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Structural formulas I-IV

Figure 1: Structural formulas I-IV

Abstract

Full Text

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On the Structure of 9-Aminoacridine

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In works by various authors, arguments have already been advanced both in favor of the amino-structure ([1–5]) (I) and in favor of the imino-structure ([6–9]) (II) of 9-aminoacridine.

(I) (II) (III) (IV)

In some of these works ([3,6,7]), infrared-spectrum data were used; a more detailed consideration of these data was carried out in the work of A. V. Karyakin and A. V. Shablya ([8]), who proposed the idea of an internally ionized imino structure of 9-aminoacridine (III). This idea was based by the authors on the closeness of the ν(N—H) bands in the IR spectrum of 9-aminoacridine, 9-acridone, and acridinium hydrochloride, and on the assignment of the bands at 1650 and 1570 cm^{-1} in the spectrum of 9-aminoacridine to the deformation vibration of the group C—$\overline{\text{N}}$—H and, respectively, of the group $\geqslant \overset{+}{\text{N}}$—H.

However, the assignments of the spectral bands made by these authors and the conclusions obtained thereby raise objections. Thus, in a recent work by Mason ([10]), it was shown that the position of the ν(N—H) bands in the spectrum of 9-aminoacridine is in good agreement with the amino-, and not the imino-, structure of this compound. The assignment of the 1570 cm^{-1} band to the deformation vibration

$$\geqslant \overset{+}{\text{N}}\text{H}$$

contradicts the systematic presence of this band in the spectra of the majority of heterocyclic amines and other isomeric aminoacridines that have an amino-structure and therefore do not contain the grouping

$$\geqslant \overset{+}{\text{N}}\text{H}.$$

Fig. 1. IR spectra: a—9-aminoacridine, b—N-methyl-9-acridonimine and their N-deutero derivatives

Figure 2: Fig. 1. IR spectra: a—9-aminoacridine, b—N-methyl-9-acridonimine and their N-deutero derivatives

The assignment of the second band, 1650 cm^{-1}, is not supported in the work ([8]) by any comparisons and does not agree with the literature data ([11]).

The incorrectness of assigning the 1650 cm^{-1} band to the deformation vibration C—$\overline{N}$—H is also revealed when considering the IR spectrum obtained by us of N-methyl-9-acridonimine (IV), which has a definitely fixed imino structure. In the spectrum of this compound, absorption bands are absent in the indicated region, and the first intense absorption band is observed at 1613-1600 cm^{-1} (Fig. 1); moreover, as will be seen below, it is not related to the deformation vibration C—$\overline{N}$—H, but is evidently due to the stretching vibration of the exocyclic bond C = N.

If one assumes the amino-structure of 9-aminoacridine, the 1650 cm^{-1} band may be assigned to the deformation vibration of NH_2, and the 1570 cm^{-1} band—

to the vibration of the heterocyclic nucleus of the molecule. At the same time, the bands under consideration can also be interpreted satisfactorily if the imino structure is assumed (the band at 1650 cm^{-1}—the stretching vibration of the exocyclic imino bond C=N; the band at 1570 cm^{-1}—a vibration of the heterocyclic nucleus or a deformation vibration C=N–H). The choice of the correct assignment of the bands at 1650 and 1570 cm^{-1} in the spectrum of 9-aminoacridine, and consequently the solution of the question of the structure of the molecules of this compound, seemed to us possible by considering the changes in the IR spectrum of 9-aminoacridine upon its deuteration at the amino group. Indeed, if 9-aminoacridine is an amine, then upon deuteration the band at 1650 cm^{-1} in the IR spectrum should shift sharply into the long-wavelength region, since the frequency of this vibration depends directly on the mass of the atoms participating in the vibration. If, however, the compound under investigation is an imine and the band under consideration is due to stretching vibrations of the exocyclic C=N bond, then deuteration can cause only a small shift of the corresponding band.

Fig. 1. IR spectra: *a*—9-aminoacridine, *b*—N-methyl-9-acridonimine and their N-deutero derivatives

The data available in the literature on aliphatic amines and aniline ([12,13]) show that, indeed, the band δNH_2 (at 1620—1630 cm^{-1}) disappears upon deuteration, while a new band, evidently due to vibrations of δND_2, appears in the region 1190—1200 cm^{-1}. The latter band in N-deuteroaniline is distinguished by low intensity. Exactly the same picture is observed in the comparison we carried out of the spectra of a series of heterocyclic amines with the spectra of their N-deutero derivatives (Fig. 2)—upon deuteration the band δNH_2 in these

Fig. 2

Figure 3: Fig. 2

Fig. 3

Figure 4: Fig. 3

compounds (1620–1650 cm^{-1}) practically completely disappears without the appearance of new absorption bands in the immediate vicinity. In the spectra the bands at 1530–1600 cm^{-1}, evidently due to vibrations of heterocycles, remain practically unchanged. In the IR spectrum of 9-aminoacridine upon deuteration, the absorption band at 1660 cm^{-1} likewise disappears, and the band at 1565 cm^{-1} remains unchanged (the bands at 1650 and 1570 cm^{-1} according to ([8])).

Deuteration of N-methylacridonimine—a substance with a fixed imine structure —practically does not change the position of its most intense split band (1600–1613 cm^{-1}), but causes only some broadening of it (1623–1595 cm^{-1}) (Fig. 1). In this case one may also note the disappearance of the band at 1555 cm^{-1}.

From the data presented it follows that the imino structure of the compound corresponds to the band at 1600–1613 cm^{-1} ($\nu C = N$; it does not change upon deuteration) and the band at 1555 cm^{-1} ($\delta C = N—H$; upon deuteration it shifts to another region)—both bands are absent in the spectrum of 9-aminoacridine. The amino structure corresponds to the bands at 1660 cm^{-1} (δNH_2; upon deuteration ···

shifts to another region) and 1565 cm^{-1} (vibrations of the heterocyclic nucleus; unchanged on deuteration)—are both present in the spectrum of 9-aminoacridine. Thus, it follows from the results obtained that 9-aminoacridine is an amino compound.

Fig. 2. IR spectra: *a*—aniline, —2-aminopyridine, —2-aminoquinoline, —2-aminothiazole, and their N-deuterio derivatives

Another independent confirmation of the conclusion reached is provided by consideration of the spectral data for 9-acetylaminoacridine. If 9-aminoacridine were an acridonimine, then its monoacetyl derivative should all the more have an imine structure, since the acidifying action of the acetyl group can only strengthen the tendency of the compound to exist in the imino form ([15]). However, from the infrared (Fig. 3) and ultraviolet spectra it follows unambiguously that 9-acetylaminoacridine has the amino structure (see also ([14])), and, consequently, so does 9-aminoacridine.

Fig. 3. IR spectra: *a*—9-acetylaminoacridine, —9-trichloroacetylaminoacridine, and —N-methyl-9-trichloroacetylacridonimine

Only the introduction into the amino group of 9-aminoacridine of a considerably more strongly acidifying substituent (the residue of trichloroacetic acid) causes

the appearance of the acridonimine form in solutions and the conversion of the compound into this form in crystals (Fig. 3). On the basis of an estimate of the cont-

···of the imino form of 9-trichloroethylaminoacridine in solutions, one may consider that, in its tendency to pass into the imino form, 9-aminoacridine occupies an intermediate position between 2-aminoquinoline and 2-aminothiazole ([15]), for which, according to approximate data ([16]), the value of $K^{\text{imine}}_{\text{amine}}$ in solutions is of the order of 10^{-5}.

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Note: Figure translations are in progress. See original paper for figures.