INVESTIGATION OF AROMATIC HETEROCYCLES

XVII.* PECULIARITIES OF THE STRUCTURES OF COMPOUNDS OF THE DEHYDRO-1,2,3-BENZODITHIAZOLIUM CHLORIDE SERIES

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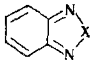
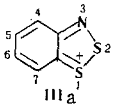
The PMR spectra of a number of 1,2,3-dithiazolium chloride derivatives were examined from the point of view of the peculiarities of the structures of these compounds. In deuterosulfuric acid the investigated compounds dissociate completely into ions, and the organic part of the molecule bears a single positive charge. Different variants of the distribution of this charge in the heteroring of the cation were analyzed, and it was established that it is predominantly concentrated on the sulfur atom bonded directly to the benzoid ring. A tendency for delocalization of the positive charge over other atoms of the heteroring was also noted. On the whole, the benzoid ring is distinguished by disruption of the uniformity of bonds according to the quinoid type, which, however, does not lead to a total loss of the aromatic character.

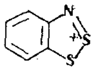
The structures of benzo-2,1,3-X-diazoles, in which the X atom (I X = Se, II X = S) is the variable fragment, were investigated in [1-4]. There are also data that dehydro-1,2,3-benzodithiazolium derivatives (IIIa or IIIb) have a different structure [5]. This makes it possible to consider compounds of the III type to be electronic analogs of diazoles I-II.



I, II



IIIa



IIIb

I X = Se;
II X = S

We have obtained compounds of the III type as individual chlorides or double salts with zinc chloride. In deuterosulfuric acid, these salts (Herz salts) give PMR spectra with a resolved structure [6].

In this communication we present an analysis of the PMR spectra and make an attempt to estimate the degree of delocalization and distribution of positive charge in the cation portion of the Herz salts. An examination of the data from the PMR spectra of structurally similar heterocyclic systems demonstrates that there are great differences in the degree of aromaticity even in a number of isomeric heterocycles. Thus 1,2,5-oxadiazole is quite similar to benzene [4], while the absence of effective conjugation in the molecule is characteristic for 1,2,4-oxadiazole [7,8]. It is clear that the conclusion previously drawn for thiadiazoles that they have pronounced aromatic character cannot be automatically transferred to Herz salts, although their π-electron systems are equivalent.

To ascertain whether doubly charged cations form when Herz salts are dissolved in concentrated deuterosulfuric acid, we obtained the spectra of several of them in hexametapol. It turned out that the PMR spectra in both solvents are identical. We used tetramethylsilane (TMS) as the standard for the hexametapol solutions and sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as the standard for the deuterosulfuric acid solutions. Tetramethylammonium chloride (TMA) was also used in place of DSS. The shape of

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* See [1] for communication XVI.

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TABLE 1. Chemical Shifts in the PMR Spectra of Dehydro-1,2,3-benzodithiazolium derivatives[a]

No	Substituent position				Chemical shifts, ppm							
					benzene ring protons				substituent protons			
	4	5	6	7	4	5	6	7	4	5	6	7
1	—	—	C_6H_5	—	8,20 8,50	8,20 8,50	—	8,20 8,50	—	—	7,31 7,60	—
2	—	—	Cl	—	8,51	7,83	—	8,37[b]	—	—	—	—
3	—	Cl	Cl	—	8,63	—	—	8,49	—	—	—	—
4	Cl	—	Cl	—	—	7,90	—	8,23	—	—	—	—
5	—	—	CH_3O	—	8,30	7,45	—	7,80[a]	—	—	3,81	—
6	—	CH_3O	CH_3O	—	7,82	—	—	7,82	—	3,81	3,92	—
7	NO_2	CH_3O	CH_3O	—	—	—	—	7,78	—	3,92	3,92	—
8	NO_2	—	CH_3O	—	—	7,90	—	8,24	—	—	3,90	—
9	CH_3O	—	Cl	—	—	7,17	—	7,93	3,93	—	—	—
10	—	CH_3O	Cl	—	7,77	—	—	8,35	—	3,79	—	—
11	CH_3O	—	Cl	CH_3O	—	7,06	—	—	3,78[c]	—	—	3,78[c]
12	—	CH_3O	—	—	7,5	—	8,55[b]	8,10	—	3,98	—	—

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[a] Relative to DSS.

[b] The spin–spin interaction constants are: $J_{6-7} = J_{4-5} = 10$ Hz, $J_{5-7} = 2$ Hz, and $J_{4-7} = 0$.

[c] The methoxyl protons give an unresolved, rather broad signal.

the spectrum in deuterosulfuric acid is independent of the nature of the standard used, but a deviation of the chemical shifts from the values calculated relative to DSS was observed in the case of TMA. Complexes are apparently formed when Herz salts are dissolved in deuterosulfuric acid that contains TMA. Similar complexes are also formed when nitrobenzene is dissolved in carbon tetrachloride that contains tetra-n-butylammonium bromide [9].

