Study of intermolecular interactions and complex formation of aminofurazans by IR spectroscopy

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The IR spectra of 3-amino-4-nitrofurazan (**1**) and 4-amino-4'-nitroazoxyfurazan (**2**) in the crystalline state and in solutions in CH_2Cl_2, CCl_4, and MeCN have been studied. It was shown that both compounds exist in the solid state as self-associates, which are destroyed on dissolution in an organic solvent. Compouns **1** and **2** form associate complexes with MeCN, the energies of formation of which are -5 and -3 kcal mol^{-1}, respectively.

Key words: aminofurazans; IR spectra; associate complexes; energy of formation.

The role of the intermolecular interactions in chemistry is extremely great, and the investigation of its various aspects is being carried out every year.[1] The present work is devoted to an IR-spectroscopic study of intermolecular interactions typical of some derivatives of aminofurazan using 3-amino-4-nitrofurazan (**1**) and 4-amino-4′-nitroazoxyfurazan (**2**) as examples. The IR spectra of compounds **1** and **2** in the solid state (pellets with KBr) and in dichloromethane and acetonitrile solutions of various concentrations were studied over a wide temperature range.

The most dramatic distinctions in the spectra are manifested in the region of stretching vibrations of the amino group. Therefore, we paid primary attention to the analysis of the variations in the 3600—3300 cm^{-1} spectral region.

The IR spectrum of a solution of a sample of **1** in dichloromethane exhibits two narrow absorption bands with similar intensities, which correspond to the stretching vibrations of the amino group (3520 and 3410 cm^{-1}) (Fig. 1, *a*). The decrease in the concentration of **1** in dichloromethane from 0.15 to 0.003 *M* causes no variations in the spectrum, which indicates the absence of intermolecular interactions involving the amino group. To find out whether the bands at 3520 and 3410 cm^{-1} correspond to free (*i.e.*, not involved in an intramolecular hydrogen bond) amino groups, we compared the spectrum of compound **1** recorded in a dilute dichloromethane solution with the corresponding spectrum of 3-amino-4-methylfurazan, which certainly forms no intramolecular hydrogen bonds. The positions of bands, their relative intensities, and their half-widths in the spectra of both compounds are identical, which confirms the absence of an intramolecular hydrogen bond in 3-amino-4-nitrofurazan in a CH_2Cl_2 solution. On the basis of this result, we assigned the bands at 3520 and 3410 cm^{-1} to vibrations of the free amino group.[2]

In the spectrum of solid **1** (in KBr) these bands are substantially broadened and shifted to lower frequencies: the high-frequency band of the NH_2 group is exhibited as a doublet at 3482 and 3462 cm^{-1}, and the low-frequency band is at 3352 cm^{-1}. The intensities of the bands are close (Fig. 1, *b*). These variations of the IR spectrum of **1** in the solid state compared with its spectrum in CH_2Cl_2 (broadening of bands and shifting to lower frequencies) indicate that molecules **1** exist in the crystal in a bound form, *i.e.*, they are self-associated due to H-bonds. The IR spectra of compound **2** recorded under similar conditions display similar changes, and we explained these changes by the fact that molecules of **2**, like molecules of **1**, exist in the crystalline state as self-associates, which are destroyed when the sample is dissolved in CH_2Cl_2 or CCl_4 (Fig. 2, *a*, *b*).

We studied the spectra of compounds **1** and **2** in MeCN. In the 3600—3300 cm^{-1} region, they differ substantially from the corresponding spectra recorded in dichloromethane (see Fig. 1, *a*, *c*, 2, *a*, *c*). The bands associated with the stretching vibrations of the amino groups are broadened and displaced to lower frequencies and have noticeably dissimilar intensities. This suggests that in MeCN, as in the solid state, molecules of these amines are bound, *i.e.*, interact with the solvent to give, probably, molecular complexes due to H-bonds.

