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Self-Association of Trifluoromethanesulfonamide in Inert Solvents

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Abstract—Trifluoromethanesulfonamide exists in inert solvents as an equilibrium mixture of the monomer and self-associates of the structure depending on the solvent polarity. In low-polarity CCl_4 and C_2Cl_4, a cyclic tetramer is formed, in which the NH_2 group is involved in two NH···O=S hydrogen bonds; in moderately polar $CHCl_3$, the compound forms cyclic trimers in which one of the hydrogen atoms of the NH_2 group is not involved in hydrogen bonding; in highly polar C_2HCl_5 and $C_2H_4Cl_2$, the compound forms chain-like dimers.

Trifluoromethanesulfonamide and *N*-methyltrifluoromethanesulfonamide exhibit high acidity (pK_a 6.39 and 7.56, respectively [1]) and undergo reversible self-association in the gas phase at 385–458 K, forming various oligomeric species [2, 3]. In inert solvents, N-methyltrifluoromethanesulfonamide forms cyclic and chain-like dimers [3]; their relative content is determined by the strength of the NH···O=S hydrogen bond and by the energy of nonspecific solvation. Data on the structure of N-unsubstituted perfluoroalkanesulfonamides in solutions are lacking. Less acidic methanesulfonamide (pK_a 10.8 [1]) exists in dilute CCl_4 solutions in the form of monomeric molecules [4].

In this study we examined experimentally and theoretically the self-association of perfluoroalkanesulfonamides $CF_3SO_2NH_2$ (**I**), $C_2F_5SO_2NH_2$ (**II**), and $CF_3SO_2NHCH_3$ (**III**) in inert aprotic solvents and in protophobic chloroform, and also the effect of the solvent polarity on the structure of the associates. For this purpose, we used IR spectroscopy, dielectrometry, and DFT B3LYP/6-31G* calculations.

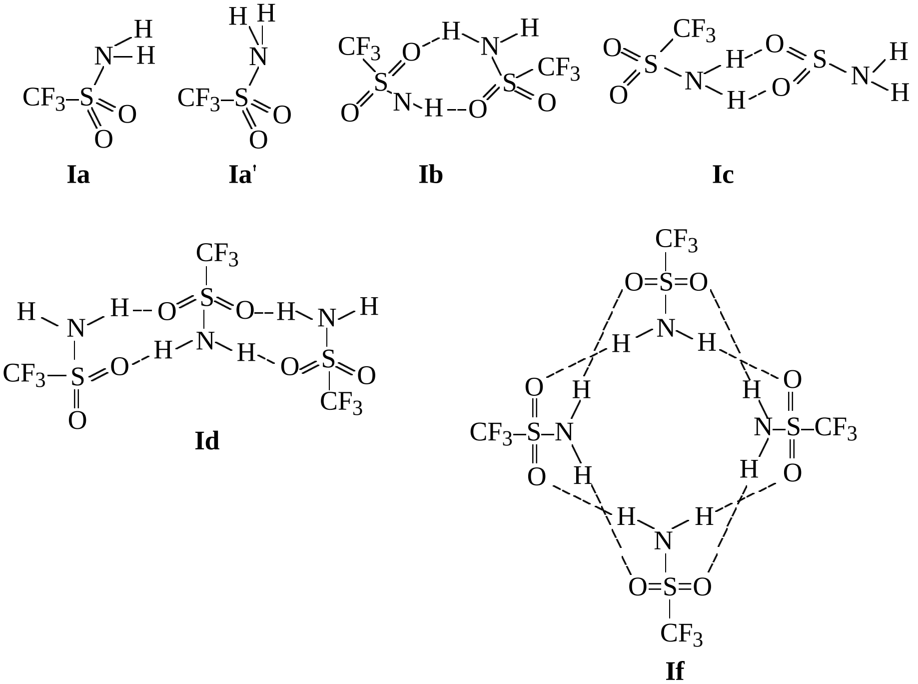
Various self-associates of amides **I**–**III** are formed via NH···O=S hydrogen bonds of various strengths; therefore, as the parameter characterizing the structure of the associates we used the stretching vibration frequencies of the free and bonded NH groups. An equilibrium between the monomeric molecules of amide I and its self-associates **Ia**–**If** (Scheme 1) gives rise to a complex pattern in the range 3000–4000 cm^{-1} with a set of overlapping bands, even in the gas phase [2].

