PARAMAGNETIC RING CURRENT IN THE DIAZEPINE RING OF THE 1H-BENZO-1,5-DIAZEPINIUM MONOCATION

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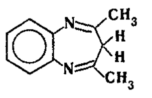
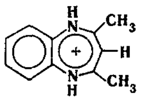
The signals of all of the protons in the PMR spectrum of 2,4-dimethyl-1H-benzo-1,5-diazepine hydrochloride are shifted to stronger fields by 0.5-1.0 ppm relative to the signals of the analogous protons in model compounds. This shift is explained by the considerable paramagnetic contribution of the eight π electrons of the diazepine ring of the 1H-benzo-1,5-diazepinium monocation to the magnetic susceptibility of the molecule. Calculations of the π-electron ring current and the π-electron component of the magnetic susceptibility of this monocation by the MO LCAO method showed that the ring current in the seven-membered ring is paramagnetic and depends markedly on the magnitude of the coulombic integral for nitrogen.

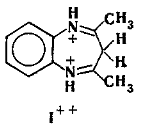
During a study of the PMR spectra of 2,4-dimethyl-1H-benzo-1,5-diazepine (I), its hydrochloride (I^+Cl^-), and a solution of I in H_2SO_4 ($I^{++} \cdot 2HSO_4^-$), our attention was drawn to the unusual relationship between the magnitudes of the chemical shifts of the phenyl and methyl protons in base I and ionic forms I^+ and I^{++}.



I

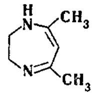


I^+

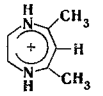


I^{++}

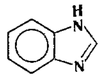
In the spectrum of monocation I^+, the signals of these protons are found at stronger fields than in the case of base I, while in the case of dication I^{++} they are found at weaker fields (Table 1). The signal of the methylene protons in the 3 position, with an intensity of 2 proton units (p.u.), which is characteristic for base I and dication I^{++}, is absent in the spectrum of monocation I^+, in which the singlet with an intensity of 1 p.u. at 4.0-4.2 ppm is affiliated with the 3-H proton.



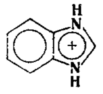
II



II^+



III



III^+

It should be noted that Barry and co-workers, who studied the PMR spectra of 1H-benzo-1,5-dizepines [1], assigned the signal in the region of the resonance of aromatic protons to the 3-H proton of monocation I^+. This assignment raises some doubt. It might be assumed that exchange of the 3-H proton of monocation I^+ with the protons of the COOH groups of the solvent occurs in the solvents used by Barry and co-workers [1]–CF_3COOH and $CDCl_3 + CH_3COOH$– and the signal at 4.0-4.2 ppm is very markedly broadened.

The unusual strong-field position of the signals of all of the protons of monocation I^+ is particularly noticeable on comparing the chemical shifts of the protons of I^+ with those of model compounds containing

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TABLE 1. Chemical Shifts of the Protons of the Bases and Cations of I, II, and III*

Formula	Solvent	δ, ppm				
		CH_3	3-H	6-H, 9-H	7-H, 8-H	
I^1	$CDCl_3$	2,32	2,80†	7,3		
I	CD_3OD	2,38	2,90†	7,3		
I	$(CD_3)_2SO$	2,29	2,80†	7,22		
I^+Cl^-	CD_3OD	1,82	4,19	6,48	6,87	
I^+Cl^-	$(CD_3)_2SO$	1,80	4,08	6,65	6,85	
I	$CD_3OD+D_2SO_4$	1,82	4,20	6,47	6,87	
I^2	H_2SO_4	3,6	4,70†	8,4		
I^1	CF_3COOH	1,87		6,1	7,1	
		CH_3	6-H			CH_2
II^2	$CDCl_3$	1,88	4,40			3,42
II^+Cl^-	CD_3OD	2,21	5,01			3,63
II^+Cl^-	$(CD_3)_2SO$	2,17	4,87			3,52
II^+Cl^-	1 *N* DCl	2,17	5,00			3,60
				4-H, 7-H	5-H, 6-H	2-H
III	CD_3OD			7,61	7,24	8,12
III	$(CD_3)_2SO$			7,60	7,19	8,21
III^+Cl^-	CD_3OD			7,88	7,66	9,50
III^+Cl^-	$(CD_3)_2SO$			7,80	7,61	9,69

*The PMR spectra were obtained with a JNM-4H-100 spectrometer.

