4H-3, 1-BENZOXAZINES.

5.* PMR AND MASS SPECTROMETRIC STUDY OF 2,4-SUBSTITUTED 1,2-DIHYDRO-4H-3,1-BENZOXAZINES

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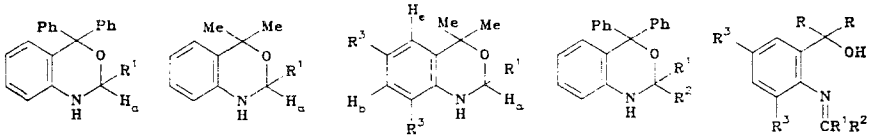
The formation of 2,4-substituted 1,2-dihydro-4H-3,1-benzoxazines from tertiary o-aminophenylcarbinols and carbonyl derivatives has been demonstrated by means of PMR and mass spectrometry. Interconversion of the six-membered heterocycle of the half-chair ⇌ half-chair type has been established on the basis of the PMR data when identical substituents are present in positions 2 and 4. The cis-arrangement of the protons in the H—$C_{(2)}$—N—H fragment of the heterocycle has been determined. The general laws governing the initial fragmentation of 1,2-dihydro-4H-3,1-benzoxazines under the effects of electron impact have been revealed.

We previously synthesized [2] a number of 1,2-dihydro-4H-3,1-benzoxazines by reacting tertiary o-aminobenzyl alcohols with carbonyl compounds and established their cyclic structure by chemical methods [3], as well as by IR and UV spectroscopy [2]. However, substituted 1,2-dihydro-4H-3,1-benzoxazines are still compounds which have been studied to a small extent, despite the data in [4-8].

The purpose of the present work was to use PMR and mass spectrometry to establish the structures of compounds I-XVIII, which we synthesized and which can exist in the cyclic 1,2-dihydro-4H-3,1-benzoxazine form (A-D) or the alternative azomethine form (E).



In I, IX, XVI, and XVIII $R^1 = CH_3$; in III, X, XIII, and XIV $R^1 = CCl_3$; in II $R^1 = n\text{-}C_3H_7$; in IV and XI $R^1 = C_6H_5$; in V R^1 = 2-furyl; in VI R^1 = 5-bromo-2-furyl; in VII, XII, and XV R^1 = 5-nitro-2-furyl; in VIII R^1 = 2-(5-methyl-2-furyl)-2-ethyl; in XVI $R^2 = CH_3$; in XVII R^1, $R^2 = (CH_2)_5$; in XVIII $R^2 = C_2H_5$; in XIII $R^3 = NO_2$; in XIV and XV R^3 = Br.

It is known that 1,3-oxazine and its derivatives have a chair conformation, according to the PMR data in [9]. In the case of the 2,3-dihydro-6H-1,3-oxazines with one double bond in the ring, a half-chair conformation is realized [10]. In compounds I-XVII, which we examined, the 1,3-oxazine ring is annelated to a benzene ring, causing the heterocycle to have a half-chair conformation with a planar configuration for the four $C_{(4)}$—C = C − N atoms in the plane of the benzene ring and protrusion of the $C_{(2)}$—O grouping of two atoms from this plane.

*For Communication 4, see [1].
†Deceased.

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TABLE 1. PMR Spectra of 1, 2-Dihydro-4H-3, 1-benzoxazines

