

MASS SPECTRA AND STRUCTURE IN THE GAS PHASE OF ISOMERIC  
2-AROYLBENZAMIDES

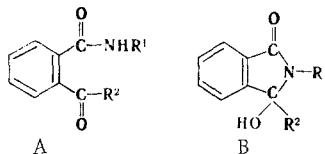
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The electron-impact mass spectra of various derivatives of 2-arylbenzamides were studied. The principal pathways of fragmentation of the open and ring isomeric forms were described on the basis of an analysis of the high-resolution spectra and the DADI spectra. It is shown that peaks of ions formed in the fragmentation of the ring form, the intensities of which decrease as the volume of the substituent increases, are observed in the spectra of compounds with substituents  $R^1 = H, CH_3$ , and  $C_2H_5$ . Thermal isomerization of the ring form was proved on the basis of a study of the temperature effect on the intensities of the peaks of ions due to fragmentation of the open and ring forms when the samples are introduced through an inlet cylinder.

Mass spectrometry is a convenient method for obtaining information regarding the structures of compounds in the gas phase, in which any solvation and intermolecular effects are absent. The forms realized in the gas phase can often be determined for compounds that are capable of isomeric and tautomeric transformations from mass-spectrometric-fragmentation data when data on the individual fragmentation of each of the possible structures are available. We have previously studied [1-3] the mass spectra of derivatives of various nitrogen- and sulfur-containing heterocycles that are capable of amino-imine or ring-chain tautomeric transformations and have drawn conclusions regarding their structure under the conditions of mass-spectrometric analysis.

The present research is devoted to the study, from this point of view, of the mass spectra of N-substituted 2-arylbenzamides, which can exist in two isomeric forms, viz., open form A and ring form B:



It has been previously established [4-6] by IR spectroscopy that compounds with substituents  $R^1 = H, CH_3, C_2H_5, C_6H_5, CH_2C_6H_5$ , and  $n-C_3H_7$ , (I-VIII, Table 1) exist in the B form in the solid state and do not undergo isomerization when they are heated to  $200^\circ C$ . Thermal conversion of the B form to the A form was observed for compounds with substituents  $R^1 = iso-C_3H_7$ , and *tert*- $C_4H_9$ , (IX and XI). The reverse transformation (from A to B) was realized under alkaline-catalysis conditions.

It seemed of interest to study the isomerism of this class of compounds under mass-spectrometric conditions. For this, we studied the electron-impact mass spectra of I-XII (Table 1). An analysis of the mass-spectrometric data (Tables 2 and 3) showed that the spectra of III, IV, and VIII-XII are characterized primarily by the presence of intense peaks of ions formed as a result of cleavage of the amide bond with the elimination of an  $NHR^1$  group from the molecular ion ( $M^+$ ). Peaks of the same fragments but with lower intensities are also observed in the spectra of II and VII. This type of fragmentation should be characteristic for the open form of the molecular ion (structure A). The advantageousness of

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TABLE 1. Investigated Compounds and Their Isomeric Compositions in the Crystalline State and in the Gas Phase

Com- ound	R <sup>1</sup>	R <sup>2</sup>	Form realized	
			solid state (IR spectrum)	gas (mass spectrum)
I	H	C <sub>6</sub> H <sub>5</sub>	B	B + traces of A
II	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	B	B + A
III	C <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	B	A + B
IV	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	C <sub>6</sub> H <sub>5</sub>	B	A + traces of B
V	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	B	A + traces of B
VI	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	B	A + traces of B
VII	CH <sub>3</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	B	B + A
VIII	C <sub>2</sub> H <sub>5</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	B	A + B
IX	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	C <sub>6</sub> H <sub>5</sub>	B	A + traces of B
X	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	C <sub>6</sub> H <sub>5</sub>	A	A
XI	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	A	A
XII	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	B	A