†These are the protons of the CH_2 group.

individual fragments of the I^+ molecule (Table 1). 5,7-Dimethyl-2,3-dihydro-1H-1,4-diazepine (II) and its hydrochloride (II^+Cl^-), in which the 6-H proton and the CH_3 group in the 5 and 7 positions are analogous, respectively, to the 3-H proton and CH_3 group in the 2 and 4 positions of I^+Cl^-, and benzimidazole (III) and its hydrochloride (III^+Cl^-), the 4- and 5-H protons of which are analogous to 6- and 7-H of I^+Cl^-, respectively, were used as model compounds of this kind.

The signal of the 3-H proton of I^+Cl^- is found at stronger fields (0.8 ppm stronger) than the signal of the corresponding 6-H proton in II^+Cl^- (Table 1). The signal of the protons of the methyl substituents of the seven-membered ring in I^+Cl^- is shifted to stronger fields by 0.38 ppm relative to II^+Cl^-. The values found should be corrected for the effect of the diamagnetic ring current of the benzene ring* in I^+Cl^-. This effect was evaluated from the tables in [3] as being 0.18 and 0.14 ppm for 3-H and CH_3, respectively. Consequently, the excess shift to strong field of the signals of the 3-H and CH_3 signals in I^+Cl^- relative to the positions expected on the basis of an examination of model compound II^+Cl^- are ~1 and 0.5 ppm, respectively.

A comparison of the chemical shifts of the protons of the benzene ring of I^+Cl^- with the corresponding values for III^+Cl^- shows that the shift to strong field is 1.3 ppm for the 6-H proton in I^+Cl^- relative to 4-H in III^+Cl^- and 0.78 ppm for 7-H in I^+Cl^- relative to 5-H in III^+Cl^-. The diamagnetic ring current in the five-membered ring of benzimidazole probably makes a certain contribution to the above differences in the chemical shifts. When this effect is taken into account, the excess shift to strong field of the signals of the protons of the benzene ring of I^+Cl^- relative to the values expected on the basis of a study of model compound III^+Cl^- was ~ 0.8 ppm for 6-H and ~ 0.6 ppm for 7-H.†

It is interesting to note the reverse effect of protonation of the nitrogen atom on the chemical shifts of the protons of I, on the one hand, and of II and III, on the other. It follows from Table 1 that on passing from bases II and III to the corresponding monocations II^+ and III^+ the signals of all of the protons are shifted to weaker field; this is also characteristic for other nitrogen heterocyclic compounds.

The excess shifts to strong field ($\Delta\delta$) of the signals of the protons of I^+Cl^- are presented in Table 2.

Let us examine the possible reasons for this effect. One of the factors that affect the chemical shifts of protons in conjugated systems is the density of the π-electron charge on the carbon atom to which a proton is connected [4]. The differences in the π-electron densities (Δq^π) on the carbon atoms in I^+ and the

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*It was assumed that the indicated effect is determined only by the distance between the proton and the center of the benzene ring.

†In the calculation of the correction for the ring current of the five-membered ring in III^+Cl^- it was assumed that this current is of the same magnitude as that of the benzene ring.

TABLE 2. $\Delta\delta$ and R Values for the Protons and Δq^{π} Values for the Carbon Atoms of Monocation I^+

Parameter	3-H	2-CH_3	6-H	7-H
$\Delta\delta$, ppm	−1,0	−0,5	−0.8	−0,6
Δq^{π}	+0,030	−0,073	+0.030	+0,008
R, Å	2,7	3,7	3.7	5,0

TABLE 3. π-Electron Ring Currents I_6 and I_7 in the Six-Membered and Seven-Membered Rings of Monocation I^+, Contributions of χ_{66}^{π}, χ_{67}^{π}, and χ_{77}^{π} to the π-Electron Component of the Magnetic Susceptibility of the Two-Ring System, and Their Summation ($\Sigma\chi^{\pi}$) for Various Values of Coulombic Parameter h_N ($I_{C_6H_6}$ and $\chi^{\pi}{}_{C_6H_6}$ were assumed to be unity)

h_N	I_6	I_7	χ_{66}^{π}	χ_{67}^{π}	χ_{77}^{π}	$\Sigma\chi^{\pi}$
0	−0,285	−2,473	1,37	−3,32	−1,80	−3,75
0,5	0,323	−1,638	1,23	−1,80	−1,40	−1,97
1.0	0,592	−1,097	1,135	−1,08	−1,00	−0,944
1.5	0,730	−0,753	1,08	−0,703	−0,701	−0,324
2,0	0.810	−0,532	1,055	−0,486	−0,503	0,066

corresponding model compounds (II^+ for C_3 and $C_{2,4}$, and III^+ for C_6 and C_7) are indicated in Table 2.* The relatively small differences in the π-electron densities and the constancy of the sign of differences $\Delta\delta$ vis-à-vis the difference in the sign of differences Δq^{π} attest that it is not this effect that determines the shift in the signals of the protons of I^+Cl^- to strong field.

