



XIII



XIV

TABLE I  
Comparison of intensities of characteristic ions in the mass spectra

Compound <sup>a</sup>	Formula	Ion	
		$m/z$	% $\Sigma I$
Dehydroadamantane	<i>III</i>	134	10.8
Dehydrodiamantane	<i>VI</i>	186	16
4,6-Dehydroadamantanone	<i>IX</i>	148	5.7
2,4,6,9-Didehydroadamantane	<i>XII</i>	132	9.6

Compound <sup>b</sup>	Formula	Ion	
		$m/z$	% $\Sigma I$
Aziadamantane	<i>II</i>	134	1.8
Azidiamantane	<i>V</i>	186	3.2
4-Aziadamantanone	<i>VII</i>	148	1.7
6-Aziadamantanone	<i>VIII</i>	148	0.8
2,4-Bis-aziadamantane	<i>X</i>	132	1.1
2,6-Bis-aziadamantane	<i>XI</i>	132	1.2

<sup>a</sup> Dehydrodiamantoid structure; <sup>b</sup> structure with spirodiazirine ring.

The ratio of intensity of the ion *C* in the spectra of both the bis-azi derivatives *X* and *XI* to the intensity of the molecular ion *C* in the spectrum of didehydroadamantane (*XII*) remains the same as the ratio of the intensity of the ion *A* in the spectrum of compound *II* to the intensity of the molecular ion *A* in the spectrum of compound *III* — see Table I. The intensity of ion at *m/z* 131 which has no analogy in the case of *II* and *III*, remains almost the same for the three compounds *X*, *XI* and *XII*.

In connection with the above-mentioned study we determined the spectra of adamantanone azine (*XIII*) and diamantanone azine (*XIV*). Also the spectra of these compounds contain the respective ions *A* and *B*, their intensity is, however, low. The main fragmentation path is cleavage of the *N*—*N* bond to give ions  $\text{Ad}=\overset{+}{\text{N}}\text{H}_2$ ,  $\text{Ad}=\overset{+}{\text{N}}\text{H}$  and  $\text{Ad}=\overset{+}{\text{N}}\text{I}$  (*m/z* 150, 149 and 148) for the adamantane system and ions  $\text{Dia}=\overset{+}{\text{N}}\text{N}_2$ ,  $\text{Dia}=\overset{+}{\text{N}}\text{H}$  and  $\text{Dia}=\overset{+}{\text{N}}\text{I}$  (*m/z* 202, 201 and 200) for the diamantane skeleton (*Ad* denotes adamantane, *Dia* diamantane skeleton). The same fragmentation also takes place<sup>7</sup> in the pyrolysis of azines *XIII* and *XIV*.

## EXPERIMENTAL

Synthesis, purity and physicochemical constants of aziadamantane and azidiamantane derivatives and several related compounds were published previously<sup>1,8</sup>.

Mass spectra of the adamantane derivatives were measured at the Institute of Organic Chemistry, USSR Academy of Sciences in Moscow on a Varian MAT CH-6 (EI spectra) and KRATOS MS-30 (CI spectra) instrument. Spectra of the diamantane derivatives were obtained with an LKB 9000 spectrometer at the Prague Institute of Chemical Technology. Samples of pure compounds were introduced using the direct inlet technique (ion source temperature 130—150°C, for LKB 250G310°C, ionizing electron energy 70 eV). In the CI spectral measurements (on KRATOS instrument) the ion source temperature was 150°C, ionizing gas isobutane, pressure 0.03 kPa.

The ion intensities are given in relative intensity % of the base ion. For better comparison, Table I gives the intensities in total ionization % (%  $\Sigma_I$ ). Unless stated otherwise, the data relate to EI mass spectra; the CI spectra are specifically mentioned.

*Hydraziadamantane* (I): 165(10), 164(59), 163(9), 149(14), 148(20), 147(9), 146(12), 135(11), 133(15), 132(22), 123(27), 122(32), 121(31), 120(12), 119(17), 118(10), 117(10), 109(20), 108(15), 107(28), 106(41), 105(37), 104(13), 96(12), 95(27), 94(27), 93(42), 92(30), 91(70), 83(12), 82(14), 81(33), 80(37), 79(86), 78(30), 77(77), 70(9), 69(15), 68(13), 67(35), 66(19), 65(38), 57(10), 56(22), 55(27), 54(39), 53(54), 52(17), 51(22), 43(35), 42(19), 41(100), 40(15), 39(86).