Generally, these bands can belong to the stretching vibrations of free NH_2 groups (monomers **Ia** and **Ia**'; chain-like dimer **Ic**), NH_2 groups fully involved in hydrogen bonding (tetramer **If**), and those containing one free NH group (dimer **Ib**; trimers **Id** and **Ie**). Amide **III**, according to our previous study [3], in low-polarity CCl_4 exists in the form of monomer **IIIa** and cyclic dimer **IIIb**, and in more polar CH_2Cl_2, in the form of chain-like dimers **IIIc** having a higher dipole moment (Scheme 2) [3].

The energy of the NH···O=S hydrogen bond, according to quantum-chemical calculations, only slightly depends on the structure of the self-associates and is approximately equal to 26 kJ mol^{-1} per bond. The experimentally determined enthalpy of formation of chain-like dimer **IIIc** is 20 kJ mol^{-1} [5].

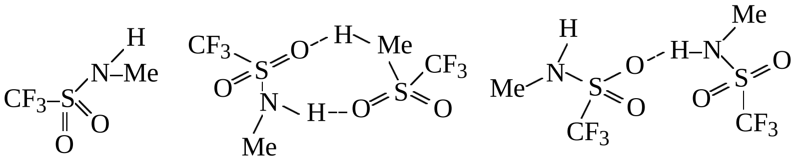
We estimated in this study the enthalpy of formation (ΔH) of cyclic dimer **IIIb** in CCl_4 by the procedure applied in [5] to chain-like dimer **IIIc** and based on measuring the integral intensities of ν(NH) bands of the free and hydrogen-bonded NH groups in relation to the amide concentration and temperature. At high concentrations of **III**, a shoulder appears on the high frequency wing of the band belonging to NH···O vibrations in cyclic dimer **IIIb**, suggesting the presence of a small fraction of chain-like dimer **IIIc**. The ν(NH) frequency for this species is lower than for the monomer but higher than for the cyclic dimer [3]. Because of the partial overlap of the bands belonging to the monomer and dimers, we resolved the overall IR band into three Lorentzian components. The integral absorption coefficients of the vibration bands of the monomer (A_m) and cyclic dimer (A_d) in CH_2Cl_2 are 1.3 and 1.8×10^4 l mol^{-1} cm^{-2} [5]. Taking into account the ratio of these bands, we determined the contribution of the free NH group of this dimer into the total integral intensity of the band observed in the

Scheme 1.



Ia **Ia'** **Ib** **Ic** **Id** **If**

Scheme 2.



IIIa **IIIb** **IIIc**

range of vibrations of free NH groups and made the necessary correction. For solutions of **III** in CCl_4, the integral intensities of the absorption bands of cyclic dimer **IIIb** [ν(NH) 3310 cm^{-1}] and monomer **IIIa** [ν(NH) 3400 cm^{-1}] were determined from the linear correlation between $B_{3310}/([M]_0d)$ and $B_{3400}/([M]_0d)$:

$$B_{3310}/([M]_0d) = (12.3 \pm 1.3) - (1.6 \pm 0.3)B_{3400}/([M]_0d),$$
$$r\ 0.912,\ Sd\ 1.5,\ n\ 9. \qquad (1)$$

Here B_{3310} and B_{3400} are the integral intensities of the corresponding bands, $[M]_0$ is the initial amide concentration, and d is the layer thickness (Fig. 1). The coefficients A_m and A_d corresponding to the intercepts on the coordinate axes are 0.7 and 1.2 × 10^4 l mol^{-1} cm^{-2}. The dimerization constants K_d of **III** at $[M]_0$ 0.085 M were found from the equation $K_d = [D]/[M]^2$ in the range 282–323 K.