Compound	Solvent	Chemical shifts, δ ppm						Spin–spin coupling constant, Hz
		R_a (c)	R_e (c)	H(R^1)	H_a(R^2)	H–N (1H, br.s)	C_6H_4* (4H, m)	
I	CCl_4	7,08 (5H)	7,20 (5H)	1,33 (3H, d)	4,45 (1H, q)	3,72	6,57	$^3J_{CHCH_3}=6,0$
II	CCl_4	7,06 (5H)	7,20 (5H)	1,51 (4H, m, α,β-CH_2); 0,70 (1H, t, γ-CH_3)	4,38 (1H, t)	3,84	6,54	$^3J_{CHCH_2}=6,0$; $^3J_{CH_2CH_3}=6,0$
III	CCl_4	7,10 (5H)	7,25 (5H)	—	4,83 (1H, d)	4,60	6,50	$^3J_{CHNH}=1,5$
IV	CCl_4	7,10 (5H)	7,20 (5H)	7,00 (5H, m)	5,23 (1H, s)	3,93	6,50	—
	$(CH_3)_2CO$	7,50 (5H)	7,50 (5H)	7,30 (5H, s)	5,55 (1H, d)	5,80	6,80	$^3J_{CHNH}=1,5$
V	CCl_4	7,00 (5H)	7,18 (5H)	6,35 (1H, d) 5′-H); 6,20 (1H, d, 3′-H); 6,12 (1H, t, 4′-H)	5,35 (1H, s)	4,35	6,55	$^3J_{5,4}=3,0$; $^3J_{3,4}=2,0$
	$(CH_3)_2CO$	7,25 (5H)	7,40 (5H)	6,62 (1H, d, 5′-H); 6,50 (1H, d, 3′-H); 6,45 (1H, t, 4′-H)	5,62 (1H, d)	6,00	6,83	$^3J_{5,4}=3,0$; $^3J_{3,4}=2,0$ $^3J_{CHNH}=3,0$
VI	CCl_4	7,09 (5H)	7,25 (5H)	6,35 (1H, d, 4′-H); 6,20 (1H, d, 3′-H)	5,50 (1H, s)	4,20	6,65	$^3J_{3,4}=3,5$
VII	$CDCl_3$	7,18 (5H)	7,30 (5H)	6,62 (1H, d, 3′-H); 7,12 (1H, d, 4′-H)	5,62 (1H, s)	5,08	6,80	$^3J_{3,4}=4,0$
VIII	CCl_4	7,10 (5H)	7,22 (5H)	1,86 (2H, m, α-CH_2); 2,60 (2H, t, β-CH_2); 2,03 (3H, s, CH_3); 5,58 (2H, s, 3′-H, 4′-H)	4,47 (1H, t)	3,72	6,57	$^3J_{CHCH_2}=5,0$; $^3J_{CH_2CH_2}=6,5$
IX	CCl_4	1,40 (3H)	1,45 (3H)	1,31 (3H, d)	4,70 (1H, q)	3,56	6,50	$^3J_{CHCH_3}=6,0$
X	CCl_4	1,51 (3H)	1,56 (3H)	—	4,96 (1H, s)	4,36	6,75	—
XI	CCl_4	1,43 (3H)	1,49 (3H)	7,20 (5H, m)	5,38 (1H, s)	3,70	6,55	—
XII	$CDCl_3$	1,52 (3H)	1,60 (3H)	6,70 (1H, d, 3′-H); 7,28 (1H, d, 4′-H)	5,72 (1H, d)	4,12	6,97	$^3J_{3,4}=4,0$; $^3J_{CHNH}=1,5$
XIII	$CDCl_3$	1,45 (3H)	1,56 (3H)	—	5,27 (1H, s)	9,30	8,87 (1H, d, H_B); 8,00 (1H, d, H_c)	$^3J_{Bc}=3,0$
XIV	$CDCl_3$	1,51 (3H)	1,60 (3H)	—	5,01 (1H, s)	5,33	7,41 (1H, d, H_B); 7,14 (1H, d, H_c)	$^3J_{Bc}=3,0$
XV	$CDCl_3$	1,55 (3H)	1,47 (3H)	6,65 (1H, d, 3′-H); 7,20 (1H, d, 4′-H)	5,70 (1H, d)	4,70	7,35 (1H, d, H_B); 7,00 (1H, d, H_c)	$^3J_{3,4}=4,0$; $^3J_{Bc}=3,0$ $^3J_{CHNH}=1,5$
XVI	$CDCl_3$	7,18 (5H)	7,18 (5H)	1,27 (3H, s)	1,27 (3H, s)	3,80	6,67	—
XVII	$CDCl_3$	7,18 (5H)	7,18 (5H)		1,40 (10H, s)	4,27	6,59	—
XVIII	$CDCl_3$	7,14 (5H)	7,20 (5H)	1,10 (3H, s)	0,88 (3H, t, β-CH_3); 1,57 (2H, q, α-CH_2)	3,80	6,66	$^3J_{CH_2CH_3}=6,0$

* I—XII, XVI—XVIII R^3=H, XIII $R^3=NO_2$, XIV, XV R^3=Br.