The protons of the unsubstituted benzodithiazolium chloride in the PMR spectrum of a deuterosulfuric acid solution give a complex, poorly resolved multiplet centered at 8.87 ppm, which is absolutely unlike the PMR spectra of naphthalene and its symmetrical heteroanalogs [2,3]. This fact unambiguously attests to substantial nonequivalency of the protons of the benzoid ring in III. In addition, the difference in the chemical shifts of these protons is extremely small; the deviation of the molecule from symmetry is less than might have been expected on the basis of the hypothesis of complete localization of the positive charge in the 1-position (structure IIIa). At the same time, there is an extremely strong (approaching unity) positive charge on the organic portion of the III molecule. This sort of conclusion follows from a comparison with the PMR spectrum of benzo-2,1,3-thiadiazole in CCl_4 (a multiplet centered at 7.48 ppm at weak field relative to TMS [2]). It is seen that the proton signals for the Herz salt are shifted by ~1.4 ppm to weak field. A comparison of the spectra of 6-methoxybenzothiadiazole in tetrachloroethylene demonstrates that the signals of the protons in the 4- and 7-positions of the Herz salt are shifted to weak field by ~0.7 ppm. Thus Herz salts are practically completely dissociated into ions when they are dissolved in deuterosulfuric acid, and the lifetime of the possible ion pairs does not exceed 10^{-4} sec.

For a more detailed study of dehydro-1,2,3-benzodithiazolium derivatives, we obtained and analyzed the PMR spectra of a number of compounds substituted in the benzene ring (Table 1).

Analysis of the values obtained shows that the electron density on the condensed benzene ring of these compounds is markedly depressed. Thus two systems can be isolated in the PMR spectrum of the 6-phenyl derivative (No. 1 in Table 1). The protons of the phenyl group form the multiplet of monosubstituted benzene (δ 7.31-7.60 ppm), which is close to the chemical shifts of nitrobenzene (δ 7.4-7.9 ppm). The protons of the condensed benzene ring together with the protons of the 6-phenyl substituent form the system of lines of m,p-disubstituted biphenyl, for which a multiplet at 8.20-8.50 ppm is characteristic. The PMR spectrum of unsubstituted biphenyl is a multiplet at 7.15-7.7 ppm. Thus the shift to weak field of the signals of the biphenyl system of the 6-phenyldithiazolium salt indicates that the electron density in it is appreciably depressed.

The presence of a positive charge on the cationoid portion of the Herz salts is also responsible for the peculiarities in the properties of the compounds. It is apparently necessary to consider four variants of the distribution of the positive charge (q) in the dithiazolium ring: a) charge q is concentrated on the

TABLE 2. Dependence of the Difference in the Chemical Shifts in the α- and β-Positions of the Benzoid Ring of the Dehydrobenzodithiazolium Cation on the Position of the Charge in the Heteroring

Computational variant	Δ 4,5	Δ 7,6
a	0,17	0,20
b	0,06	0,06
c	0,11	0,13
d	1,0	1,0

sulfur atom in the 1-position; b) charge q is concentrated on the sulfur atom in the 2-position; c) both sulfur atoms are equivalent in the sense of distribution of charge q between them; d) charge q is delocalized over all of the atoms of the heteroring. We will assume that the dehydrobenzodithiazolium cation is planar and that the interatomic distances and angles between the bonds are typical for the corresponding combinations of atoms. One can then easily calculate the electrical field strength at the site of the position of each of the resonating protons as a function of the method of distribution of the electrical point charge (q) via the variants indicated above. The calculations of the chemical shifts caused by this electrical field from the linear approximation of the Buckingham–Masher formula is the difference in the chemical shifts of the protons in the 4- and 5- and 7- and 6-positions (see Table 2).

The 4- and 7-positions in the cations of Herz salts are nonequivalent, and this hinders the measurement of the internal shift ($\Delta_{\alpha,\beta}$). According to a rough estimate, $\Delta_{\alpha,\beta}$ is 0.5 ppm. It is apparent from Table 2 that the calculated $\Delta_{\alpha,\beta}$ value obtained by variant *a* is least out of line with the experimental value. It is also apparent that variant d gives an extremely high estimate of the $\Delta_{\alpha,\beta}$ shift; i.e., total delocalization of charge q is repudiated by the PMR data. It is most natural to assume that all of the examined effects coexist in the real molecule and that there may be a certain delocalization of the positive charge in the heteroring.