T, K	282	293	303	313	323
K_d, l mol^{-1}	69.15	49.16	31.00	20.00	13.74

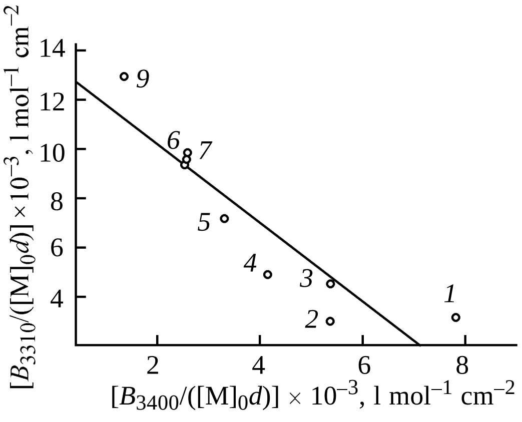


Fig. 1. Correlaton between the reduced integral intensities of the absorption bands of the stretching vibrations of associated and free NH groups in the IR spectra of solutions of *N*-methyltrifluoromethanesulfonamide in CCl_4. $[M]_0$, M: (*1*) 0.003, (*2*) 0.006, (*3*) 0.012, (*4*) 0.024, (*5*) 0.048, (*6*) 0.057, (*7*) 0.085, (*8*) 0.096, and (*9*) 0.192.

The enthalpy of formation of cyclic dimer **IIIb** was calculated by the van't Hoff equation to be 30.5 ± 6.3 kJ mol^{-1}. Thus, the values of $-\Delta H$ per H bond of the dimers are 15.5 ± 3.3 kJ mol^{-1} for **IIIb** in CCl_4 and 20.1 ± 1.7 kJ mol^{-1} for **IIIc** in CH_2Cl_2. Taking into account the determination error, these values differ insignificantly, in agreement with the theory.

The calculated energies of formation of self-associates of amide **I** per H bond are close ($-\Delta E_H$ ~23.5 kJ mol^{-1}) and, on the whole, somewhat lower compared to **III** (26.0 kJ mol^{-1}). The dipole moments μ of these species, however, differ significantly. This fact suggests that the polarity of a nonspeficically solvating medium is also a decisive factor affecting the self-association equilibrium.

Comp. no.	**Ia**	**Ia'**	**Ib**	**Ic**	**Id**	**Ie**	**If**
$-\Delta E_H$, kJ mol^{-1} (B3LYP/6-31G*)	0	3.3	26.0	21.8	23.9	21.5	23.4
μ, D	3.36	4.23	0.36	9.54	3.16	3.75	0.05

Indeed, the number and position of bands in the relevant range of the IR spectrum of amide **I** depend on the solution concentration and solvent polarity/polarizability (see table), quantitatively described by the Kamlet–Taft solvatochromic parameter π^* [6, 7] characterizing the capability of a medium to stabilize dipolar molecules by the mechanism of nonspecific solvation. In particular, the IR spectra of very dilute solutions of **I** in CCl_4 contain only two bands corresponding to the stretching vibrations of the NH_2 group, with maxima at 3475 and 3366 cm^{-1}. With an increase in the concentration of **I**, two additional bands appear with maxima at lower frequencies (3387 and 3280 cm^{-1}), and at concentrations exceeding 0.01 M these bands start to prevail. A similar pattern was observed for solutions of amide **I** in C_2Cl_4. At a high solvent polarity (CH_2Cl_2, π^* 0.82; $C_2H_2Cl_4$, π 0.95), only two bands are detected in the spectrum; the frequencies of their maxima decrease with increasing π^*. Such a solvatochromic behavior is typical of compounds with free NH or NH_2 groups [8–10].

According to the previous study [3], for **III** the theoretically calculated shifts of the NH vibration frequencies of the dimers (cyclic **IIIb**, 111 cm^{-1}; chain-like **IIIc**, 62 cm^{-1}) relative to the monomer are in good agreement with the experimental data [3]. According to the experiment, the shift for **IIIb** is 110 cm^{-1} in the gas phase and 93 cm^{-1} in CCl_4; for **IIIc**, it is 60 cm^{-1} in CCl_4 and 50 cm^{-1} in CH_2Cl_2. Therefore, when determining the structure of the self-associates in inert solvents of different polarities, we used the theoretically found NH vibration frequencies.