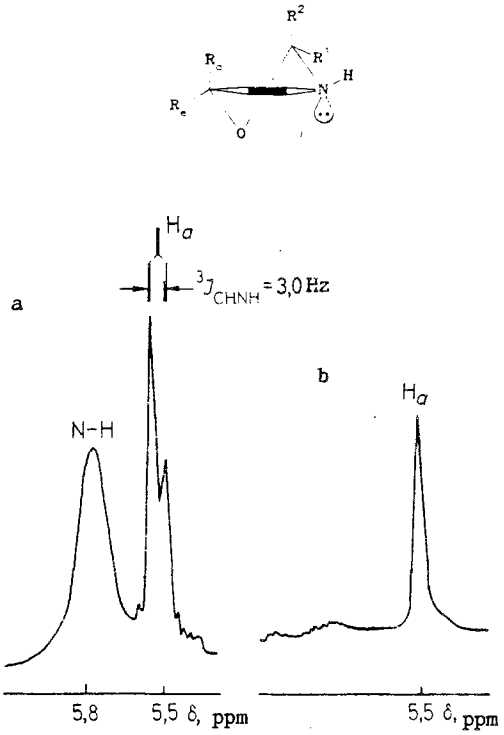


Fig. 1. PMR spectra of 2,4,4-triphenyl-1,2-dihydro-4H-3,1-benzoxazine (IV): a) In acetone; b) in an acetone–D_2O mixture.

In the PMR spectra of compounds I-XV and XVIII, the presence of two singlet signals of the protons of the gem-dimethyl (or diphenyl) grouping attest to their inequivalence. This finding allows us to assert that the molecules of the compounds indicated have cyclic structures A-D and exist predominantly in a half-chair conformation (Table 1). The spectra of compounds III-V, XII, and XV display doublet splitting of the signal of the proton at the $C_{(2)}$ atom of the ring and the presence of a diffuse resonance band of the proton at the N atom (Table 1). In the case of the 1, 2-dihydro-4H-3, 1-benzoxazines without substituents at the nitrogen atom, it is potentially possible to determine the vicinal spin-spin coupling constant of the protons of the H–$C_{(2)}$–N–H fragment. However, owing to the fact that the nucleus of the ^{14}N atom has a spin number equal to 1 and, therefore, has a quadrupole moment, the resonance signals of the N–H protons are strongly broadened. For this reason, it is possible to determine the spin–spin coupling constant $^3J_{HCNH}$ only on the basis of the spectra of compounds III-V, XII, and XV when D_2O is added to the solutions under investigation. As a result, the resonance band of the N–H group vanishes due to the exchange of the protons for deuterium, and the split resonance signal of the proton at the $C_{(2)}$ atom of the ring becomes a singlet (Fig. 1). According to [11], a Karplus dependence may be expected for the heteroatomic H–$C_{(2)}$–N–H fragment. The values of the spin–spin coupling constant $^3J_{HCNH}$, which are equal to 1.5 and 3.0 Hz (Table 1), attest to the cis configuration of the $C_{(2)}$–H and N–H bonds with an axial methine proton and an equatorial proton at the nitrogen atom. The orbital of the lone pair of the N atom has an axial direction.

The absence of doublet splitting of the signal of the $C_{(2)}$–H proton in the spectra of compounds I, II, VI-XI, XIII, and XIV does not contradict their cyclic structure, since the chemical shift of this proton is equal to 4.38-5.27 ppm, rather than 8.12-8.36 ppm, as is observed upon the transition to the azomethine form [12, 13].

The PMR spectrum of compound XVI reveals the singlet nature of the resonance signals of the geminal substituents in positions 2 and 4 of the ring at 1.27 and 7.18 ppm, respectively, which attest to interconversion of the six-membered heterocycle of the half-chair $\rightleftharpoons$ half-chair type. Similar inversion of the heterocycle also takes place in the case of compound XVII. In the case of 1, 2-dihydro-4H-3, 1-benzoxazine XVIII, which has different substituents at the $C_{(2)}$ atom (R^1 = CH_3, R^2 = C_2H_5), interconversion is not observed. When the measurement temperature is increased to 130°C, the spectroscopic parameters of 1, 2-dihydro-4H-benzoxazine remain unchanged, i.e., the two lines of the gem-diphenyl grouping do not merge.