Another factor that affects the magnitudes of the chemical shifts of the protons in conjugated cyclic systems is the induced ring current. The effect of the ring current should be identical in sign for all of the protons situated in the plane of the ring and should decrease as the distance from the center of the ring increases. A comparison of the $\Delta\delta$ values found with the distances of the corresponding protons from the center of the seven-membered ring in I^+ (R, Table 2) shows that these conditions are basically satisfied, and the sign of the effect of the ring current turns out to be the opposite of the sign of this effect in aromatic systems.

Thus the data obtained in this study make it possible to conclude that the magnetic field in the seven-membered ring of the 1H-benzo-1,5-diazepinium monocation induces a paramagnetic ring current, in contrast to the diamagnetic ring current in aromatic systems.

This conclusion is confirmed by calculation of the magnitudes of the π-electron ring currents and the π-electron component of the magnetic susceptibility of the 1H-benzo-1,5-diazepinium monocation within the framework of the MO LCAO method by the procedure in [5] (Table 3). The calculation was made for different values of the coulombic integral for nitrogen, during which it was assumed that by virtue of the symmetry of the I^+ monocation the coulombic integrals for N_1 and N_5 are equal, i.e., $\alpha_{N_1}=\alpha_{N_5}=\alpha_C+h_N\beta$. It was further assumed that all of the resonance integrals are equal to β and that both of the rings of the two-ring system are regular polyhedra.

According to Table 3, the calculation predicts the existence of a paramagnetic ring current in the seven-membered ring, the magnitude of which decreases as coulombic parameter h_N for the nitrogen atom increases. The ring current for the six-membered ring is paramagnetic for very low h_N values and diamagnetic for very high h_N values and approaches the magnitude of the ring current in benzene as h_N increases. The contributions of the six- and seven-membered rings to the π-electron component of the magnetic susceptibility of the two-ring system change correspondingly: the paramagnetism decreases as h_N increases. However, the contributions of χ_{67}^{π} and χ_{77}^{π} are paramagnetic and considerable with respect to their absolute value over the entire range of h_N values used in the literature [6]. The anisotropy of the

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*The π-electron densities were calculated by the simple Hückel method (Hückel MO) with $h_N=1$ and $k_{CN}=1$.

magnetic susceptibility of the 1H-benzo-1,5-diazepinium monocation ($\Delta\chi_{I^+}$) should therefore be markedly depressed or even have a sign that is the opposite of the sign of $\Delta\chi_{C_6H_6}$; this is in agreement with the experimental data from the PMR spectrum of I^+Cl^-.

In a number of studies it has been shown that the character of the ring current in a conjugated carbocyclic system (or of individual rings of a polycyclic ring) is determined by the number of π-electrons: the current is diamagnetic for $4n+2$ π-electrons and paramagnetic for $4n$ π-electrons (n is the whole number) [7-10]. Cyclic systems with $4n$ π-electrons have been singled out from conjugated molecules with respect to a number of properties and have been called antiaromatic systems [11, 12].

The existence of a paramagnetic ring current has been reliably established in a study of the PMR spectra of annulenes [10, 13, 14] and condensed conjugated carbocycles (three- and four-ring systems) [15, 16]. The influence of this effect on the chemical shifts of the protons in some heterocyclic compounds has also been contemplated [17, 18].

The conjugated system of the 1H-benzo-1,5-diazepinium monocation is formed by 12 π-electrons, of which eight belong to the system of the seven-membered diazepine ring. Consequently, this ring in I^+ is isoelectronic with respect to the antiaromatic system of the tropylium anion, for which, in accordance with the Hückel MO method, two π-electrons are found in a doubly degenerate antibonding orbital, and the ring current is paramagnetic and infinite in magnitude [10]. The introduction of heteroatoms into the tropylium system and condensation with a benzene ring lower the energy and remove the degeneracy of the upper occupied level. However, the unfilled character of the electron shell is retained [7, 19] as, for example, in the antiaromatic pentalene system (eight π-electrons), for which calculations give a magnetic susceptibility (of opposite sign) that is greater than that of benzene by a factor of 2.5 [8, 9].

Thus all of the data obtained in this study indicate the existence of a paramagnetic ring current in the conjugated heterocyclic 1H-benzo-1,5-diazepinium monocation as one of the manifestations of the antiaromatic character of the diazepine ring in this system.

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