TABLE 2. Mass Spectra of I-XII\*

Com- ound	m/z values (intensities of the ion peaks in percent of the maximum peak)
I	225 (18), 209 (11), 208 (38), 207 (41), 206 (21), 181 (7), 180 (12), 179 (23), 178 (14), 166 (6), 165 (38), 153 (9), 152 (18), 151 (12), 149 (11), 148 (100), 131 (7), 130 (85), 105 (32), 104 (34), 103 (7), 102 (28), 78 (87), 77 (71), 76 (80), 75 (18), 74 (11), 70 (7), 68 (7), 51 (46), 50 (35), 44 (41), 40 (9)
II	239 (8), 223 (f), 222 (15), 210 (29), 209 (17), 195 (2), 181 (6), 163 (11), 162 (100), 153 (8), 152 (15), 133 (17), 118 (6), 105 (19), 102 (6), 91 (8), 78 (33), 77 (38), 76 (15), 51 (18), 50 (8), 40 (9)
III	254 (10), 253 (42), 236 (10), 224 (8), 211 (6), 210 (34), 209 (100), 208 (7), 196 (4), 181 (12), 177 (9), 176 (66), 162 (16), 153 (20), 152 (32), 148 (24), 131 (6), 130 (48), 105 (28), 104 (8), 102 (14), 91 (6), 78 (20), 77 (44), 76 (16), 63 (6), 51 (16), 50 (6), 44 (54)
IV	268 (7), 267 (27), 250 (5), 210 (20), 209 (100), 190 (8), 162 (11), 153 (11), 152 (19), 151 (8), 148 (8), 130 (14), 105 (18), 104 (6), 102 (6), 78 (7), 77 (22), 76 (8), 75 (5), 58 (8), 57 (5), 51 (8), 46 (24), 45 (68), 44 (89), 43 (13), 42 (6), 41 (8), 40 (6)
V	301 (4), 285 (5), 284 (5), 210 (16), 209 (100), 208 (5), 153 (6), 152 (14), 105 (7), 77 (18), 51 (5)
VI	315 (0,1), 298 (1), 238 (0,2), 210 (12), 209 (5), 181 (9), 160 (6), 152 (6), 107 (9), 106 (100), 105 (7), 91 (29), 79 (5), 77 (15), 65 (10), 51 (8)
VII	275 (6), 273 (18), 256 (10), 245 (9), 243 (20), 209 (5), 163 (12), 162 (100), 152 (19), 151 (5), 139 (9), 113 (5), 112 (7), 111 (14), 106 (13), 104 (6), 102 (5), 77 (20), 76 (16), 75 (13), 51 (10), 50 (8), 42 (33)
VIII	289 (13), 288 (8), 287 (40), 272 (5), 271 (5), 270 (11), 258 (8), 256 (7), 246 (8), 245 (37), 244 (25), 243 (100), 242 (7), 181 (8), 177 (8), 176 (60), 153 (7), 152 (50), 151 (12), 148 (19), 141 (7), 140 (8), 139 (18), 138 (8), 130 (43), 113 (8), 112 (6), 111 (22), 105 (10), 104 (8), 103 (6), 102 (16), 77 (20), 76 (23), 75 (17), 63 (7), 51 (10), 50 (11), 44 (80)
IX	267 (11), 252 (7), 250 (2), 210 (22), 209 (100), 208 (6), 190 (5), 181 (5), 153 (9), 152 (17), 148 (12), 130 (12), 105 (14), 102 (5), 77 (20), 76 (6), 58 (26), 51 (6), 44 (5), 40 (10)
X	281 (6), 210 (16), 209 (100), 153 (6), 152 (13), 148 (9), 105 (14), 77 (18), 41 (5)
XI	315 (7), 246 (6), 245 (32), 244 (18), 243 (100), 153 (5), 152 (22), 151 (5), 148 (12), 139 (9), 130 (5), 111 (8), 105 (8), 77 (6), 76 (6), 75 (5), 57 (5), 44 (6), 41 (9), 40 (10)
XII	315 (7), 246 (6), 245 (39), 244 (21), 243 (100), 153 (5), 152 (25), 151 (5), 149 (10), 148 (11), 139 (9), 130 (8), 111 (10), 105 (9), 102 (5), 77 (7), 76 (7), 75 (6), 44 (6), 42 (5), 41 (10), 40 (13)

\*The peaks of the M<sup>+</sup>, C, D, and E ions, as well as the peaks of ions with intensities  $\geq 5\%$ , are presented.