To confirm this inference we studied the IR spectra of mixtures of compounds **1** and **2** with MeCN in CH_2Cl_2 and CCl_4 at various concentrations and various amine : acetonitrile molar ratios over a wide temperature range. The IR spectrum of **1** in CH_2Cl_2 or CCl_4 at the above-specified concentrations of the amine exhibits two narrow bands associated with the stretching vibra-

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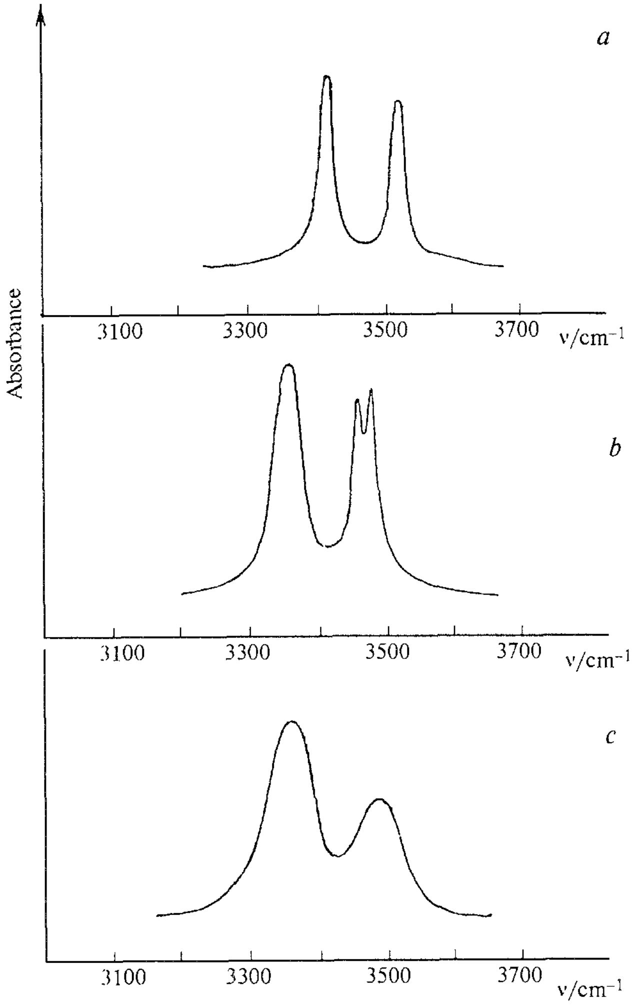

Fig. 1. The IR spectra of **1** in the ν(NH_2) region in CH_2Cl_2 (*a*), in pellets with KBr (*b*), and in MeCN (*c*).