TABLE 2. Mass Spectra of Dihydrobenzoxazines

Compound	Value of m/z (I_{rel}, %)*
III**	403 (3), 286 (100), 256 (10), 254 (6), 208 (42), 180 (13), 165 (13), 152 (4), 105 (9), 77 (8), 51 (4)
IV	363 (61), 286 (12), 258 (24), 257 (32), 256 (100), 254 (17), 180 (40), 152 (8), 105 (24), 77 (26), 52 (7)
V	353 (32), 257 (20), 256 (100), 202 (20), 180 (33), 95 (24), 81 (59), 77 (15),
VI**	69 (92), 57 (48), 55 (42)
	431 (12), 352 (7), 300 (15), 258 (9), 257 (20), 256 (100), 254 (11), 180 (33), 165 (5), 105 (9), 77 (19)
VII	398 (29), 381 (11), 286 (8), 258 (14), 257 (9), 256 (100), 254 (10), 180 (31), 165 (10), 105 (10), 77 (13)
VIII	395 (58), 286 (56), 258 (100), 256 (37), 208 (43), 202 (15), 180 (30), 165 (18), 95 (59), 58 (17), 56 (18)
IX	177 (57), 162 (83), 157 (71), 144 (100), 133 (60), 132 (58), 118 (33), 117 (29), 91 (34), 77 (37), 57 (20)
X**	279 (3), 162 (100), 144 (43), 134 (11), 132 (8), 118 (6), 117 (7), 106 (8), 94 (9), 91 (13), 77 (7)
X-D***	280 (4), 163 (100), 162 (24), 145 (53), 144 (28), 135 (21), 134 (9), 133 (11), 132 (5), 119 (10), 118 (13), 117 (9), 107 (8) 106 (9), 95 (9), 94 (11), 92 (9), 91 (17), 77 (11)
XI	239 (23), 224 (10), 133 (100), 132 (34), 130 (6), 118 (20), 117 (11), 105 (21), 91 (19), 77 (35), 51 (15)
XII	274 (28), 259 (14), 133 (100), 132 (38), 130 (6), 118 (18), 117 (10), 115 (7), 91 (13), 77 (7), 51 (8)
XVI	315 (24), 300 (100), 258 (14), 256 (57), 180 (24), 165 (10), 150 (33), 81 (25), 77 (14), 69 (46), 55 (26)
XVIII	329 (11), 314 (15), 300 (100), 258 (11), 256 (32), 254 (6), 180 (55), 165 (15), 152 (15), 105 (7), 77 (13)

*The peaks for M^+ and the 10 most intense ions are presented.

**The values of m/z of the molecular ions were calculated for the light isotope of the halogen (^{79}Br and ^{35}Cl).

***Dihydrobenzoxazine X labeled with deuterium.

TABLE 3. Intensity of the Peaks of the Principal Characteristic Ions in the Mass Spectra of Compounds III-XII, XVI, and XVII (Σ_{50}, %)

Compound	W_M	F_1	F_2 (RDA + H)	F_3 (RDA)	F_4 (RDA−H)	F_5	F_6	F_7	F_8	F_9
III	1,4	26,9	—	—	2,6	3,4	—	—	11,2	3,4
IV	10	1,9	3,8	5,2	16,4	6,5	—	—	—	1,1
V	4,3	—	0,8	2,7	13,7	4,5	—	—	—	1,2
VI	7,2	—	2,9	6,3	30,9	10,1	—	—	—	1,5
VII	10,1	2,8	4,9	3,1	34,7	10,6	—	—	—	3,4
VIII	8,8	8,5	15,3	—	5,6	4,6	—	—	6,6	2,8
IX	8,2	12,0	1,9	8,7	8,5	4,7	4,9	14,5	—	—
X	1,4	24,6	2,6	0,8	1,9	1,5	3,3	10,6	—	—
XI	4,3	0,7	—	18,7	6,4	4,0	3,6	—	—	—
XII	5,9	0,8	—	20,9	8,0	4,0	2,7	—	—	—
XVI	4,9	20,8	2,8	—	11,8	4,9	—	—	—	2,0
XVIII*	3,2	31,4	3,2	—	10,0	17,2	—	—	—	4,6

*The intensity of the peak for F_1' is 4.5.

