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MASS-SPECTRAL BEHAVIOR OF SUBSTITUTED 2-ALKYLAMINOBENZOXAZOLES AND 3-METHYL-2-ALKYLIMINOBENZOXAZOLINES

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Schemes that reflect the peculiarities of each of the investigated groups of compounds and make it possible to distinguish the amino and imino forms are given on the basis of a study of the dissociative ionization processes of 18 2-alkyl(dialkyl)-aminobenzoxazoles and six 3-methyl-2-alkyliminobenzoxazolines. A qualitative relationship between the electronic properties of the substituents in the aromatic ring and the formation of the imino forms of the molecular ions in the gas phase was found.

The problem of the possibility of the use of mass spectrometry as a method for the determination of the existence of tautomeric equilibria in various organic compounds has been discussed repeatedly [1-3]. Relatively recently Ogura and co-workers [4] described the mass spectra of a series of N-alkylaminobenzothiazoles. In a comparison of some peculiarities of the mass-spectral behavior of 2-methylaminobenzoxazole and 3-methyl-2-iminobenzoxazoline (as well as their thiazole analogs) they erroneously concluded that the mass spectra of these compounds are virtually identical, whereas a more thorough analysis of the mass spectra† presented in [4] makes it possible to note that higher stability of the molecular ions, a higher probability of the loss of a hydrogen atom or a CH_3N fragment by the molecular ion, and a lower probability of elimination of H_2CN or $CH_3N{-}CN$ fragments are characteristic for the 2-methylamino derivatives as compared with the isomeric 2-imino compounds.

In order to find distinctive features that are characteristic for the mass spectra of 2-alkylaminobenzoxazoles (I) and 2-alkyliminobenzoxazolines (II) we studied the dissociative ionization of a large series of Ia-r and IIa-f compounds that contain electron-donor or electron-acceptor substituents in the benzene ring.

The synthesis of these compounds [5] and their IR spectra [6] have been previously described. A comparison of the mass spectra of Ia,l,n,q that we obtained with the spectra presented in [4] showed good agreement for the peaks with intensities greater than 90%, and this

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*Deceased.

†The mass numbers of the ions in the mass spectra of these and many other compounds published in [4] are frequently presented, but the intensities of their peaks are not indicated. In addition, the presence in them of $[M-12]^+$, $[M-13]^+$, and $[M-24]^+$ ion peaks and the increased (as compared with the theoretically possible values) intensities of the $[M+1]^+$ ion peaks make it possible to assert that some of the investigated compounds were not sufficiently pure for mass-spectral analysis.

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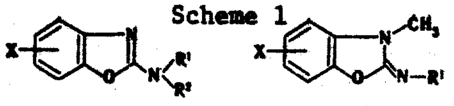
Scheme 1



I a-r II a-f

I	R^1	R^2	X	II	R^1	X
a	n-C_4H_9	H	H	a	CH_3	6-NO_2
b	n-C_4H_9	H	5-CH_3	b	n-C_3H_7	6-NO_2
c	n-C_4H_9	H	5-SO_2NH_2	c	n-C_4H_9	6-NO_2
d	n-C_4H_9	H	6-SO_2NH_2	d	*cyclo*-C_6H_{11}	6-NO_2
e	n-C_4H_9	H	5-Cl	e	*cyclo*-C_6H_{11}	5-SO_2NH_2
f	n-C_4H_9	H	6-Cl	f	*cyclo*-C_6H_{11}	H
g	n-C_4H_9	H	5-NO_2			
h	n-C_4H_9	H	6-NO_2			
i	n-C_4H_9	H	6-Br			
j	n-C_4H_9	H	5-SO_2CH_3			
k	n-C_4H_9	H	6-SO_2CH_3			
l	$C_6H_5CH_2$	H	H			
m	C_6H_5	H	H			
n	$-(CH_2)_2-O-(CH_2)_2$		H			
o	$-(CH_2)_2-O-(CH_2)_2$		5-NO_2			
p	$-(CH_2)_5-$		5-NO_2			
q	CH_3	CH_3	H			
r	C_2H_5	C_2H_5	5-NO_2			

makes it possible in a number of cases to compare the data that we obtained with the data described in [4].