To explain the differences in the degree of electron shielding of the protons in various positions of the benzoid ring of the Herz compounds, we made a comparison of the PMR spectra of a number of derivatives. All of the investigated compounds give well-resolved spectra, and, in the case of 6-chloro and 6-methoxy derivatives, for example, one can isolate the signal of the isolated proton in the 7-position with confidence. Alternate substitution of the ring protons of the 6-chloro- and 6-methoxydehydro-1,2,3-benzodithiazolium cations by a chlorine atom makes it possible to ascribe the signal at weaker field to the 4-position and the signal at stronger field to the 5-position (see Nos. 2-4 and 5-7 in Table 1). An examination of the spectra of 5,6-dimethoxy derivatives makes it possible to compare the degree of shielding of the 5- and 6-positions in the dehydrobenzodithiazolium cation. In fact, the methoxyl groups of 5,6-dimethoxydehydro-1,2,3-benzodithiazolium (No. 6 in Table 1) form a split signal; the introduction of a nitro group into the 4-position of this molecule should cause a low-field shift of the signals of the methoxy protons in the 5-position and have a weak effect on the position of the signal of the methoxy protons in the 6-position. This is, in fact, what happens. As a result, the spectrum of 4-nitro-5,6-dimethoxybenzodithiazolium (No. 7 in Table 1) contains a single signal from the protons from the two methoxy groups, and its intensity is greater by a factor of exactly six than the intensity of the signal from the lone ring proton. Thus it can be concluded that the 5- and 6-positions in the benzothiazothionium molecule are not equivalent; the carbon atom in the 6-position bears more positive charge than the 5-carbon atom.

A comparison of the chemical shifts of the protons in the 4- and 7-positions of the investigated cations demonstrates that the positive charge in the 4-position is greater than in the 7-position (see Table 1), but this difference is small. The same conclusion can be drawn by comparing the spectra of 6-methoxy- and 5,6-dimethoxybenzodithiazolium salts. In fact, the introduction of a methoxy group into the 5-position of the 6-methoxydehydro-1,2,3-benzodithiazolium ion should primarily shift the signal from the 4-proton to strong field; this actually occurs (see Nos. 5-6 in Table 1): the chemical shifts of the protons in the 4- and 7-positions are equal.

A study of the effect of substituents on the chemical shift of the protons of the condensed benzoid ring and a comparison of the results obtained with data on compounds of the benzene series make it possible to correlate the bond orders in the carbocyclic portion of the investigated cations.

The multiplet of meta protons in the PMR spectrum of anisole is situated at 7.2-7.3 ppm; i.e., the signals are shifted to strong field by no more than 0.1 ppm from the signal of the protons of unsubstituted benzene. The center of the joint multiplet from the ortho and para protons of anisole is found at 6.6 ppm. Other than this, the shielding effect of the methoxy group in anisole is transmitted approximately equally to the ortho and para positions and is estimated to be 0.3-0.4 ppm.

The introduction of a methoxy group in the 4- or 5-positions of the 6-chlorobenzodithiazolium ion (Nos. 9-10 in Table 1) does not affect the chemical shift of the signal of the proton in the meta position relative to the methoxy group but shifts the signal of the proton para to it by 0.44 ppm and the signal of the proton ortho to it by 0.66-0.74 ppm to strong field. Thus the shift of the electron density within the limits of the 4−5 and 5−6 bonds is almost double that in the benzene series for the investigated benzodithiazolium derivatives. The same conclusion can also be drawn on comparing the spectra of the 6-chloro- (No. 4 in Table 1) and 6-chloro-4, 7-dimethoxybenzodithiazolium ions (No. 11 in Table 1).

The examined data consistently indicate that the positive charge in the condensed system of benzodithiazolium cations is to a certain degree delocalized between the atoms of the benzoid ring and that disruption of the equality of the bonds according to the quinoid type (formula IIIa) is characteristic for the benzoid ring.

EXPERIMENTAL

Solid chlorides of the dithiazolium derivatives (sometimes as the double salts with zinc chloride) were used for the investigation. The solvent was 99.5% D_2SO_4. The solutions obtained from the zinc chloride salts were filtered before they were introduced into the ampuls. The PMR spectra were recorded with a Perkin-Elmer R-12 spectrometer with an operating frequency of 60 MHz at a block temperature of 33.5 deg. The spectra were recorded in both normal and integral form. The standards were sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) and tetramethylammonium chloride (TMA). The TMA signal in D_2SO_4 has a chemical shift of 3.15 ppm relative to DSS. Dilution of the prepared deuterosulfuric acid solutions does not affect either the character of the spectrum or the relative position of the signals. Storage of solutions of the benzothiazothionium compounds in deuterosulfuric acid (at a salt concentration of ~1 g/liter) at room temperature for 20-40 days did not lead to changes in the PMR spectra.

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