Thus, the PMR data for the series consisting of 1, 2-dihydrobenzoxazines I-XV and XVIII indicate that fixation of the half-chair conformation and the absence of its inversion are stipulated by the different structures of the substituents in the second position of the ring.

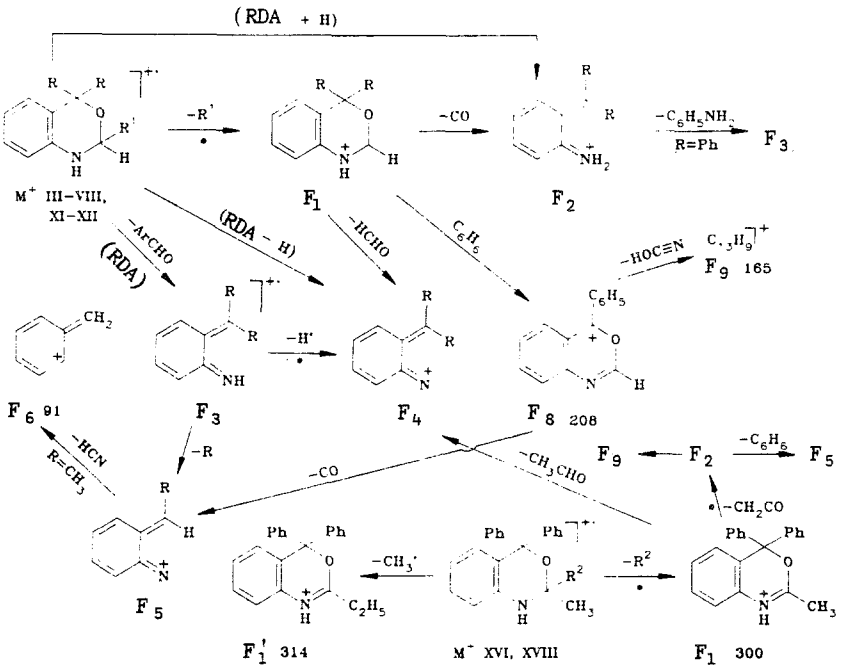
A comparison of the PMR spectra of benzoxazines I, II, and IX, which have alkyl substituents in the second position of the heterocycle, with 2-alkyltetrahydro-1, 3-oxazines [9] reveals downfield displacement of the signals of the protons at the $C_{(2)}$ atoms of all the benzoxazines ($\Delta\delta$ = 0.29-0.60 ppm), which is caused by the anisotropic magnetic influence of the aromatic ring condensed with the heterocycle.

In the series of 1, 2-dihydro-2-[furyl-2-(alkyl, phenyl)]4H-3, 1-benzoxazines I-XII, downfield displacement of the chemical shift of the 2-H proton is also observed as the acceptor influence of the substituent in position 2 is enhanced ($\Delta\delta_{I\text{-}IV, V}$ = 0.78 and 0.90, $\Delta\delta_{IX\text{-}XI}$ = 0.68 ppm, Table 1). This effect is most clearly expressed when electron-acceptor groups (Br, NO_2) are introduced into the furan ring ($\Delta\delta_{I\text{-}VI,VII}$ = 1.05 and 1.17, $\Delta\delta_{IX\text{-}XII}$ = 1.02 ppm).

The nature of the substituent at the $C_{(2)}$ atom also has an influence on the position of the chemical shifts of the signals of the proton of the N—H group. An effect of deshielding of the proton of the NH group is observed in the 2-nitrofuryl-, 2-bromofuryl-, and 2-trichloromethyl-1, 2-dihydro-4H-3, 1-benzoxazines (III, VI, VII, X, and XII) (Table 1). If the furan ring is separated from the heterocycle by several methylene fragments (compound VIII), its influence on the signals of the C_2—H and NH protons is not manifested. The introduction of acceptor substituents into the aromatic ring condensed with the heterocycle causes significant downfield displacement of the signal of the proton of the NH group ($\Delta\delta_{X\text{-}XIV}$ = 0.97, $\Delta\delta_{XII\text{-}XV}$ = 0.58, $\Delta\delta_{X\text{-}XIII}$ = 4.94 ppm). In the case of compound XIII, the drastic downfield displacement of the signal of this proton may be attributed to the existence of an intramolecular hydrogen bond between the proton of the amino group of the heterocycle and the oxygen atom of the nitro group.

