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INTEGRAL INTENSITY OF THE BANDS OF DEFORMATION VIBRATIONS OF THE PRIMARY AMINO GROUP

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The integral intensity of absorption bands in infrared spectra is one of the most important electro-optical characteristics of a molecule. To date, integral intensities have been measured for many bands corresponding to characteristic vibrations of individual bonds and groups (⁀1).

In particular, the integral intensities of the bands of antisymmetric and symmetric stretching vibrations of N—H in the infrared spectra of a series of aliphatic, aromatic, and N-heterocyclic primary amines in the region 3380-3500 cm^{-1} have been studied (^{2}-4).

It is known that in the infrared spectrum of primary amines, in the region 1600-1660 cm^{-1}, there is a band corresponding to the deformation vibration of the NH_2 group. The literature contains no data concerning the integral intensity of this vibration. At the same time, such data should be of considerable interest, since the integral intensity of the bands of deformation vibrations of NH_2 is directly related to the polarity of the N—H bonds and therefore makes it possible to observe the displacement of electron density in this bond under various changes in the molecule.

In the present work, the integral intensities of the bands of deformation vibrations δNH_2 were measured in the spectra of a series of aliphatic, aromatic, and heterocyclic primary amines in the region 1600-1660 cm^{-1}. The spectra were obtained on a double-beam infrared spectrophotometer UR-10 (Zeiss) with an NaCl prism. The spectral slit width in the region studied (1600-1700 cm^{-1}) was 8 cm^{-1}. The spectra of solutions of all amines were recorded in non-demountable standard cells with NaCl windows (absorbing-layer thicknesses 0.0609, 0.0386, and 0.0266 cm).

The integral intensity of the δNH_2 bands "*A*" was calculated by Bourgin' s method (⁀5). In those cases where the contour of the δNH_2 band on the low-frequency side overlapped with the band of an aromatic-ring vibration near 1600 cm^{-1}, the measurements were made as follows. It was assumed that the δNH_2 band was symmetrical; therefore, one half of its area was determined on the high-frequency side, where distortion of the band contour did not occur. The value obtained was doubled, and the subsequent calculation was carried out as usual.

Heptane, chloroform, and dioxane were used as solvents. The results of measurements of the integral intensity are given in Table 1. From the data obtained it is seen that the integral intensities of the δNH_2 bands in aliphatic amines have values of the order of 0.3—$0.4 \cdot 10^4$ $mole^{-1} \cdot liter \cdot cm^{-2}$.

On going to the first member of the aromatic amine series—aniline—the intensity of the δNH_2 band increases sharply, which makes it possible to speak here of an increase in the polarity of the N—H bonds due to the conjugation effect of the amino group with the phenyl nucleus. Introduction into the phenyl nucleus of aniline of electron-acceptor substituents (NO_2, Cl, Br) in the *p*-position relative to the amino group causes a further increase in the integral intensity of the δNH_2 band. A similar effect is also exerted by the second aromatic nucleus in the fused system of naphthalene.

Electron-donor substituents (OCH_3, NH_2) in the *p*-position relative to the amino group cause a decrease in the integral intensity of the band studied.

Table 1

No.	Substance	Solvent	ν_{max} δNH_2, cm^{-1}	$A \cdot 10^{-4}$, $mol^{-1} \cdot l \cdot cm^{-2}$
1	$(CH_3)_2CHCH_2NH_2$	Heptane	1625	0,31
2	$CH_3(CH_2)_6NH_2$	Heptane	1623	0,30
3	Same	Dioxane	1600	0,42
4	Cyclohexylamine	Heptane	1630	0,31
5	Same	Chloroform	1590	0,40
6	$CH_3C(=O)NH_2$	Dioxane	1621	1,00
7	$CH_3SO_2NH_2$	Heptane	1575	0,59
8	Aniline	Heptane	1620	1,02
9	Same	Dioxane	1629	1,07
10	*p*-Phenylenediamine	Chloroform	1620	0,62 (×2)
11	*p*-Anisidine	Dioxane	1628	0,68
12	*p*-Bromoaniline	Dioxane	1633	1,25
13	*p*-Chloroaniline	Dioxane	1633	1,30
14	*p*-Nitroaniline	Dioxane	1642	2,00
15	*o*-Nitroaniline	Dioxane	1628	2,40
16	*o*-Anisidine	Dioxane	1623	1,41

