

Effect of molecular and crystal structure of *N*-naphthylurethanes (carbamates) on their IR spectra

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A comparative analysis of the IR spectra in the region of 3000–400 cm⁻¹ of four urethanes (methyl-*N*-(1-naphthyl) carbamate, ethyl-*N*-(1-naphthyl) carbamate, dimethyl-*N,N'*-(1,5-naphthylene) dicarbamate, and diethyl-*N,N'*-(1,5-naphthylene) dicarbamate) with known molecular and crystal structures was carried out. The assignment of the bands related to the vibrations of the urethane and naphthyl fragments was refined on the basis of the study of the crystalline samples, melts, solutions, and deuterated analogs. The effect of the degree of conjugation of the urethane group with the naphthalene ring on the Amide II vibration frequency in the crystals was shown. It was suggested that the stretching vibrations of the C(Ar)—N bond in naphthylurethanes (unlike aliphatic derivatives) make a considerable contribution to the Amide II vibration, while the planar deformation vibration of the N—H bond was proved to be more significant for Amide III than for Amide II. In addition, strong nonspecific intermolecular interactions in the crystal can weaken valent bonds.

Key words: urethanes, IR spectra, intramolecular and intermolecular interactions.

Urethanes and polyurethanes were intensely studied by IR spectroscopy¹ mainly to establish the nature of intermolecular hydrogen bonds (IMHB) C=O...H—N. In the majority of the works the well-known bands of stretching vibrations (ν) of the NH and C=O groups (3400 and 1700 cm⁻¹) have been studied. The spectra exhibit bands at 1530, in the region of 1300–1200 and 650 cm⁻¹, which, by analogy to amides, are referred to as Amide II, Amide III, and Amide V, and their behavior was not systematically investigated. Studies on the dependence of the spectra on the molecular and crystal structures of urethanes are scarce. These studies became possible due to the appearance of published data on X-ray diffraction analysis of model urethanes.

In this respect, two urethanes close in their molecular structure are very interesting: methyl-*N*-(1-naphthyl) carbamate (**1**),² ethyl-*N*-(1-naphthyl) carbamate (**2**),³ and the disubstituted analog of **2**, diethyl-*N,N'*-(1,5-naphthylene) dicarbamate (**4**).⁴ The structural studies show that the layered packing of monourethane molecules in crystals have a similar structure: the naphthyl fragments are arranged in a herringbone pattern relative to the trunk created by the chains of C=O...H—N IMHB. The crystal structure of diurethane is characterized by a pile packing with parallel arrangement of adjacent naphthylene fragments resulting in strong nonspecific intermolecular interactions (IMI). The differences in the molecular structure are due to the values

of the dihedral angles between the planes of the naphthyl and urethane fragments: 45° (**4**), 67° (**1**), and 89° (**2**). As the angle increases, the C(Ar)—N bond elongates (0.1420–0.1428–0.1446 nm), and the conjugation of the urethane group with the aromatic ring decreases.

In this work, we studied the dependence of the IR spectra of the urethanes mentioned on their molecular and crystal structures in a wide frequency range.

Experimental

Urethanes were obtained by mixing 1-naphthyl isocyanate and 1,5-naphthylene diisocyanate with an excess of dry MeOH and EtOH. Melting points (°C): **2**, 80; **1**, 120; **4**, 234; and dimethyl-*N,N'*-(1,5-naphthylene) dicarbamate (**3**), 256. Compound **1** was deuterated by hydrogen exchange with completely deuterated ethanol. The molecular and crystal structures of deuterated **1** are identical to the starting structures. The crystal structure of **3** was not studied, but it can be assumed to be close to that of **4**, because the melting point of **3** is close to that of **4**. IR spectra in the medium region (4000–400 cm⁻¹) were measured on a Specord M80 spectrometer with a data processing system based on a PC-AT 486. Crystalline samples were molded in pellets with KBr. Melts of monourethanes between KBr glasses were placed in a thermostatted cell (140 °C). Solutions in CCl₄ with sample concentration 0.01 mol L⁻¹ were prepared for studying the spectra of isolated molecules. The main frequencies of **1** and **2** in the crystalline state, melt, and solution are presented in Table 1, and the spectra are shown in Fig. 1. Diurethanes are insoluble in CCl₄.