An analysis of the mass spectra (Table 2 and 3) reveals that the spectra of all the samples investigated contain peaks for the molecular ions (M^+), whose fragmentation is determined by the character of the substituent at the $C_{(2)}$ atom of the heterocycle. The molecular ions of 2-alkyldihydrobenzoxazines III, VIII, XVI, and XVIII initially eliminate the alkyl radicals to form ions with a 4H-3, 1-benzoxazine structure (F_1). Then fragmentation of the heterocycle is possible by means of the elimination of molecules of carbon monoxide, benzene, formaldehyde (or acetaldehyde), which gives the F_2, F_8, F_5, and F_4 ions (Scheme 1). The $F_1 \rightarrow F_8$, $F_1 \rightarrow F_4$ fragmentation processes, as well as the $F_8 \rightarrow F_5$ and $F_8 \rightarrow F_9$ processes, are confirmed for compound III by the DADI spectra of the F_1 and F_8 cations.

Scheme 1

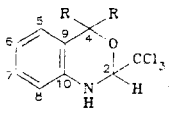


The primary fragmentation act of the molecular ions M^+ of 2-furyl(phenyl)dihydrobenzoxazines IV-VIII, XI, and XII is the loss of a molecule of the aromatic aldehyde with the formation of the F_3 ion (reverse Diels—Alder reaction, RDA [14, 15]). The ion F_3 next eliminates a hydrogen atom (F_4, the RDA − H process) or a phenyl (methyl) radical (F_5) and then an HCN molecule (F_6, when R = CH_3). The appearance of benzaldehyde and furfural molecules during the fragmentation of the molecular ions M^+ of compounds IV, XI, and V is confirmed by the presence of even-electron ions with m/z 105 and 95, respectively, in their mass spectra [16].

The formation of the F_1 ions for dihydrobenzoxazines IX, XVIII and the F_3 and F_4 ions (compound V) is confirmed by the metastable transitions.

The initial fragmentation of 2, 4-substituted dihydrobenzoxazines III-VIII, XI, XII, XVI, and XVIII with the formation of characteristic ions F_1-F_5 just described is consistent with the data on the fragmentation of 2-aryl-1, 2-dihydro-4H-3, 1-benzoxazines presented in [8] and confirms the existence of the cyclic form of the compounds investigated in the gaseous phase.

TABLE 4. ^{13}C NMR spectra of Compounds III and X



Compound	δ, ppm (in CD_2Cl_2)										
	$C_{(2)}$	$C_{(CCl_3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	$C_{(8)}$	$C_{(9)}$	$C_{(10)}$	CR	
										$C_{(1R)}$	$C_{(1e)}$
III	87,01	102,55	86,10	129,90	119,05	126,62	116,59	146,04	156,58	143,85	141,83
X	88,67	102,75	80,50	131,06	123,17	127,69	119,38	132,48	142,76	32,43	31,96

TABLE 5. 1, 2-Dihydro-4H-3, 1-benzoxazines

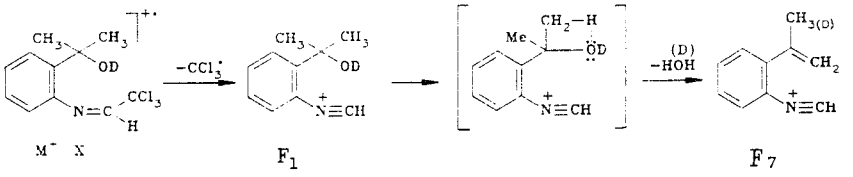
Compound	Empirical formula	mp, °C	Yield, %	Compound	Empirical formula	mp, °C	Yield, %
III	$C_{21}H_{16}Cl_3NO$	202...203	74	VII	$C_{24}H_{18}N_2O_4$	197	70
IV	$C_{26}H_{21}NO$	158	95	XI	$C_{16}H_{17}NO$	67	76
V	$C_{24}H_{19}NO_2$	165	86	XVI	$C_{22}H_{21}NO$	170...171	75

It should be noted that the molecular ion M^+ of compound VII eliminates an hydroxyl radical. Such fragmentation is characteristic of nitrofuran compounds [17], and in our case, it is confirmed by the presence of a metastable ion in the spectrum.

