RESEARCHES ON AROMATIC HETEROCYCLIC COMPOUNDS

III. The Aromatic Character Of Piazthiol*

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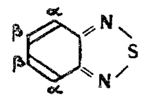
The PMR spectra of piazthiol, which is benzo[1,2-c]-[1,2,5]-thiodiazole, and of its α- and β-nitro, chloro, methyl and amino derivatives are investigated The effects of these substituents on the chemical shift is in qualitative agreement with the like effects in the benzene series. The parameters of the corresponding PMR spectra are greatly dependent on the electrophilic action of the heterocyclic ring. It is shown that there is conjugation in the thiadiazole ring, although, however, it is much weakened compared with that existing in the benzene ring.

Piazthiol, which is benzo[1,2-c]-[1,2,5]thiadiazole (I), is a condensed system, exhibiting the distinctive peculiarity of having a strongly electrophilic heterocyclic ring [1].



I

Study of the properties of piazthiol led to the conclusion that when it is formed from o-phenylenediamine, a new aromatic system is formed, which is to be compared to a naphthalene one [2,3]. However, piazthiol undergoes electrophilic substitution with much greater difficulty than naphthalene. In this connection we consider [4] that the possibility that these two systems closely resemble one another is necessary in further discussion. Actually, like naphthalene, piazthiol can be regarded as a molecule with the delocalized electrons [3], but only if it is considered that the key sulfur atom is involved in conjugation. To some extent the problem of the reality of this conjugation can be settled by high resolution proton magnetic resonance (PMR).

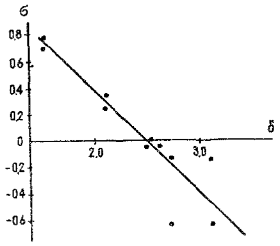


Fig. 1. Correlation between observed chemical shifts and the corresponding Hammett $\sigma_{m,p}$ constants.

The table gives the names of the compounds which have been investigated, and the values of the chemical shifts in the corresponding PMR spectra.

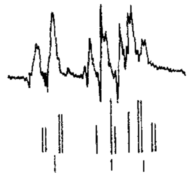


Fig. 2. PMR spectrum of 4-methylthiazole with a $2 \cdot 10^{-8}$ resolution.

In the table the compounds are arranged in order of increasing degree of shielding of protons of the benzene ring which, as is known, can be compared with the increase in electron density at these hydrogen atoms, and correspondingly, at the adjacent C atoms. Prominent is the very great effect of the nitro group, which exceeds the same effect in nitrobenzene: in the nitropiazthiols (Nos. 1 and 2) the electron density at the protons is markedly decreased. The donor effect of the amino group (Nos. 8 and 9) leads to almost the same increase in shielding of protons of the benzenoid ring as is observed with aniline. The action of chlorine (Nos. 3,4) and the methyl group (Nos. 6,7) on the chemical shifts also falls into line with the analogous effect in the PMR spectra of substituted benzenes. It would have been interesting to compare the values of the chemical shifts, with $\sigma_{m,p}$ constant, for the substituting groups. However, the complexity of precise identification of resonance lines, due to complex interaction with the 3-spin system, makes it hard to correlate δ and $\sigma_{m,p}$ correctly. Comparison of Hammett's $\sigma_{m,p}$ with the averaged, between α and β substituted piazthiols, values of the chemical shifts of the ring protons (Fig. 1), demonstrates an approximately linear relationship.

Closer consideration of this question necessitates computer treatment of the spectra. We have taken the first step in that direction with α-methylpiazthiol, for which very high resolution spectra could be obtained.

Fig. 2 gives PMR spectra of α-methylpiazthiol with ordinary resolution, and the splitting of this spectrum into quadruplets, as well as the chemical shifts resulting from such splitting. Higher resolution

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*For Part II see [10].

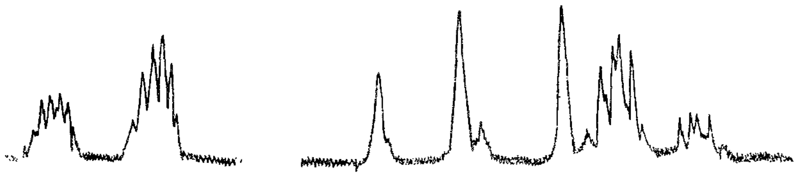


Fig. 3. PMR spectrum of 4-methylpiazthiol at limiting resolution.

reveals an additional hyperfine structure (Fig. 3) for this spectrum. The signal from the methyl protons, not shown in Fig. 3, also appeared resolved. This indicates that additional splitting is conditioned by interaction between ring protons and the CH_3 group.

