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Abstract

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Structure of 9-Aminoacridine According to Spectral Data

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In a previous work (^{1}), on the basis of a study of the absorption of solutions of aminoacridines and a number of acridine derivatives in the visible and ultraviolet regions of the spectrum, as well as in the near infrared region of the spectrum, an assumption was put forward concerning the acridone-imine form of 9-aminoacridine.

Recently, however, works have been published in which, on the basis of measurements of dipole moments (^{2}), and also on the basis of a study of infrared absorption spectra in the region of the fundamental frequencies of the NH group (^{3}), the amine structure of 9-aminoacridine is defended.

The purpose of the present work was a detailed study of the infrared absorption spectra of aminoacridines and a number of acridine derivatives in the region of the fundamental and deformation frequencies of the NH group.

Measurements of the infrared absorption spectra of a solution in CCl_4 (concentration of the order of 10^{-4}–10^{-5} mole/l and layer thickness 30 mm) in the region of the fundamental frequencies of the NH group were carried out on an IKS-11 infrared spectrometer with a LiF prism.

Infrared absorption spectra in the region of the deformation frequencies of the NH group were obtained on the same spectrometer, but with a NaCl prism. In this case, thin layers of substances sublimed at $-180°$ in vacuum (thickness 5 –20 μ) were measured by a method developed in our laboratory (^{4}). Similar results were obtained using the method of pressing KJ disks in mixture with the substance under investigation in vacuum. These methods make it possible to eliminate completely the absorption bands of the solvent, which are very intense in this region of the spectrum. The absorption spectra of solutions in CCl_4 of aminoacridines and a number of other compounds are shown in Fig. 1, and the frequencies obtained are summarized in Table 1. Examination of the figure and the table shows that 1- and 2-aminoacridines have two narrow absorption bands with frequencies of 3410 and 3485 cm^{-1}, which are usually assigned to the symmetric and antisymmetric vibrations of the NH_2 group. These frequency values agree well with the frequency values for 9-aminoanthracene.

Fig. 1. Infrared absorption spectrum of solutions in CCl_4 in the region 3400–3500 cm^{-1}: 1 —9-aminoanthracene, 2 —2-aminoacridine, 3 —9-aminoacridine, 4 —acridone, 5 —acridane.

Table 1

Absorption bands of the NH groups of aminoacridines in the region 3400–3500 cm^{-1}

Compound	Structure	NH_2, cm^{-1}	$>^{+}NH$ and $>NH$, cm^{-1}	$-NH$, cm^{-1}
1-Aminoacridine	[[chemical structure shown]]	3410, 3485	—	—
2-Aminoacridine	[[chemical structure shown]]	3410, 3485	—	—
9-Aminoanthracene	[[chemical structure shown]]	3415, 3485	—	—
9-Aminoacridine	[[chemical structure shown]]	—	3440	3520
Acridone	[[chemical structure shown]]	—	3440	—
Acridane	[[chemical structure shown]]	—	3440	—

In the absorption spectrum of 9-aminoacridine there are also two narrow absorption bands, but with different frequency values—3440 and 3520 cm^{-1}, which differ from the above-listed frequency values for the NH_2 group.

[[chemical scheme I shown]]

One of the frequencies of 9-aminoacridine, namely 3440 cm^{-1}, coincides with the frequency of the band possessed by acridone and acridane and which should be assigned to the vibration frequency of the $>NH$ group, where the nitrogen is that of the heterocycle.

Consequently, this frequency (3440 cm^{-1}) in 9-aminoacridine should also be assigned to the vibration frequency of the $>NH$ group, i.e., the presence of acridone-imine tautomerism I should be assumed. Moreover, this frequency, 3440 cm^{-1}, coincides exactly with the vibration frequency observed in the acridine ion (acridine hydrochloride in $CHCl_3$). Therefore, the frequency 3440 cm^{-1}

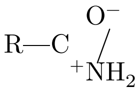
should also be assigned to vibrations of the $>^{+}NH$ group, when the nitrogen of the heterocycle is tetravalent and positively charged.

If one assumes an internally ionized structure of 9-aminoacridine in the form II, then the decrease in the vibration frequency of the $>NH$ group (3440 cm^{-1}), in comparison with secondary amines (3460 cm^{-1}) (3) and the vibration frequencies of NH in pyrrole and indole (3490 cm^{-1}) (5), can be explained by the presence of a positively charged nitrogen. Similarly, the second band, with vibration frequency 3520 cm^{-1}, which has a considerably higher value than for

of the imino group (3400–3200 cm^{-1})[6], should be assigned to vibrations of the NH group, which has divalent, negatively charged nitrogen.

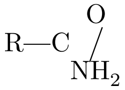
It should be noted that the presence of an internally ionized structure in the molecule of 9-aminoacridine preserves the conjugation of the benzene rings with the heterocycle, which, as is known, is energetically favorable, whereas in the simple acridone-imine structure the conjugation is disrupted.