The fragmentation of the molecular ions M^+ of dihydrobenzoxazines IX and X, which have alkyl substituents in the heterocycle, obeys the general scheme, but, in addition to the peaks for M^+ and the F_1-F_6 ions, the spectra also show a peak for the F_7 ion (m/z 144), which forms as a result of the dehydration of the F_1 cation (m/z 162). The 162 → 144 transition (in the example case of compound X) is confirmed by the metastable ion with an apparent mass of 128.5.

The investigation of compound X with the aid of deuterium labeling (Table 2) shows that the process of the dehydration of the F_1 cation takes place with the loss of both H_2O and HDO. These phenomena are specific for the mass-spectrometric fragmentation of saturated alcohols, during which cleavage of the O–C bond with the simultaneous transfer of hydrogen (deuterium) takes place [18]; this finding indicates that the compounds investigated (X) can exist in an open form in the gaseous phase (Scheme 2).

Scheme 2



In order to unequivocally resolve the question of the structure of compounds IX and X, we carried out a comparative analysis of the spectroscopic (^{13}C NMR and IR) data for compound X and dihydrobenzoxazine III, which has a fixed cyclic structure (see Table 1).

The positions of the bands of the stretching vibrations of the functional groups in the IR spectra of compounds III and X nearly coincide. IR spectrum of compound III: 3380 (N-H); 1600, 1580 ($C=C_{ar}$); 1010, 1070, 1125 cm^{-1} (N–C–O). IR spectrum of compound X: 3370 (N–H); 1605, 1580 ($C=C_{ar}$); 1025, 1080, 1110 cm^{-1} (N–C–O). The chemical shifts of the signals of the $C_{(2)}$ and $C_{(CCl_3)}$ atoms (Table 4) in the ^{13}C NMR spectra are also close.

A comparative study reveals the absence of a band for the stretching vibrations of the azomethine group in the IR spectrum of compound X [19], although the ^{13}C NMR spectrum contains a signal for a protonated sp^2 carbon atom* joined to a nitrogen atom by a multiple bond [20]. This attests to the realization of cyclic form B of compound X in the solid phase and in solution. A similar conclusion is also valid for compound IX [2]. The transition to the gaseous phase under the conditions of a mass-spectrometric experiment is accompanied by the transformation of cyclic form B into azomethine form E in the case of compounds IX and X.

*The signals in the ^{13}C NMR spectra were interpreted with consideration of the nuclear Overhauser effect [20].

Thus, an analysis of the NMR, IR, and mass spectra makes it possible to identify the structures of the compounds of types A-D in different phases and to expand our conception of the structure and properties of 2, 4-substituted 1, 2-dihydro-4H-3, 1-benzoxazines.

EXPERIMENTAL

The IR spectra were recorded on a Specord-71 spectrometer at room temperature in KBr prisms. The PMR spectra were recorded on Tesla-BS (60 MHz) and Varian HA-100D (100 MHz) spectrometers. The internal reference was HMDS. The mass spectra were obtained on Varian MAT CH-6, LKB-2091, and Hitachi M-80 B spectrometers with the use of the method of direct admission of the substance into the ion source, and ionization energy of 70 eV, and temperatures equal to 50, 100, and 140°C. The ^{13}C NMR spectra were recorded on a Bruker AC-80 (20 MHz) spectrometer at room temperature under pulse acquisition conditions with subsequent Fourier transformation and complete proton decoupling. The internal reference was TMS.

The synthesis of compounds I, II, VI, VIII-X, XII, XVII, XVIII, and XIII-XV was described in [2, 3], respectively. Dihydrobenzoxazines II-V, VII, XI, and XVI (Table 5) were obtained according to the method in [2]. The data from elemental analysis for compounds III-V, VII, XI, and XIV (C, H, and N) correspond to the calculated data. Compound X was obtained by recrystallization from CH_3OD.

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