It should first of all be noted that the presence in the benzene ring of both electron-donor and electron-acceptor has no effect on the primary pathways of fragmentation of the molecular ions of I and II. The X substituents are split out in most cases in subsequent stages of the fragmentation. This makes it possible to assume that the positive charge in the molecular ions of these compounds is localized in the region of the —N=C—N— grouping. This is also indicated by the character of the "amine" fragmentation, which consists in primary cleavage of the β-C—C bond with respect to the exocyclic nitrogen atom (the F_2 and F'_2 ions; see the scheme presented above . In the case of N,N-disubstituted aminobenzoxazoles In-p,r this process is accompanied by transfer of a proton from the second hydrocarbon grouping with the formation of stable amine fragment F_3 . A second important pathway of fragmentation of I and II, which was also noted in [4], is a McLafferty rearrangement, which leads to the F_4 (F'_4) ion. Finally, a third pathway of fragmentation of the investigated compounds entails α cleavage of the N—C bond, which leads to F_1 (F'_1) ions.

An analysis of the intensities of the indicated characteristic ions (Tables 1 and 2) makes it possible to note that the formation of F_2 and F_4 ions is characteristic for monosubstituted Ia-l and that F_1 ions are not characteristic; the ratio of the intensities of the F_2 and F_4 ion peaks ($I_{F_2}/I_{F_4} = K$) is always less than unity in this case. At the same time, intense F_1 ion peaks and low intensities of the F_4 ion peaks ($K \gg 1$) are typical for the mass spectra of N,N-disubstituted derivatives (Iq,r). In addition, very intense (usually maximum-intensity) F_3 ion peaks are characteristic for In-p,r. Let us note that our analysis of the data in [4] confirms these conclusions.