*Aziadamantane* (II): 162(G), 135(2), 134(14), 120(3), 119(24), 107(3), 106(24), 105(34), 93(52), 92(69), 91(100), 80(31), 79(62), 78(28), 77(62), 67(17), 66(14), 65(28), 63(10), 55(7), 54(7), 53(28), 52(14), 51(21), 41(48), 40(14), 39(72).

CI spectrum: 220(14), 219(80), 164(5), 163(30), 136(12), 135(100), 134(20).

*Dehydroadamantane* (III): 135(10), 134(84), 119(26), 106(11), 105(21), 93(50), 92(100), 91(64), 81(4), 80(45), 79(97), 78(33), 77(45), 66(20), 65(19), 64(15), 63(5), 56(14), 55(5), 53(8), 52(6), 51(12), 44(21), 43(10), 41(21), 39(28).

*Hydrazidiamantane* (IV): 217(21), 216(100), 215(9), 202(10), 201(27), 200(11), 199(4), 187(5), 86(9), 185(7), 184(5), 175(5), 173(6), 171(4), 159(4), 158(6), 157(6), 156(5), 145(7), 144(9), 143(11), 136(9), 135(11), 129(14), 121(13), 120(8), 119(9), 118(8), 117(61), 115(9), 109(9), 108(10), 107(12), 106(19), 105(18), 104(11), 95(18), 94(21), 93(21), 92(15), 91(40), 81(16), 80(16), 79(32), 78(11), 77(25), 67(14), 65(12), 53(11), 52(4), 43(8), 41(26), 39(16).

*Azidiamantane* (V): 215(1), 213(1), 201(1), 188(2), 187(10), 186(50), 172(2), 171(11), 158(9), 157(18), 145(14), 144(18), 143(36), 132(16), 131(32), 130(39), 129(61), 128(16), 120(7), 119(14), 118(20), 117(41), 116(16), 115(20), 108(16), 107(20), 106(77), 105(52), 104(66), 103(11), 96(7), 95(64), 94(39), 93(50), 92(55), 91(100), 82(7), 81(43), 80(41), 79(82), 78(30), 77(48), 67(27), 66(11), 65(25), 64(7), 63(11), 55(11), 54(7), 53(20), 52(10), 51(20), 50(7), 41(39), 40(7), 39(41).

*Dehydroadiamantane* (VI): 187(16), 186(100), 185(15), 171(3), 158(3), 157(5), 145(4), 144(5), 143(10), 132(4), 131(9), 130(15), 129(28), 128(6), 119(5), 118(5), 117(12), 116(5), 115(6), 108(4), 107(5), 106(16), 105(16), 104(17), 95(29), 94(22), 93(13), 92(17), 91(38), 81(12), 80(32), 79(33), 78(12), 77(18), 67(10), 66(5), 65(9), 55(4), 54(4), 53(7), 52(4), 51(6), 41(18), 39(18).

*4-Azidamantanone* (VII): 176(G), 151(6), 149(15), 148(19), 147(4), 133(6), 129(4), 128(4), 121(6), 120(29), 119(12), 117(4), 115(4), 107(14), 106(29), 105(83), 104(31), 103(6), 94(8), 93(17), 91(100), 83(8), 82(6), 81(17), 80(17), 79(100), 78(44), 77(58), 71(6), 69(12), 68(8), 67(21), 66(29), 65(21), 63(8), 60(6), 58(8), 57(8), 56(4), 55(19), 54(8), 53(31), 52(15), 51(23), 50(8), 46(27), 45(31), 44(40), 43(29), 42(8), 41(35), 40(12), 39(52).