We examined how the position of the two NH vibration bands in the spectra of **I** in the gas phase at 458 K and in CCl_4, C_2Cl_4 (~0.002 M), CH_2Cl_2, and $C_2H_2Cl_4$ correlates with the solvent parameter π^*, to confirm the assignment of these bands to the monomer. Indeed, the position of each band is described by a separate linear correlation $\nu(NH) \sim f(\pi^*)$. The high-frequency band corresponding to the antisymmetric vibrations of the NH_2 group obeys Eq. (2), and the low-frequency band (symmetric vibrations), Eq. (3). This fact directly supports the assignment of these bands to the monomer of amide **I**.

$$\nu_{as}(NH_2) = (3475 \pm 3) - (24 \pm 4)\pi^*, \tag{2}$$

$$r\ 0.967,\ Sd\ 6,\ n\ 5,$$

$$\nu_s(NH_2) = (3367 \pm 3) - (29 \pm 4)\pi^*, \tag{3}$$

$$r\ 0.969,\ Sd\ 7,\ n\ 5.$$

The regression coefficients at π^* in Eqs. (2) and (3) are similar, indicating that the antisymmetric and symmetric vibration frequencies of the NH_2 group of monomer **Ia** show similar sensitivity to the polarity/polarizability of the medium. An additional argument in favor of the assignment of the bands observed in highly polar inert solvents to the monomer is as follows. According to the calculations, the difference between the antisymmetric and symmetric vibration frequencies of the NH_2 group of **Ia**, $\Delta\nu(NH) = \nu_{as}(NH_2) - \nu_s(NH_2)$, is 117 cm^{-1}. The experimental differences $\Delta\nu(NH)$ between the frequencies of the bands assigned to the monomer are 110–120 cm^{-1} in the above-mentioned media. The experimental dipole moment μ of **I** in CH_2Cl_2, in which this compound forms no self-associates according to IR data, is 3.60 D, in agreement with the calculated value.

Two additional bands appearing in the spectra of solutions of **I** in CCl_4 and C_2Cl_4 at high amide concentrations and shifted toward lower frequencies compared to the monomer (Fig. 2) suggest formation of a self-associate of **I**. As both bands of the monomer are shifted to a similar extent (88 and 86 cm^{-1} in CCl_4; 76 and 79 cm^{-1} in C_2Cl_4), the associate contains no free NH bonds. Such a pattern is realized in cyclic tetramer **If** of C_4 symmetry (Scheme 1). A calculation of the vibration spectrum of tetramer **If** shows that its NH stretching frequencies are shifted toward lower values by 110–130 cm^{-1} relative to the monomer, and $\Delta\nu(NH) = \nu_{as}(NH_2) - \nu_s(NH_2)$ is 80–115 cm^{-1}, in full agreement with the experiment (Fig. 2). Also, for dimer **IIIb** formed in CCl_4, the spectral shift of the absorption band is 90 cm^{-1}, as in **If**, and the calculation gives 111 cm^{-1}. Thus, in a low-polarity medium, amide **I** exists as an ensemble of monomers and cyclic

Experimental and theoretical NH stretching vibration frequencies for various trifluoromethanesulfonamide species

Medium	π*	ν(NH_2), cm^{-1}	Species	ν(NH_2), cm^{-1} (B3LYP/6-31G*)
Gas	–1.10	3500	**Ia**	3633 (61)[a]
		3398		3516 (53)
Carbon tetrachloride	0.28	3475[b]	**Ia**	
		3366[b]		
		3387[c]	**If**	3507 (1263), 3505 (1301), 3492 (79), 3488 (44)
		3280[c]		3411 (533), 3389 (435), 3388 (444), 3379 (14)
Tetrachloroethylene	0.28	3465[b]	**Ia**	
		3358[b]		
		3389[c]	**If**	
		3279[c]		
Chloroform	0.58	3463	**Ia**	
		3350		
		~3470[d]	**Id**	3611 (129), 3607 (196)
		3419[d]		3506 (1138)
		3350[d]		3437 (559), 3425 (544)
		3284[d]		3391 (147)
Pentachloroethane	0.62	3463	**Ia**	
		3353		
1,2-Dichloroethane	0.81	3432	**Ia** + **Ic**	3648 (63), 3603 (46)[e]
		3315		3524 (60), 3493 (110)[e]
		3380[f]	**If**	
		3280[f]		
Dichloromethane	0.82	3449	**Ia**	
		3334		
1,1,2,2-Tetrachloroethane	0.95	3455	**Ia**	
		3343		
			Ib	3609 (163), 3608 (156)
				3426 (1097), 3405 (1)
			Ie	3612 (167), 3609 (151), 3607 (159)
				3461 (238), 3436 (1019), 3400 (389)

[a] The relative band intensities are given in parentheses. [b] ~0.002 M solution. [c] ~0.02 M solution. [d] Spectrum of the solution at 255 K. [e] Frequencies for **Ic**. [f] Spectrum of the solution at 237 K.

tetramers in which all the amide hydrogen atoms are involved in hydrogen bonding.