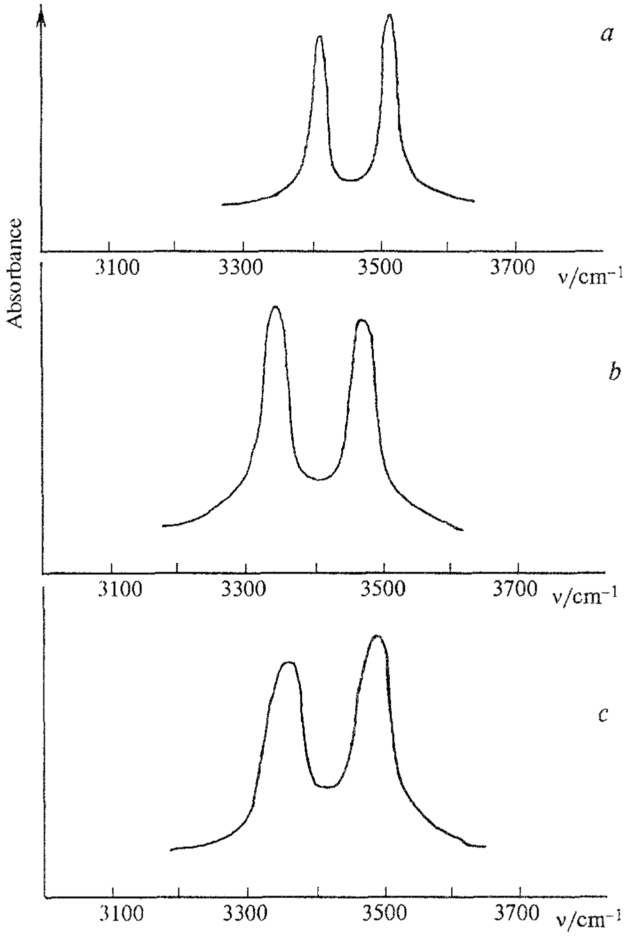

Fig. 2. The IR spectra of **1** in the ν(NH_2) region in CH_2Cl_2 (*a*), in pellets with KBr (*b*), and in MeCN (*c*).

tions of the amino group, corresponding to its "free" form (3520 and 3410 cm^{-1}). Therefore, under these conditions no self-association of the amine takes place.

When MeCN is added to the solution, alongside the narrow band corresponding to the "free" NH_2 group (3410 cm^{-1}), a broad low-frequency band of the "bound" amino group (3360 cm^{-1}) appears in the IR spectrum (Fig. 3). The other band associated with the vibrations of the amino group (ν = 3520 cm^{-1}) is broadened and shifts to the lower-frequency region. On further addition of MeCN, the intensity of the band for the "bound" amino group increases, and that for the "free" amino group decreases to the point of disappearance, *i.e.*, the amine is entirely converted into the bonded state. It should be noted that at identical **1** : MeCN molar ratios, the equilibrium in CCl_4 is shifted to the formation of the H-complex to a greater degree than in CH_2Cl_2.

We studied the effect of concentrations of 3-amino-4-nitrofurazan and acetonitrile in CH_2Cl_2, with their molar ratio remaining constant, on the IR spectrum in the ν(NH_2) region. Conditions have been found* under which the whole amine exists in the bound state, as indicated by the presence of two broad bands in the region of the amino group stretching vibrations (3485 and 3355 cm^{-1}) and the absence of any other bands in this region. When this system is diluted by dichloromethane, the associate complex starts to decompose, and the "free" form of the amine, existing in an equilibrium with the "bound" form, appears. A narrow high-frequency band associated with the "free" NH_2 group (ν = 3410 cm^{-1}) appears in the IR spectrum near the broad bands.

When the solution is further diluted, the intensity of the band corresponding to the "free" form increases, and that for the "bound" form decreases, and at [**1**] = 0.022 *M*, the amine is entirely non-associated even when a twentyfold excess of acetonitrile is added to the solution:

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* [**1**] = 0.59 *M*; **1** : CH_3CN = 1 : 20.

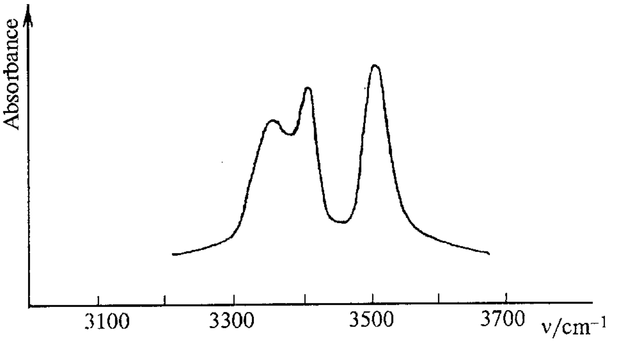

Fig. 3. The IR spectrum of **1** in the $\nu(NH_2)$ region in a $MeCN—CH_2Cl_2$ mixture at a **1** : MeCN molar ratio of 1 : 20; [**1**] = 0.134 *M*.