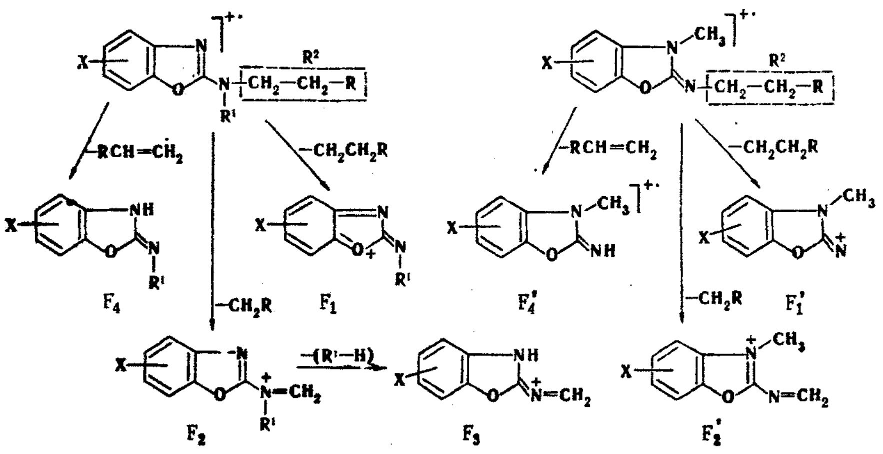


TABLE 1. Mass Spectra of I and II*

Compound	m/e values (relative intensities, %)
I a	190 (37), 173 (13), 148 (18), 147 (57), 134 (100), 120 (21), 105 (17), 91 (55), 79 (30), 78 (16)
I b	204 (71), 187 (34), 161 (90), 148 (100), 147 (49), 134 (24), 133 (36), 91 (42), 78 (32), 77 (32)
I c	269 (61), 226 (72), 213 (61), 146 (34), 91 (100), 83 (35,5), 81 (38), 79 (43), 78 (34), 77 (47)
I d	269 (100), 252 (26), 226 (71), 213 (62), 133 (25), 105 (49), 91 (82), 81 (32), 78 (50), 77 (52)
I e	226 (10), 224 (38), 207 (16), 183 (14), 182 (15), 181 (52), 170 (27), 168 (100), 113 (12), 76 (14)
I f	226 (11), 224 (38), 207 (12), 182 (14), 181 (42), 170 (25), 168 (100), 154 (15), 91 (14), 81 (13)
I g	235 (76), 193 (32), 192 (70), 179 (100), 146 (96), 133 (60), 105 (47), 91 (71), 78 (48), 77 (67)
I h	235 (91), 193 (35), 192 (70), 179 (100), 91 (91), 105 (66), 81 (44), 77 (76), 69 (68), 78 (74)
I i	270 (38), 268 (38), 227 (40), 225 (44), 214 (95), 212 (95), 91 (100), 83 (36), 81 (66), 71 (60)
I j	268 (69), 226 (27), 225 (67), 212 (70), 146 (56), 133 (100), 91 (56), 79 (30), 78 (36), 77 (46)
I k	268 (57), 226 (19), 225 (56), 212 (51), 97 (53), 91 (100), 83 (67), 82 (41), 81 (69), 71 (83)
I l	224 (25), 223 (5), 133 (1), 117 (1), 106 (2), 105 (3), 92 (7), 91 (100), 78 (2), 65 (13)
I m	210 (100), 209 (39), 106 (17), 105 (12), 91 (16), 78 (22), 77 (42), 69 (17), 65 (13), 51 (35)
I n	204 (93), 149 (4), 148 (12), 147 (100), 146 (55), 145 (3), 119 (5), 92 (7), 91 (3), 73 (3)
I o	249 (100), 203 (6), 193 (6), 192 (86), 191 (36), 178 (2), 175 (2), 161 (5), 146 (11), 145 (17)
I p	247 (100), 201 (15), 192 (19), 90 (28), 83 (15), 77 (16), 69 (75), 63 (31), 55 (69), 79 (15)
I q	162 (100), 147 (84), 133 (27), 120 (12), 119 (32), 78 (28), 77 (15), 63 (11), 51 (22), 72 (7)
I r	235 (51), 220 (26), 207 (6), 206 (34), 193 (5), 192 (100), 146 (25), 71 (20), 63 (12), 56 (14)
II a	207 (100), 192 (6), 161 (9), 160 (11), 111 (4), 81 (11), 206 (16), 81 (10), 73 (19), 60 (26)
II b	235 (8), 206 (100), 207 (11), 160 (29), 92 (4), 85 (4), 71 (8), 69 (7), 60 (5), 57 (14)
II c	249 (11), 207 (18), 206 (100), 160 (31), 98 (11), 97 (10), 92 (11), 71 (15), 69 (11), 57 (29)
II d	275 (55), 258 (6), 246 (7), 233 (15), 232 (100), 81 (11), 71 (13), 69 (21), 57 (17), 55 (11)
II e	309 (33), 292 (4), 278 (4), 266 (14), 265 (100), 227 (4), 97 (3), 57 (13), 56 (43), 55 (13)
II f	230 (28), 213 (4), 201 (3), 188 (13), 187 (100), 174 (3), 161 (3), 160 (2), 148 (4), 109 (3)

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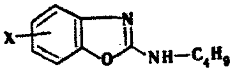
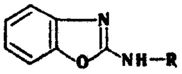
*The 10 most intense peaks are presented.

TABLE 2. Relative Intensities of the Characteristic Ions in the Mass Spectra of Some I and II ($\%\Sigma_{39}$)

Compound	W_M	F_1	F_2	F_3	F_4	$[M-X]^+$	$[M-OH]^+$
I a	5,6	0,6	8,6	—	15,2	—	2,0
I g	6,8	0,3	6,3	—	9,1	—	2,2
I r	14,4	8,8	6,7	25,8	0,6	1,2	—
I o	35,4	—	—	28,4	—	2,1	—
I n	30,7	—	—	30,2	—	—	—
I p	15,0	—	—	2,6	—	2,1	—
I h	6,7	0,4	5,9	—	7,4	—	1,8
II c	3,4	0,4	27,0	—	0,6	—	1,6
II b	4,5	0,4	49,0	—	—	—	0,3
II d	22,0	1,1	—	1,1	1,3	—	1,7
II a	19,8	1,1	—	—	—	1,8	—
II f	17,6	2,5	—	1,6	2,5	—	2,1
I g	34,8	27,2	—	—	—	—	—

The difference in the mass-spectral behavior of aminobenzoxazoles I from that of iminobenzoxazolines II consists in the appreciably lower stabilities of the molecular ions of the latter and the correspondingly higher I_{F_2}/I_M values. In the case of IIb and IIc this value

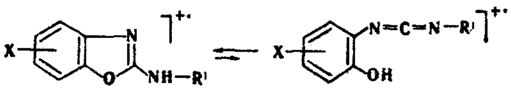
TABLE 3. K = I_{F_2}/I_{F_4} Values As a Function of Substituent X in the Benzene Ring (our data) and Substituent R (data in [4])

			
X	K	R	K
H	0,56	C_2H_5	0,45
5-CH_3	0,90	C_3H_7	0,44
5-Cl	0,52	*i*-C_3H_7	0,20
5-SO_2NH_2	1,2	*n*-C_4H_9	0,64
5-SO_2CH_3	0,96	*i*-C_4H_9	0,46
5-NO_2	0,60	*sec*-C_4H_9	0,40
6-Br	0,46	*tert*-C_4H_9	0,02
6-Cl	0,42	*n*-C_6H_{13}	0,65
6-SO_2NH_2	1,15		
6-SO_2CH_3	1,07		
6-NO_2	0,80		

is greater than 10, while in the case of the isomeric amino derivative Ig it is close to unity.