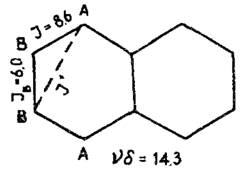


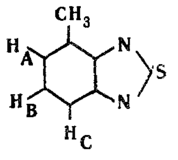
Fig. 4. Parameters of the PMR spectrum of Naphthalene, J^1 = 1.4 cps.

Use of the technic of suppression of spin-spin interaction (double proton-proton resonance) removes this splitting, finally confirming, that it is due to the stated distant spin-spin interaction. The constants for this interaction found by analyzing Fig. 3, are:

$$J(CH_3—CH_A) \approx 0.9 \text{ cps}; \quad J(CH_3—CH_B) \leqslant 0.2 \text{ cps};$$

$$J(CH_3—CH_C) \approx 0.6 \text{ cps (see II)}$$

The basis for the assignment by scheme II can be constructed as follows. In xylene the difference between the effects of the methyl group on the chemical shifts of ortho, meta, and para protons does not exceed $2 \cdot 10^{-7}$. In α-methylpiazthiol this effect is, for example, greater by a power of ten. Hence it can be assumed that in α-methylpiazthiol, the chemical shifts δ_A, δ_B, and δ_C are mainly determined by the effects of the nitrogen and sulfur atoms. Scheme II also follows from this. Alternation of spin-spin interaction according to the distance from methyl is most naturally to be compared with the ortho, meta and para charge redistributions in the benzenoid ring. Thus the effect of a methyl group on the distribution of electron density in the benzenoid ring is identical in character with the effect of substituents of the first kind. However, the basic effect on the state of the C—H ring bonds in α-methylpiazthiol is due to the adjacent heterocyclic ring. This conclusion makes one skeptical about the possibility of further more precise correlation between $\delta_{m,p}$ and $\sigma_{m,p}$ in the substituted piazthiols series.



II

Spectrum analysis (Fig. 2) and double resonance give the following values for the constants of spin-spin interaction between the ring protons of α-methylpiazthiol: J_{AB} = 6 cps; J_{AC} = 0.8 cps, and J_{BC} = 8.25 cps. Interaction of the hydrogen atoms in the corresponding case for naphthalene is characterized by very close values of J [5] (Fig. 4).

Fig. 5 gives the PMR spectrum of piazthiol juxtaposed with that of naphthalene, measured with an instrument using the same working frequency [5]. A calculation, wholly analogous to that given in a monograph [5], gives the PMR spectrum parameters shown in Fig. 6.

It should be mentioned that the difference in J for piazthiol and naphthalene is not very great. Some increase in the constant J is, for example, accompanied by a decrease in the constant J_B. These changes are naturally to be compared with the probable additional upsetting of the equality of the bonds of the benzenoid ring compared with the naphthalene ring. The previously noted closeness of the spin-spin interaction constants for α-methylpiazthiol and napthelene is obviously due to the partial compensation of the electrophilic effect of the heterocyclic ring by the electron-donor effect of the CH_3 group.

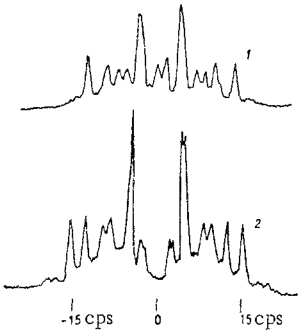


Fig. 5. PMR spectra: 1) Naphthalene; 2) Piazthiol.

The value of the chemical shift $\nu_0\delta_{AB}$ = 14.3 cps for naphthalene is in complete agreement with the calculated value obtained by considering two systems of ring currents in this molecule [5]. Our value obtained for piazthiol $\nu_0\delta_{AB}$ = 17.6 cps cannot be ascribed to the increase in ring current in comparison with naphthalene. To evaluate the value of the current in heterocyclic ring of piazthiol, it is necessary to review all factors which might affect δ_{AB}.

