INVESTIGATION IN THE FIELD OF AROMATIC HETEROCYCLES

XIII. Calculation of the Proton Magnetic Resonance Spectra of Compounds of the 2, 1, 3-Selenadiazole and 2, 1, 3-Thiadiazole Series*

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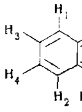
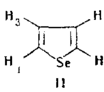
The results of complete quantum-mechanical calculations of the PMR spectra of compounds of the 2, 1, 3-X-diazole (X = S, Se) series are given. The parameters of these spectra have been used previously for a discussion of the aromaticity of the corresponding compounds.

In parts III [2] and V [3], a discussion was given of some features of the structure of compounds of the general formula I (X =O, S, Se) on the basis of data obtained from the PMR spectra.


I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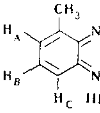
III

However, in using the spectral parameters mentioned in these parts, we did not give their basis in calculation. Below we give the results of the calculation of the PMR spectra considered previously (see table).

The spectra of naphthalene, piazthiole (I, X = S), and piazselenole (I, S = Se) were analyzed as systems of the AA'BB' type. The numbering of the corresponding hydrogen atoms of the molecules mentioned is the same for both and is shown in formula I. The spectrum of selenophene is typical for an AA'XX' system; a detailed discussion of the results of its analysis will be given later. The numbering of the atoms in the molecule of selenophene is given in formula II. The spectrum of α-methylpiazthiole was analyzed as a system of the $ABCX_3$ type (see formula III), the interaction of the three protons (X_3) of the methyl group with the terminal protons A, B and C being considered as a weak perturbation. The spectrum of naphthalene was studied earlier at a frequency of 40 MHz. We were powerfully convinced that the value of the spin-spin coupling constant $I_{1,2}$ was actually close to zero. A series of calculations that we have carried out using various positive and negative values of $I_{1,2}$ has shown that the best correspondence of the experimental and theoretical spectra of naphthalene is achieved at $I_{1,2} = 0$. Fig. 1 shows the experimental (a) and theoretical (b) spectra of piazselenole. A similar good agreement has been obtained for the other four-spin systems given in the table. Figure 2 shows the experimental (a) and theoretical (b, c) spectra of β-methylpiazthiole (frequency 60 MHz).

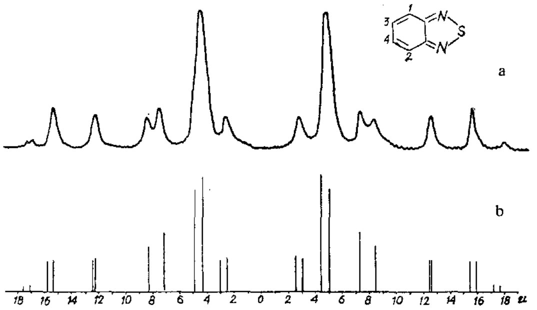

Fig. 1. PMR spectra (60 MHz) of piazselenole: a) experimental; b) theoretical.

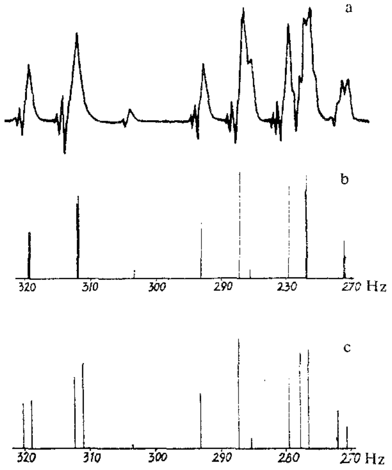

Fig. 2. PMR spectra (60 MHz) of α-methylpiazthiole: a) experimental; b) and c) theoretical, calculated for $I_{AC} < 0$ and $I_{AC} > 0$, respectively.

In connection with the difficulties arising in the performance of a complete analysis of the six-spin system $ABCX_3$, in Fig. 2 we give a comparison of the results of a theoretical calculation of an ABC system with the experimental spectrum obtained with a specially limited resolving capacity of the spectrometer. The theoretical spectra of the protons of the benzoid ring were calculated by us for the following parameters: $\delta_A = 315$ Hz, $\delta_B = 286$ Hz, $\delta_C = 275$ Hz, $I_{A,B} = 8.28$ Hz, $I_{A,C} = |0.8|$Hz, and $I_{B,C} = 6$ Hz (the chemical shifts are given relative to tetramethylsilane).

It can be seen from Fig. 2 that the best correspondence is observed between spectra a and b; the latter was obtained using a value of $I_{A,C} < 0$.

When the resolving power of the spectrometer was increased, an additional splitting of some of the components of the spectrum of β-methylpiazthiole was observed (see [2]).

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*For part XII, see [1].

Calculation of the PMR spectra of the 2, 1, 3-X-Diazoles (X = S, Se) and Related Systems

Compound	Working frequency of the spectrometer, MHz	Resonance frequencies, Hz**		Spin-spin coupling constants, Hz			
		$\nu_1=\nu_2$	$\nu_3=\nu_4$	$I_{1,2}$	$I_{1,3}=I_{2,4}$	$I_{2,3}=I_{1,4}$	$I_{3,4}$
Naphthalene	40	−7.15	+7.15	0.00	+8.60	+1.40	+6.00
Piazthiole	40	−8.80	+8.80	+0.10	+9.70	+1.20	+5.30
Piazselenole	60	−14.15	+14.15	+1.00	+8.50	+1.18	+5.25
Selenophene	100	−29.35	+29.35	+1.20	+6.00	+0.10	+6.00

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*Reckoned from the center of gravity of the spectrum.

As mentioned previously [2], the signal of the methyl protons also proved to be resolved. We have used in the first order of the theory of perturbation the following values of the constants of long-range spin-spin c coupling:

$$I_{CH_3-CH_A} \approx 0.9 \text{ Hz};$$
$$I_{CH_3-CH_B} \leqslant 0.2 \text{ Hz};$$
$$I_{CH_3-CH_C} \approx 0.6 \text{ Hz}.$$

In this case, spectrum b illustrated in Fig. 2 is modified so that its complete coincidence with the experimental spectrum recorded at limiting resolution is achieved. The experimental procedure has been described previously [2, 3]. The calculations were carried out on a "Minsk-1" electronic computer using the program described by Shmyrev et al. [5]. We thank I. K. Shmyrev for cooperation in the performance of the calculation.

REFERENCES

1. Z. V. Todres, V̄. Sh. Tsveniashvili, S. I. Zhdanov, and D. N. Kursanov, DAN, **181,** 138, 1968.
2. E. I. Fedin, Z. V. Todres, and L. S. Efros, KhGS [Chemistry of Heterocyclic Compounds], **3,** 297, 1967.
3. E. I. Fedin and Z. V. Todres, KhGS [Chemistry of Heterocyclic Compounds], 4, 416, 1968.
4. J. Pople, W. Schneider, and H. Bernstein, High Resolution Nuclear Magnetic Resonance [Russian translation], IL, Moscow, p. 182, 1962.
5. I. K. Shmyrev, A. D. Barskaya, A. B. Donner, L. Braier, P. V. Petrovskii, and E. I. Fedin, ZhSKh, **6,** 625, 1965.

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