The internally ionized structure also occurs for acridone III. This is confirmed by the fact that in acridone the frequency of the carbonyl group (1640 cm^{-1}) is considerably lowered in comparison with anthraquinone (1675–1690 cm^{-1})[7], but agrees well with the value of the frequency in amides:



$$R\text{—}C\begin{smallmatrix}O^{-}\\ {}^{+}NH_2\end{smallmatrix}$$

(1650–1740 cm^{-1}), which is explained in them by an internally ionized structure of the type[6,7]:



$$R\text{—}C\begin{smallmatrix}O\\ NH_2\end{smallmatrix}$$

The presence of an internally ionized structure in 9-aminoacridine and acridone is confirmed by studying solid films of these substances in the region of the fundamental frequencies of vibration of the NH group. 9-Aminoacridine and acridone, in contrast to all aminoacridines and acridane, exhibit very strong intermolecular interaction, leading to a large shift of the NH-group absorption bands into the long-wavelength region and to their strong broadening.

The assumption of an acridone-imine internally ionized structure of 9-aminoacridine is additionally confirmed by studying the absorption spectra in the region from 1700 to 700 cm^{-1}, which are given in Fig. 2. The frequencies of several bands are collected in Table 2.

From consideration of the spectra and the data of Table 2 it is seen that 1-, 2-aminoacridines and 9-aminoanthracene have one absorption band with a frequency of 1640–1650 cm^{-1}, which is assigned to the deformation vibration

Fig. 2. Infrared absorption spectra of sublimed layers in vacuum: I—1-aminoacridine, II—2-aminoacridine, III—9-aminoacridine, IV—acridone, V—acridan

Figure 1: Fig. 2. Infrared absorption spectra of sublimed layers in vacuum: I—1-aminoacridine, II—2-aminoacridine, III—9-aminoacridine, IV—acridone, V—acridan

of the NH_2 group, whereas 9-aminoacridine gives two absorption bands with frequencies of 1650 and 1570 cm^{-1}. In the absorption spectrum of acridone and acridane there is one absorption band with a frequency of 1570 cm^{-1}, which coincides with one of the bands of 9-aminoacridine. Consequently, this frequency (1570 cm^{-1}) should be associated with deformation vibrations of the group $>^{+}$ NH, where the nitrogen is that of the heterocycle.

The second band of 9-aminoacridine with a frequency of 1650 cm^{-1} should be assigned to the imino group (deformation vibration of the group $-\overline{N}-H$), and not to the amino group, despite the coincidence of their frequency values.

Table 2

Absorption bands of aminoacridines in the region 1700–700 cm^{-1}

Compound	NH_2, cm^{-1}	$-\overline{N}H$, cm^{-1}	C–O^-, cm^{-1}	ring, cm^{-1}	> NH, $>^+$ NH, cm^{-1}	ring, cm^{-1}	ring, cm^{-1}	ring, cm^{-1}	?, cm^{-1}
1-aminoacridine	1640	–	–	1610	–	1560	1520	1460	–
2-aminoacridine	1640	–	–	1610	–	1530	1490	1450	–
9-aminoanthracene	1650	–	–	1590	–	1560	1490	1460	–
9-aminoacridine	–	1650	–	1610	1570	1520	1490	1460	1280
Acridane	–	–	–	1615	1580	1500	1490	–	1280
Acridone	–	–	1640	1590	1570	1510	1480	–	1280
Methylacridone	–	–	1630	1590	–	1500	1460	–	1280

Fig. 2. Infrared absorption spectra of sublimed layers in vacuum: **I**—1-aminoacridine, **II**—2-aminoacridine, **III**—9-aminoacridine, **IV**—acridone, **V**—acridan

In addition, in the infrared absorption spectra of 9-aminoacridine, acridone, methylacridone, and acridan there is a band with a frequency of 1280 cm^{-1}, which is absent in all the other aminoacridines and in acridine. This band may be assigned to some vibration of the heterocyclic ring in the presence of a substituent at nitrogen (H, CH_3).

In the absorption spectrum of 9-aminoacridine in the region from 1500 to 700 cm^{-1}, additional differences from the other aminoacridines were observed, which are difficult to interpret.

Thus, spectral data in the infrared region additionally confirm the conclusion made initially regarding the structure of 9-aminoacridine as an acridone-imine with an internally ionized structure ([1]). L. V. Levshin and A. P. Khovanskii arrived at the same conclusion in studying the luminescence spectra of aminoacridines at various pH values of the medium ([8]).

An attempt to detect a similar phenomenon for aminopyridines was unsuccessful. The absorption spectra of α-, β-, and γ-aminopyridines, both in the region of stretching and deformation vibrations of the NH group, differed little from one another, and the values of the frequencies of the absorption bands agreed quite well with the literature data ([9]).

As a consequence, it must be considered that the spectral study of aminopyridines gives no indication of the presence of tautomerism in them.

In all probability, an analogous conclusion should also be drawn for aminoquinolines when analyzing the literature spectral data ([9]).

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