TABLE 3. High-Resolution Spectra of I, IV, and VI

Fragment	I			IV			VI		
	observed	calc.	composition	observed	calc.	composition	observed	calc.	composition
[M-OH] <sup>+</sup>	208,0830	208,0762	C <sub>14</sub> H <sub>10</sub> NO				298,1252	298,1231	C <sub>21</sub> H <sub>16</sub> NO
[M-H <sub>2</sub> O] <sup>+</sup>	207,0734	207,0684	C <sub>14</sub> H <sub>9</sub> NO						
[M-R <sub>2</sub> ] <sup>+</sup>	148,0394	148,0398	C <sub>8</sub> H <sub>6</sub> NO <sub>2</sub>	190,0928	190,0868	C <sub>11</sub> H <sub>12</sub> NO <sub>2</sub>	238,0833	238,0868	C <sub>15</sub> H <sub>12</sub> NO <sub>2</sub>
[M-NHR <sub>1</sub> ] <sup>+</sup>				209,0636	209,0602	C <sub>14</sub> H <sub>9</sub> O <sub>2</sub>	209,0609	209,0602	C <sub>14</sub> H <sub>9</sub> O <sub>2</sub>
[M-R <sub>2</sub> , -OH, -R <sub>1</sub> ] <sup>+</sup>	130,0262	130,0292	C <sub>8</sub> H <sub>4</sub> NO	130,0275	130,0292	C <sub>8</sub> H <sub>4</sub> NO	130,0318	130,0292	C <sub>8</sub> H <sub>4</sub> NO
[M-NHR <sub>1</sub> , -CO] <sup>+</sup>				181,0577	181,0653	C <sub>13</sub> H <sub>9</sub> O	181,0629	181,0653	C <sub>13</sub> H <sub>9</sub> O
[M-NHR <sub>1</sub> , -2CO] <sup>+</sup>				153,0592	153,0578	C <sub>11</sub> H <sub>7</sub> O			
[M-NHR <sub>1</sub> , -CO, -HCO] <sup>+</sup>				152,0568	152,0500	C <sub>11</sub> H <sub>6</sub> O			
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> NH <sup>+</sup>							106,0653	106,0656	C <sub>7</sub> H <sub>8</sub>
C <sub>6</sub> H <sub>5</sub> CH=NH <sup>+</sup>				105,0413	105,0340	C <sub>7</sub> H <sub>5</sub> O	105,0574	105,0576	C <sub>7</sub> H <sub>7</sub>
C <sub>6</sub> H <sub>5</sub> CO <sup>+</sup>							105,0355	105,0340	C <sub>7</sub> H <sub>5</sub> O

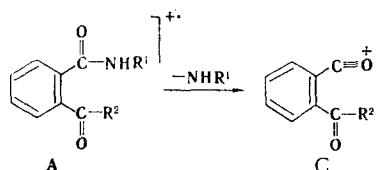
TABLE 4. Ratios of the Intensities of the Ion Peaks I<sub>C</sub>/I<sub>D</sub> and I<sub>C</sub>/I<sub>E</sub> of I-V, VII, VIII, and X

Compound	R <sup>1</sup>	I <sub>C</sub> /I <sub>D</sub>	I <sub>C</sub> /I <sub>E</sub>
I	H	0,3	0,1
II	CH <sub>3</sub>	1,1	0,2
III	C <sub>2</sub> H <sub>5</sub>	10	1,6
IV	n-C <sub>3</sub> H <sub>7</sub>	20	12
V	C <sub>6</sub> H <sub>5</sub>	23	100
VII*	CH <sub>3</sub>	2,2	0,3
VIII	C <sub>2</sub> H <sub>5</sub>	8,5	2,3
X†	t-C <sub>4</sub> H <sub>9</sub>	~	~

\*The intensities of the peaks of C and D ions, which contain <sup>35</sup>Cl and <sup>37</sup>Cl, were taken into account for VII and VIII.

†The peaks of D and E ions are absent in the mass spectra of X-XII.

the elimination of the NHR<sub>1</sub> group in this case is evidently explained by the ease of stabilization of the charge on the amide oxygen atom in fragment C:



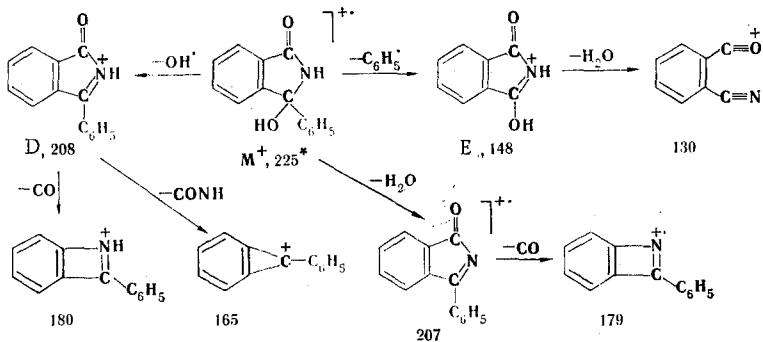
An analysis of the spectra obtained by the DADI method for IV and V showed that the subsequent fragmentation of ion C takes place with the successive detachment of two molecules of CO or a molecule of CO and an HCO radical. The introduction of a benzyl group as substituent R<sup>1</sup> in VI leads to the appearance in the spectrum of intense ion peaks with m/z 210 and 106, which are absent in the spectra of the other compounds. The compositions of the ions were determined from the high-resolution spectra (Table 3). A comparison of the mass spectra obtained by the DADI method and the high-resolution spectra of VI showed that the formation of ions with mass number 210 occurs through stepwise elimination of C<sub>6</sub>H<sub>5</sub> and

TABLE 5. Relative Intensities of the Peaks of C, D, and E Ions of III for Different Inlet Systems and Temperatures

Fragment	Direct introduction, 50°C	Introduction through an inlet cylinder				
		40°	80°	100°	120°	140°
$[M - NH_2C_2H_5]^+$	100	100	100	100	100	100
$[M - OH]^+$	10	89	62	54	46	37
$[M - C_6H_5]^+$	64	50	62	56	60	66

$N=CH_2$  radicals from  $M^+$ . The ion with  $m/z$  106 ( $C_6H_5CH=NH_2^+$ ) is formed directly from  $M^+$  and is the principal product of fragmentation of the latter.