First and foremost ring current depends on the geometry of the molecule, since

$$\nu_0\delta_i = iQ\left(\frac{1}{R_1^3} - \frac{1}{R_2^3}\right) \qquad (1)$$

where δ_i is the contribution to the chemical shift made by the current i, Q is the area embraced by this current contour, R_1 is the distance between the center of this contour and the protons A, R_2 is the distance between the contour center and protons B.

Using structural analysis data [6–8], it is possible to show that the decrease Q in piazthiol as compared with naphthalene, is compensated by increase in the distance R_1^{-3}–R_2^{-3}, with an accuracy which corresponds completely to the accuracy of the dipole approximation (1)

It might have been important to know the chemical shift between the PMR signals of the benzenoid ring of such a molecule, which would have, at positions 1 and 2, identical electron accepting groups, but unlike piazthiol, the molecule had only one ring contour. With this end in view we investigated the PMR spectrum of o-dinitrobenzene, where $\nu_0\delta_{AB}$ = 25 cps. According to Primas's additive scheme [9], one oxygen separated by four bonds from the proton under consideration, at a frequency of 40 Mcps imparts a shift of about 10 cps. While for two O atoms in the NO_2 group we obtain a contribution of about 20 cps, and about 5 cps remains for the share of the nitrogen atom. That is close to 3.6 cps, the evaluated inductive effect for the nitrogen atom according to the scheme of [9].

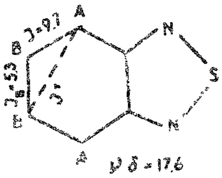
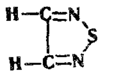


Fig. 6. Parameters of the PMR spectrum of piazthiol. $J' = 1.15$ cps.

The sulfur atom, whose electronegativity is equal, for example, to 70% of the electronegativity of oxygen, should shift the signal separated by four bonds from the proton, by 7 cps. This value is to be split into halves between the oxygen atoms in the two α positions of the piazthiol benzenoid ring. Hence for the polar effect of the heterocyclic ring on the chemical shift of the α hydrogen atoms, we obtain a value of the order of cps. This 10 cps is to be deducted from the value $\nu_0\delta_{AB}$ = 17.66 cps found for piazthiol, in order to evaluate the contribution of the current, $\nu_0\delta_i$. Referring the value of $\nu_0\delta_i$ thus obtained to 14.3 cps (shift due to ring current in benzenoid rings of naphthalene), we find that the postulated ring current in the thiazole ring is reduced approximately twofold as compared with benzene. It is important to emphasize that it is not possible to obtain an evaluation of the current i = 0, by reasonable changes in the increments δ given here. In other words, the piazthiol system contains a conducting system in its heterocyclic ring, i.e. there is conjugation between the atoms going to make up the skeleton of the ring. The current due to the presence of this conductivity, arising when the specimen is put in a magnetic field, is appreciably weakened as compared with aromatic systems (benzene, naphthalene, cyclopentadienyl anion, tropylium cation) but is not zero. This conclusion is in good agreement with that reached by Momany and Boham [8], that replacement of C atoms at positions 2 and 5 in thiophene by N atoms is without appreciable effect. Electron diffraction data indicate the approximately equal characters of the bonus in thiophene and 1,2,5-thiadiazole (III).



III

PMR Spectra of Substituted Piazthiols

No.	Compound investigated	Chemical shift	
		Ring protons	Substituent protons
1	α-Nitropiazthiol	8.5	—
2	β-Nitropiazthiol	8.5	—
3	β-Chloropiazthiol	7.9	—
4	α-Chloropiazthiol	7.6	—
5	Piazthiol	7.48	—
6	β-Methylpiazthiol	7.5	2.4
7	α-Methylpiazthiol	7.4	2.5
8	α-Aminopiazthiol	7.3; 6.5	5.0
9	β-Aminopiazthiol	6.9	4.7

EXPERIMENTAL

For registering the PMR spectra, solutions of the compounds in CCl_4 or dioxane were used, while liquid compounds were used neat. A sealed ampule 4.7 mm diameter was used, with a TsLA-5535 spectrometer with a working frequency 40 Mc. PMR of ring protons of α-methylpiazthiol was investigated with a JNM-3H-60 spectrometer. The accuracy of measurement of chemical shifts was restricted by the complex character of the spectra, but it was not less than $\pm 1 \cdot 10^{-7}$.

Most of the o-phenylenediamines needed to synthesize the piazthiols were obtained by the simple method of reducing the appropriate nitroanilines with Na hydrosulfite in alkaline solution.

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