Thus N-alkylaminobenzoxazoles and N-alkyliminobenzoxazolines behave substantially differently under electron impact. If it is assumed that the F_2 ion is characteristic only for the imino form (IIb, c), whereas the rearranged F_4 ion reflects the contribution of the amino form to fragmentation, one might have expected existence of a correlation between the K value and the σ constants of the X substituents in the Ia-k series. An examination of the data in Table 3, in which our results and the results obtained in [4] are presented, makes it possible to note the existence of a qualitative correlation between the character of the substituent in the benzene ring and the K value, viz., the K value is larger in the case of the presence of electron-acceptor substituents in the 6 (but not the 5) position of 2-butylaminobenzoxazole, i.e., these substituents promote a shift of the equilibrium in the direction of the imino form. Similarly, lengthening of the hydrocarbon chain attached to the exocyclic nitrogen atom also evidently promotes an increase in the fraction of the imino form. Nevertheless, we were unable to make any quantitative estimates of the effect of the substituents.

A peculiarity of the mass spectra of all I and II except for dialkylamino-substituted In-r and 2-phenylaminobenzoxazole Im is the presence in them of rather intense $[M-OH]^+$ ion peaks from 0.3 to 3.0% of the Σ_{39} total ion current (demonstrated by means of the high-resolution mass spectra). A partial ($\sim$20%) shift of the mass of this ion by one unit is observed in the mass spectrum of Ig. This makes is possible to assume that an amine hydrogen atom participates in its formation, i.e., at least some of the molecular ions of the aminobenzoxazoles may exist in the open hydroxyphenylcarbodiimide form:



In addition $[M-OH]^+$ ions are also observed in the mass spectra of aminobenzoxazoles presented in [4].

EXPERIMENTAL

The mass spectra were obtained with MKh-1303 and MS-30 (AEI) mass spectrometers at ionization energies of 50 and 70 eV, respectively, with direct introduction of the samples into the ionization region.

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ACIDIC PROPERTIES AND STRUCTURES OF HETEROCYCLIC AMINOVINYL KETONES AND AMINOVINYL THIONES*

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V. A. Bren', and V. I. Minkin

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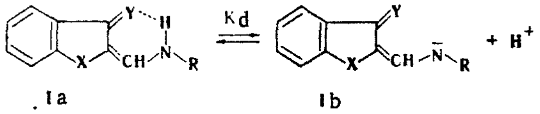
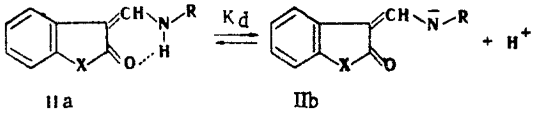
The ionization constants of 33 keto and thiono amines of the benzo[b]furan, benzo[b]thiophene, indan, and 1-methylindole series were determined by potentiometric titration in acetonitrile. The effect of various structural factors on the acidities of these compounds was ascertained. The effect of N-aryl substituents on the free energies of the deprotonation reactions was evaluated quantitatively by means of correlation analysis.

Keto and thiono amine structures are characteristic for heterocyclic azomethines Ia and IIa [2-7]. The proton of the NH group participates in the formation of an intramolecular hydrogen bond (IHB), the strength of which depends on the peculiarities of the structures of imines Ia and IIa.



(1)



(2)

I a,b X=O, S, CO, CH_2, SO_2, Y=O, S; R=Ar, Alk; IIa,b X=S, NCH_3; R=Ar, Alk

We have previously investigated the relationship between the basicities of compounds of the Ia and IIa type and the nature of the R grouping attached to the imine nitrogen atom. In the present research we set out to determine the acidities of aminomethylene ketones and aminomethylene thiones Ia and IIa and to investigate the effect of substituents R, heteroatoms X and Y, and other structural factors of Ia and IIa on their ability to undergo acidic ionization via Eqs. (1) and (2).

With this end in mind we measured the acid dissociation constants (K_d) of Ia and IIa and, by means of correlation analysis, evaluated the structure-acidity relationships in these reaction series. For the determination of the K_d values we selected nonaqueous potentiometric titration in acetonitrile [8, 9], which we used in [1] for the study of the basic properties of compounds of the Ia type.

According to the results of previous studies [9-11], equilibria (1) and (2) may be complicated by the formation of homoconjugates of the Ia·Ib and IIa·IIb type, which exist in equilibrium with the unassociated forms. The titration curves of the majority of the Ia and IIa compounds in the buffer region differ little from the theoretically calculated curves,

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*Communication 19 from the series "Basicities and structures of azomethines and their structural analogs"; see [1] for Communication 18.

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