*6-Azidamantanone* (VIII): 176(G), 138(6), 133(6), 130(14), 129(6), 120(20), 118(6), 117(6), 117(23), 115(6), 106(6), 105(46), 104(6), 93(17), 92(91), 91(100), 80(9), 79(9), 78(34), 77(51), 67(9), 66(29), 65(17), 63(9), 57(6), 55(29), 53(17), 52(11), 51(23), 50(9), 41(29), 40(9), 39(46).

*4,6-Dehydroadamantanone* (IX): 149(10), 148(60), 133(6), 130(10), 129(5), 120(31), 119(10), 117(11), 115(8), 107(11), 106(28), 105(35), 104(7), 103(7), 94(8), 93(16), 92(78), 91(80), 70(24), 79(100), 78(71), 77(61), 70(6), 67(10), 66(70), 65(33), 63(13), 58(8), 57(8), 55(26), 53(24), 52(17), 51(34), 50(12), 41(36), 40(14), 39(60).

*2,4-Bis-azidamantane* (X): 188(G), 134(1), 133(2), 132(11), 131(30), 129(7), 128(5), 118(10), 117(66), 116(26), 115(41), 105(18), 104(39), 103(24), 102(5), 93(10), 92(16), 91(100), 90(16), 89(10), 80(13), 79(46), 78(59), 77(46), 76(5), 75(4), 74(4), 67(29), 66(37), 65(49), 64(10), 63(23), 62(6), 55(4), 54(13), 53(27), 52(24), 51(41), 50(10), 41(39), 40(12), 39(66).

*2,6-Bis-azidamantane* (XI): 188(G), 132(9), 131(22), 129(6), 18(6), 117(70), 115(36), 105(13), 104(26), 103(15), 93(9), 92(20), 91(100), 79(43), 78(48), 77(52), 67(6), 66(11), 65(35), 64(6), 63(17), 54(9), 53(22), 52(17), 51(30), 50(11), 41(24), 40(9), 39(61).

*2,4,6,9-Didehydroadamantane* (XII): 133(3), 132(56), 131(20), 118(5), 117(98), 116(8), 115(20), 105(5), 104(20), 103(5), 92(5), 91(100), 79(8), 78(70), 77(16), 67(7), 66(8), 65(11), 64(5), 63(5), 54(44), 53(5), 52(5), 51(10), 43(10), 41(5), 39(26).

*Adamantanone azine* (XIII): 297(15), 296(64), 295(8), 255(14), 254(7), 253(18), 239(26), 228(11), 216(8), 215(8), 190(8), 188(8), 176(10), 175(30), 163(9), 151(7), 150(48), 149(28), 148(34), 135(11), 134(11), 133(7), 132(8), 131(11), 121(20), 120(12), 119(12), 118(7), 117(8), 108(13), 107(23), 106(48), 105(23), 104(8), 95(12), 94(27), 93(66), 92(42), 91(72), 82(19), 81(54), 80(55), 79(95), 78(28), 77(81), 71(8), 70(21), 69(12), 68(17), 67(72), 66(21), 65(28), 57(8), 56(23), 55(57), 54(35), 53(41), 43(21), 42(11), 41(100), 39(33).

*Diamantanone azine* (XIV): 402(5), 401(25), 400(100), 399(13), 398(3), 385(2), 306(2), 305(3), 293(2), 291(3), 280(2), 279(2), 278(4), 267(2), 240(3), 228(2), 227(6), 203(8), 202(46), 210(28), 200(28), 199(5), 173(5), 172(3), 158(5), 149(4), 146(4), 145(4), 144(5), 143(4), 133(3), 132(5),

131(9), 130(4), 129(5), 121(4), 120(6), 119(5), 118(5), 117(9), 116(4), 115(4), 108(4), 107(5), 106(9), 105(9), 104(5), 95(7), 94(6), 93(16), 92(7), 91(22), 81(13), 80(7), 79(23), 78(7), 77(11), 69(5), 67(12), 66(3), 56(5), 57(3), 56(3), 55(8), 54(4), 53(5), 43(4), 41(14).

## CONCLUSION

The obtained results show marked analogy between the behaviour of azi derivatives of adamantane and diamantane in their photolysis and pyrolysis, and fragmentation of their molecular ions  $M^+$ , generated in the mass spectrometer by electron impact.

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