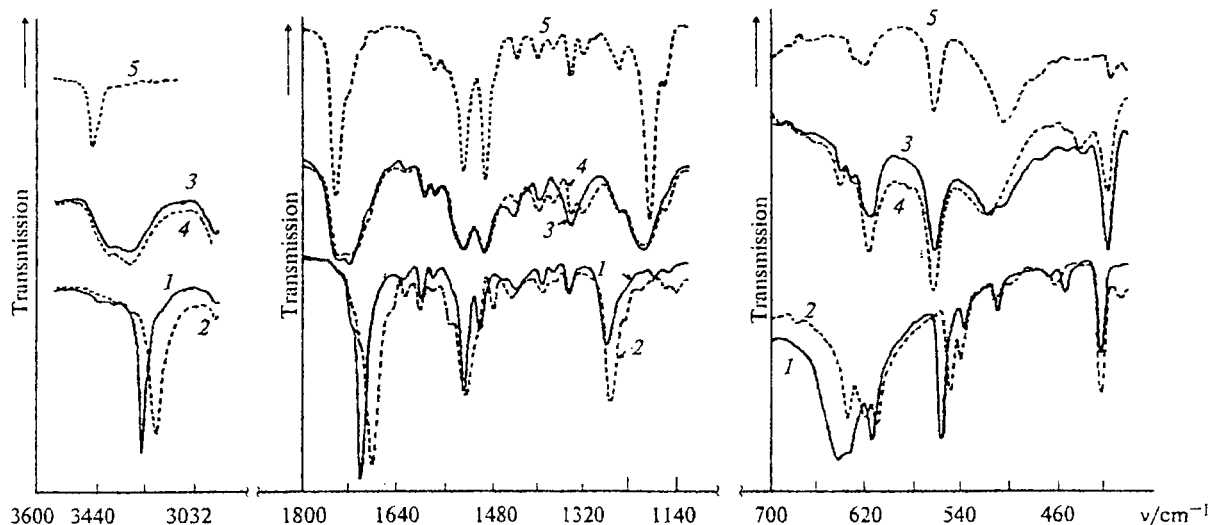


Fig. 1. IR spectra of *N*-(1-naphthyl)urethanes: crystal of **1** (**2**), (spectrum **1**, **2**); melt of **1** (**2**) (spectrum **3**, **4**); **5**, dilute solution of **2**. The regions of 3600–3000 cm^{-1} , 1800–700 cm^{-1} , and 700–400 cm^{-1} are presented in different scales.

Results and Discussion

The behavior of the $\nu(\text{NH})$ bond in crystalline naphthylurethanes and other related compounds with $\text{C}=\text{O}\dots\text{H}-\text{N}$ IMHB with different IMHB geometries has been considered previously.^{4–5} As follows from the data in Table 1, for crystalline **1** and **2** the shift of the $\nu(\text{NH})$ frequency due to the formation of IMHB is 172 and 220 cm^{-1} , respectively. When the $\nu(\text{NH})$ band for

dilute solutions of diurethanes is assumed to be also observed at 3464 cm^{-1} , the frequency shift on going to the crystalline state is equal to 172 cm^{-1} (**3**) and 183 cm^{-1} (**4**).

When the sample melts, the band typical of the crystal disappears, and bands appear at 3340, 3400, and 3460 cm^{-1} , which can be assigned to $\nu(\text{NH})$ of NH bound to $\text{C}=\text{O}$ by IMHB, NH interacting with the π -electronic system of naphthalene rings, and "free" NH. A decrease in the $\nu(\text{NH})$ of NH bound by IMHB ($\text{C}=\text{O}\dots\text{H}-\text{N}$) in the melt indicates that these interactions weaken when the crystal lattice is broken.