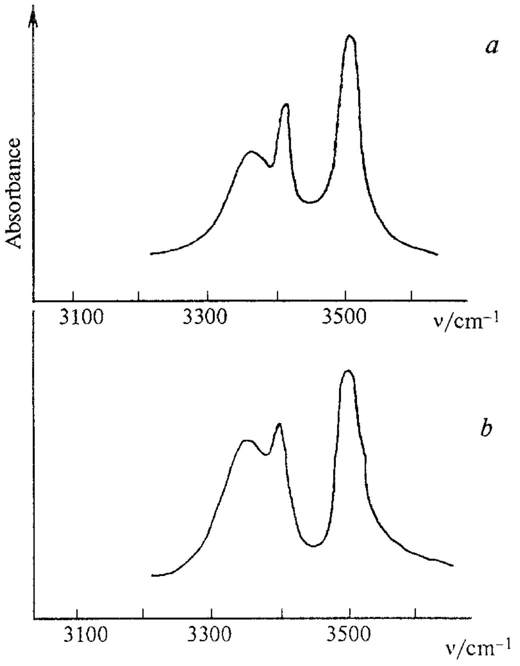

Fig. 4. The IR spectrum of **2** (*a*) and **1** (*b*) in the $\nu(NH_2)$ region in a $MeCN—CH_2Cl_2$ mixture at [amine] = 0.134 *M* and an amine : MeCN molar ratio of 1 : 20.

the IR spectrum contains two narrow absorption bands of the "free" NH_2 group, at 3520 and 3410 cm^{-1}. Increasing the temperature acts similarly to dilution: the H-complex formed decomposes, which is manifested in the spectrum as a decrease in the intensity of bands attributed to the "bound" amino group and an increase in the intensity of the bands relating to the "free" form of the NH_2 group. Thus, the IR spectra of compound **1** recorded with variation of the concentrations, of the amine : acetonitrile molar ratio, and of the temperature, reflect the formation of an associate complex between 3-amino-4-nitrofurazan and acetonitrile, owing to intermolecular hydrogen bonds.

A similar picture is observed for compound **2**. The absorption bands of the amino group in the spectrum of a solution of **2** in acetonitrile are also shifted to lower frequencies ($\nu(NH_2)$ = 3482 and 3355 cm^{-1}) compared with those for a solution in CH_2Cl_2. Their displacements are smaller than those observed on going to the spectrum of compound **2** in KBr (see Fig. 2). It is likely that, in this case, interaction of molecules of **2** with acetonitrile with the formation of intermolecular hydrogen bonds also occurs.

Dilution of the **2** : MeCN : CH_2Cl_2 (CCl_4) ternary system, in which the amine is entirely bonded, with dichloromethane or CCl_4 (with the amine : acetonitrile molar ratio remaining constant) results in the decomposition of the complexes and the appearance of nonbonded molecules of **2**. This is reflected in the spectra as the appearance of a high-frequency band associated with the stretching vibrations of the "free" NH_2 group, and the intensity of this bond increases as the solvent is added, whereas the intensity of the band of the "bound" amino group simultaneously decreases. An increase in the temperature also results in the decomposition of the H-complex of **2** with MeCN.

Thus, in the behavior of compounds **1** and **2** a general regularity can be followed: these amines form H-complexes with acetonitrile; these complexes readily decompose when the solution is diluted with a nonpolar solvent (CCl_4, CH_2Cl_2) or heated. At the same time, some distinctions exist. From the IR spectra of **1** and **2** recorded under identical conditions, it can be seen that the relative intensity of the low-frequency band of the "bound" amino group is always greater in the case of **1** than in the case of **2** (Fig. 4). This implies that the H-complex of molecule **1** with acetonitrile is probably more stable than the corresponding complex of **2**. To verify this suggestion, we determined the energies of formation of the H-complexes of amines with acetonitrile. The resulting values were −5 kcal mol^{-1} for **1** and −3 kcal mol^{-1} for **2**, *i.e.*, as has been expected, the complex of molecule **1** with MeCN is stronger than that of **2**. The resulting energies of formation of the amine—acetonitrile associate complexes are typical of normal H-bonds; both complexes are weak and exist only in concentrated solutions.