Peaks of  $[M - OH]^+$  (D) and  $[M - R^2]^+$  (E) ions, which can be ascribed to fragmentation of the ring form (see the scheme), are observed in the spectra of I-III, VII, VIII, and, to a lesser extent, IV-VI and IX. Of these ions, the most characteristic is evidently the peak of ion D, since the elimination of substituent  $R^2$  can, in principle, also be expected for the fragmentation of the open structure of  $M^+$  (A). However, it should be noted that the intensity of ion E in the spectra of V, VI, and X-XII, which have an open form, is low or generally equal to zero. However, the peak of ion E has the maximum intensity in the spectra of I, II, and VII. This fact and the similar character of the change in the relative intensity of ions E and D as a function of substituent  $R^1$  provide a basis for the assumption that ion E is also due to a considerable degree of fragmentation of the ring form of  $M^+$ . The overall scheme of the fragmentation of the ring form of the molecular ion, which was proved on the basis of the DADI spectra and high-resolution spectra, is presented below in the case of I:



An analysis of the spectra of compounds with various  $R^1$  substituents shows (see Table 4) that the ratios of the intensities of the ion peaks  $I_C/I_D$  and  $I_C/I_E$  depend markedly on the volume of substituent  $R^1$  and increase rapidly in the order  $R^1 = H < CH_3 < C_2H_5 < iso-C_3H_7 < C_6H_5 < tert-C_4H_9$ . The spectrum of I ( $R^1 = H$ ) is primarily due to fragmentation of the ring form, the ring form still predominates in the spectra of II and VII ( $R^1 = CH_3$ ),<sup>†</sup> while when  $R^1 = C_2H_5$ , the percentages of the ring and open form are comparable. The overall intensity of the peaks of ions due to the fragmentation of the B form is low in the mass spectra of IV-VI and IX. Compounds X-XII have spectra that correspond to the fragmentation of only the A form, and the spectra of isomers XI and XII are virtually identical. Considering the data from the IR spectra [4] indicating thermal isomerization of compounds with substituents  $R^1 = tert-C_4H_9$  and  $iso-C_3H_7$ , it may be assumed that the fragmentation of IV-VI and IX-XII is explained by partial (or complete for some compounds) ring opening during vaporization and heating of the sample in the mass spectrometer. In this connection, we attempted to study the temperature dependence of the intensities of the peaks of ions formed in the fragmentation of the open and ring forms in the spectrum of

\*The  $m/z$  values.

<sup>†</sup>One must, of course, take into account the fact that the ratio of the intensities will also be determined by the ease of cleavage of the C-NH $R^1$  bond and the subsequent fragmentation of the resulting ion. The ratio of the intensities may therefore indicate only substantial predominance of one of the forms or their comparability but cannot be a quantitative characteristic of the ratio of the forms.

III ( $R^1 = C_2H_5$ ) when the sample is introduced through an inlet cylinder and to compare these data with the mass spectra obtained when the sample is introduced directly into the source. The results are presented in Table 5. It can be seen that an increase in the temperature leads to a decrease in the intensity of the peak of ion D, which indicates thermal isomerization of the sample. The more complex character of the temperature dependence of the intensity of the peak of ion E is possibly explained by its formation from both forms.

Of particular interest is the large difference in the relative intensities of the peak of ion D in the spectra obtained by the different methods for introduction of the sample into the ion source. It is apparent from Table 5 that a sharp decrease in the intensity of the peak of ion D occurs in the case of direct introduction of the sample into the source as compared with its intensity when an inlet cylinder is used. This can be explained by thermal isomerization of the sample in the immediate proximity of the heated ionization chamber of the source.

The small difference in the  $I_C/I_D$  and  $I_C/I_E$  values for II and VII and III and VIII, respectively (Table 4), although one might have expected greater stabilization of  $M^+$  of the ring form of VII and VIII because of introduction of an electron-acceptor  $R^2$  substituent ( $C_6H_4Cl$ ), is possibly explained by the same effect.

#### EXPERIMENTAL

The electron-impact and DADI mass spectra were obtained with a Varian MAT-112 spectrometer at an ionizing-electron energy of 70 eV and an ionization-chamber temperature of 180°. Systems for direct introduction of the samples into the source and through an inlet cylinder were used. The substance was introduced into the inlet cylinder in the form of a solution in  $C_2H_5OH$ , after which the alcohol was removed by evacuation. The temperature of the cylinder was varied from 40°C to 120°C. The high-resolution mass spectra were obtained with Varian MAT-212 and JEOL JMS-01-SG-2 spectrometers at 70 eV.

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