It is known that the $\nu(\text{C}=\text{O})$ band (Amide I) is also sensitive to the formation of IMHB. This band shifts on going from crystalline **1** and **2** to dilute solutions to lower frequencies relative to Amide I by 52 and 72 cm^{-1} , which coincides with the behavior of $\nu(\text{NH})$. An almost straight linear dependence between the $\nu(\text{NH})$ and $\nu(\text{C}=\text{O})$ frequencies is observed for four crystalline urethanes. At least three bands appear in this region for the melt of monourethanes: a noticeable shoulder at 1700–1710 cm^{-1} is due to $\nu(\text{C}=\text{O})$ perturbed by the $\text{C}=\text{O}\dots\text{NH}$ IMHB, which is weaker than that in the crystal; the band at 1720 cm^{-1} can be related to $\nu(\text{C}=\text{O})$ of the urethane group, whose NH group participates in IMHB; and the band at 1740 cm^{-1} corresponds to $\nu(\text{C}=\text{O})$ of the "free" urethane group. The difference in the Amide I frequencies of the "free" urethane groups in the melt and dilute solution is understandable, because this band is very sensitive to other types of IMI rather than to IMHB.⁶

In the crystalline samples, bands at 1544 (**4**), 1528 (**3**), 1530 (**1**), and 1524 cm^{-1} (**2**) were attributed to the Amide II vibration. The nature of this band and Amide III in the spectra of amide has been discussed for a long time,⁷ and presently it is assumed that these bands are

Table 1. The most intense bands in the IR spectra attributed to the absorption of the urethane fragment

Compound	ν/cm^{-1}		
	Crystal ^a	Melt	Solution ^a
1	3292, 1700, 1530, 1504, 1282, 808, 774, 630 ^b	3460 sh, 3400, 3344, 1742, 1724, 1708 sh, 1534, 1498, 1256, 1230 sh, 1214, 794, 774, 518	3464, 1752, 1534, 1498, 1206, 504
2	3244, 1676, 1524, 1512 sh, 1270, 808 w, 778, 620 ^b	3460 sh, 3394, 3336, 1736, 1720, 1700 sh, 1530, 1496, 1254, 1234 sh, 1210, 796, 778, 520	3464, 1748, 1538, 1498, 1206, 504
3	3292, 1714 sh, 1701, 1528, 1499, 1263, 792, 778, 640 ^b		
4	3279, 1692, 1544, 1500, 1237, 780, 771 sh, 696		

^a At room temperature. ^b The frequency value was obtained after separation of the bands.

due to the sum of several vibrations. The planar deformation vibration $\delta(\text{NH})$ and $\nu(\text{C}-\text{N})$ of the amide group contribute mainly to this sum. One of the main arguments in favor of the participation of NH in the Amide II vibration is the high-frequency shift of this band on the formation of IMHB. This behavior of Amide II is observed for aliphatic urethanes.⁸ As mentioned previously,¹ the shift of Amide II can reach 40 cm^{-1} . In mononaphthylurethanes for the solution-melt-crystal transition, the shift of Amide II is insignificant, and it is shifted to the opposite, low-frequency range. At the same time, three crystalline urethanes exhibit a tendency of the Amide II frequency to decrease as the $\text{C}(\text{Ar})-\text{N}$ bond elongates in the 4-1-2 series. It can be assumed that $\nu(\text{C}(\text{Ar})-\text{N})$ in naphthylurethanes makes a noticeable contribution to the Amide II vibration, equalizing or perhaps exceeding the contribution of $\delta(\text{N}-\text{H})$.

The relative intensity of the band at 1500 cm^{-1} increases sharply on melting and is maximum in a dilute solution; however, it almost disappears in the spectrum of deuterated 1. This band is absent in the spectra of aliphatic urethanes and phenylurethanes⁹⁻¹¹ and observed in those of 3 and 4 and (according to our data) crystalline 1- and 2-naphthylamines; a low-intensity band is observed in the spectrum of crystalline naphthalene.¹² It can be assumed that this band is caused by the vibration of the naphthalene ring, and its intensity is enhanced due to the substituent which is capable of conjugation with the aromatic π -electronic system.

The band usually related to the Amide III vibration is very sensitive to the formation of IMHB.^{10,11} In the spectra of solutions of 1 and 2, we assigned the band at 1206 cm^{-1} to Amide III, since it is absent in deuterated 1. In crystalline 1 and 2, the Amide III frequency is sharply increased on the average by 70 cm^{-1} . In aliphatic urethanes, the shift of Amide III due to the formation of IMHB is substantially lower ($\sim 20 \text{ cm}^{-1}$). The inversion observed in shifting the Amide II and Amide III bands in naphthylurethanes compared to aliphatic urethanes can be explained by the fact that the naphthyl ring affects the form of the vibrations in such a way that the contribution of $\delta(\text{NH})$ to Amide III is greater than to Amide II. In the melts in the 1260-1200 cm^{-1} region, a superposition of several bands is observed, which reflects the complicated structure of the melt and different characters of IMI.