Judging from the spectra, the formation of the complexes of molecules of **1** and **2** with MeCN affects to the greatest degree their NH_2 groups. The frequencies corresponding to the nitro groups and the furazan rings vary to a lesser degree (Table 1). On the basis of the data obtained, we suggested that the process described involves not only the amino groups, but also the nitro groups and the furazan rings.[3,4]

Table 1. The vibration frequencies (ν/cm^{-1}) in the IR spectra of 3-amino-4-nitrofurazan (**1**) and 4-amino-4'-nitroazoxyfurazan (**2**)

Amine	Medium	$\nu(NH_2)$	$\delta(NH_2)$	ν of the ring	$\nu(NO_2)$	$\nu(NO_2)$	δ of the ring
1	CH_2Cl_2	3520 m, 3410 m	1640 m	1599 w, 1495 w, 1440 m	1540 s	1372 s, 1360 sh	1035 m, 840 s
	KBr	3482 s, 3462 s 3352 s,	1645 s	1592 w, 1505 m, 1440 m	1532 s	1375 s, 1352 sh	1045 m, 835 s
	MeCN	3485 m, br, 3355 m, br	1645 s	1610 m, 1505	1545 m	1370 m, 1360 m	1040 m, br, 835 s
2	CH_2Cl_2	3510 m, 3405 m	1632 s	1580 s, 1490 m, 1430 w	1508 m	1350 m, 1360 sh	1042 m, 835 m
	KBr	3472 s, 3342 s	1642 s	1586 s, 1495 s, 1410 m	1512 s	1355 s, 1365 sh	1050 m, 1035 sh, 840 s
	MeCN	3480 m, br, 3355 m, br	1640 s	1587 s, 1495 m, 1415 m	1512 m	1360 m	1045 w, br, 835 s

In order to study the behavior of acetonitrile (the second component participating in the complex formation), we compared the spectra of MeCN and of saturated solutions of compound **1** in MeCN. It was shown that in the spectra of the solutions, the intensities of the bands corresponding to C≡N and C—H vibrations change, whereas their frequencies remain practically unchanged. According to the literature data,[5] the band of the stretching CN vibrations shifts on complex formation in one or another direction depending on the type of coordination (at the N or at the C atom). One may suggest that in our case both types of coordination occur, and their effects on ν(CN) cancel one another.

Thus, crystalline compounds **1** and **2** exist as self-associates, which are destroyed on dissolution in organic solvents; these amines form complexes with acetonitrile.

Experimental

IR spectra were recorded on a UR-20 instrument. KBr cells with a layer thickness of 0.02 to 1.0 mm were used. The experiments were carried out in anhydrous solutions.

The energies of the intermolecular H-bonds of molecules **1** and **2** with acetonitrile were determined from the temperature dependence of the optical density of the absorption band corresponding to NH_2 stretching vibrations using the van't Hoff's equation brought to the following form:[6]

$$-\Delta H = \frac{RT_1T_2}{T_2-T_1} \ln \frac{(D_1^0 - D_1)D_2}{(D_2^0 - D_2)D_1} ,$$

where $D^0{}_1$ and $D^0{}_2$ are the optical densities of the stretching band of the NH_2 group of the amine without acetonitrile, and D_1 and D_2 are those for the "free" NH_2 group in the system containing acetonitrile at T_1 and T_2, respectively. The temperature dependences of the intensity of the band corresponding to the "free" NH_2 group of the amines were studied; this allowed us to apply the corresponding corrections to the calculation.

The measurements were carried out in amine—MeCN—CCl_4 ternary systems at amine : acetonitrile molar ratios of 1 : 40 and 1 : 60 and at a constant concentration of an amine (0.003 *M*) at which no self-association of these amines occurs. Specially designed quartz cells 5 mm thick were used. The spectra were recorded at 20 and 70 °C using a thermocouple placed into a special pocket directly in the cell; a constant temperature was ensured by a thermostat. Random errors were minimized by repeating the measurements many times. The error evaluated according to the known procedure[7] was 15 %.

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