No.	Substance	Solvent	ν_{max} δNH_2, cm^{-1}	$A \cdot 10^{-4}$, $mol^{-1} \cdot l \cdot cm^{-2}$
17	*o*-Aminophenol	Dioxane	1623	1,53
18	1-Naphthylamine	Dioxane	1642	2,10
19	2-Naphthylamine	Dioxane	1635	2,20
20	Aminoquinoline	Chloroform	1625	3,25
21	Aminopyridine	Chloroform	1613	3,00
22	Nitroaminopyridine	Dioxane	1635	4,00
23	Aminothiazole	Dioxane	1627	1,40
24	Aminothiadiazole	Dioxane	1628	1,90
25	Aminobenzothiazole	Dioxane	1633	2,30
26	Aminoacridine	Dioxane	1644	2,80

Comparison of the values of the integral intensity of δNH_2 with the values of σ according to Hammett makes it possible to speak of the existence of a linear relationship between these quantities, i.e., of the subordination of the intensities of the δNH_2 bands in *n*-substituted anilines to Hammett’ s rule. The increase or decrease in the polarity of the N—H bonds, manifested in the corresponding changes in the intensity of the δNH_2 band, is evidently due to displacement of the electron cloud from the amino group toward the aromatic nucleus; this displacement is intensified by electron-acceptor substituents and weakened by electron-donor substituents in the nucleus.

An analogous increase in the intensity of the δNH_2 band (from $0.4 \cdot 10^4$ to $1 \cdot 10^4$ units) is observed in acetamide in connection with withdrawal of electrons from the NH_2 group toward C=O, and to a somewhat lesser degree in methanesulfonamide.

This effect is the cause not only of the corresponding changes in the intensity of δNH_2, but also of other properties of substituted aromatic compounds (the character of the basic and acidic properties of aromatic amines and phenols, the position of frequencies in vibrational spectra, and others).

It is interesting that such different substituents as NO_2 and OCH_3 (as well as OH), when located in the *o*-position to the amino group, cause only an increase in the intensity of the δNH_2 band. Apparently, this is connected with the peculiarities of the *o*-arrangement, in which intramolecular hydrogen bonds N—H . . . . O arise, and owing to this an increase in the polarity of the N—H bonds takes place. In heteroaromatic amines (2- and 4-aminopyridine) the intensity of the δNH_2 band increases to values considerably higher than in aniline. The nitrogen atom of the pyridine ring exerts a strong electron-acceptor effect. Introduction into the heteroaromatic ring of 2-aminopyridine of the electron-acceptor substituent NO_2 (moreover in the *o*-position) intensifies this effect still further.

2-Amino-3-nitropyridine has an integral intensity value of the δNH_2 band equal to $4 \cdot 10^4$ units. On the other hand, amines of heterocycles containing a sulfur atom in the ring (2-aminothiazole, 2-aminothiadiazole) show comparatively low intensity values of the δNH_2 band. Consequently, the sulfur atom in these compounds is an electron-donor center. In 2-aminobenzothiazole, condensation of the heterocyclic nucleus with a benzene nucleus causes an increase in intensity analogous to that observed in the aniline—naphthylamine series. From the point of view considered, the magnitude of the δNH_2 intensity in 2-aminoacridine is also understandable (a strong increase in comparison with aniline owing to condensation with a heterocyclic nucleus).

Whereas the integral intensities of δNH_2 change, in passing from one amine to another, quite regularly for all the diversity of the compounds examined, the δNH_2 frequencies show a similar dependence only within a narrow, uniform group of compounds (n-substituted anilines) and change quite chaotically in passing from one type of compound to another. The reason for this evidently lies in the fact that the values of the integral intensity of δNH_2 are determined practically only by the polarity of the N—H bonds, whereas the δNH_2 frequencies depend on a whole series of factors, the accounting for which is usually very difficult.

In this connection, the integral intensity of the δNH_2 band in compounds containing a primary amino group should be regarded as a very sensitive and selective characteristic of the polarity of N—H bonds, very useful in studying the influence of various structural factors on the displacement of electron density in the amino group.

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