In 3 (1263 cm^{-1}) and 4 (1237 cm^{-1}), the bands of Amide III are located substantially lower than in 1 and 2. This is especially surprising in the case of 3, since all the other bands caused by the vibrations of NH almost coincide with similar bands in the spectrum of 1. The difference between the frequencies of ethyl homologues (30 cm^{-1}) is too great, when it is taken into account that the geometric parameters of the urethane groups are close, and a weaker IMHB in 4 cannot be the reason for the strong decrease in the Amide III frequency in 4. We believe that the pile packing of diurethanes in the

crystal can be one of the reasons for the phenomenon observed. Strong IMI can result in a change in the electronic structures of the molecules,¹³ which is manifested, e.g., in the Raman spectra. Perhaps, the intramolecular bonds, whose vibrations contribute to Amide III, are weakened in diurethanes.

The bands in the 800-770 cm^{-1} region are characteristic of the urethanes under study. 1-Substituted naphthalenes usually exhibit two bands:^{12,14} 810-785 and 760-735 cm^{-1} ; the high-frequency band is caused by the nonplanar vibrations of three adjacent CH groups of the substituted ring, and the low-frequency band is due to the vibrations of four CH groups of the nonsubstituted ring.¹⁴ Analysis of the spectra obtained shows that this assignment is ambiguous. In fact, the spectrum of 1, as that of 1-naphthylamine, contains two intense bands at 808 (790) and 774 (770) cm^{-1} , the equal ratios of the intensities. Deuteration of 1 has almost no effect on these bands. At the same time, the spectrum of 2 contains only a low-frequency band at 778 cm^{-1} . The band at 808 cm^{-1} is weak, and that at 790 cm^{-1} has a shoulder. Moreover, the character of the bands in the spectra of 4 and 2 is the same, while in 3 the band at 806 cm^{-1} in 1 is shifted to 794 cm^{-1} , and its relative intensity is increased, while the position of the band at 774 cm^{-1} remained almost unchanged. In fact, the bands of crystalline 3 coincide with the bands of the melt of 1. Thus, it can be assumed that the character of these bands in the spectra of substituted naphthalenes is determined to a certain extent by the nature of the substituent. The band at 770 cm^{-1} is observed in all conceivable urethane compounds. It is usually attributed to the nonplanar vibrations of $\text{C}=\text{O}$ (Amide VI),¹ although phenylurethanes can exhibit in this region the $\delta(\text{CH})$ bands of the aromatic ring. Therefore, superposition of the bands of Amide VI and the naphthyl fragment is observed in the spectra of naphthyl- and naphthyleneurethanes.

The bands at 630 and 620 cm^{-1} (in crystalline 1 and 2, see Ref. 15), Amide II at 520 cm^{-1} (in the melts), and at 504 cm^{-1} (in the solutions) are attributed to the nonplanar vibration of NH (Amide V). In deuterated 1, the complex band at 640-610 cm^{-1} is substantially less intense, and two new bands appear at 480 and 448 cm^{-1} , which disappear on melting. One of them undoubtedly belongs to the nonplanar vibration of N-D.

A sufficiently narrow band, which is absent in the spectra of diurethanes, is observed in the 550-560 cm^{-1} range in the spectra of crystalline 1 and 2, their melts and solutions, and in the spectrum of 1-naphthylamine. This band is likely related to the vibrations of 1-substituted naphthalene.

Thus, the characteristic bands in the IR spectra of naphthylurethanes are interpreted more exactly, the dependences of the characteristic frequencies of the molecular and crystal structures are established, and the conjugation of the urethane group with the naphthyl ring is assumed to change the form of the Amide II and

III vibrations in such a way that $\nu(\text{C}(\text{Ar})-\text{N})$ contributes noticeably to Amide II, and $\delta(\text{NH})$ is more substantial for Amide III than for Amide II. It is supposed that strong nonspecific IMI in crystal can weaken valence bonds.

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