Dielectric measurements confirm the above conclusions. The dipole moment of **I** in C_2Cl_4 (0.003 M solution), μ 2.1 D, is appreciably lower than that of the monomer, μ 3.6 D. This is due to the formation in a low-polarity solvent of a cyclic self-associate with the dipole moment close to zero. Amide **III**, as noted in [3], also forms a cyclic self-associate under similar conditions with μ ~ 0.

The IR spectra of solutions of **I** in $C_2H_4Cl_2$ and C_2HCl_5 (π* 0.81 and 0.62, respectively), irrespective of the amide concentration, exhibit only two broad asymmetric bands. The asymmetry of the high-frequency bands becomes more pronounced with increasing concentration, especially in $C_2H_4Cl_2$ (Fig. 3). As a result, the frequencies measured in 1,2-dichloroethane do not obey Eqs. (2) and (3). The deviation from the corresponding regression lines is ~20 cm^{-1}. According to theoretical estimations, such a distortion of the spectrum of the monomer is possible only with formation of chain-like dimer **Ic** (Fig. 3, see table). The calculated shift of one of its high-frequency bands relative to the band of the monomer is 30 cm^{-1}, with a slight change in the transition intensity, and that of the low-frequency band is 23 cm^{-1}. In the related chain-like dimer **IIIc**, the shift of the vibration frequency of the associated NH group in CH_2Cl_2 is 60 cm^{-1}. It is interesting that cyclic associate **If** is stabilized in 1,2-dichloroethane with a decrease in the temperature from 298 to 237 K (Fig. 3).

In contrast to $C_2H_4Cl_2$, the frequencies ν(NH)

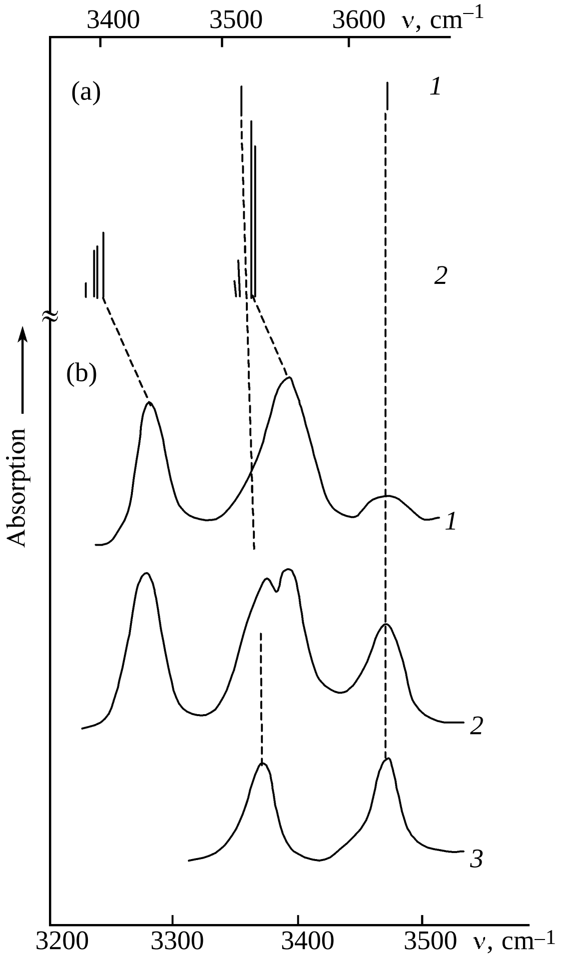


Fig. 2. IR spectra of amide **I**: (a) theoretical (B3LYP/6-31G*) spectra of (*1*) monomer **Ia** and (*2*) cyclic tetramer **If**, upper frequency scale; (b) spectra of **I** in CCl_4 at 298 K, $[M]_0$, M: (*1*) ~0.02, (*2*) 0.004, and (*3*) 0.002.

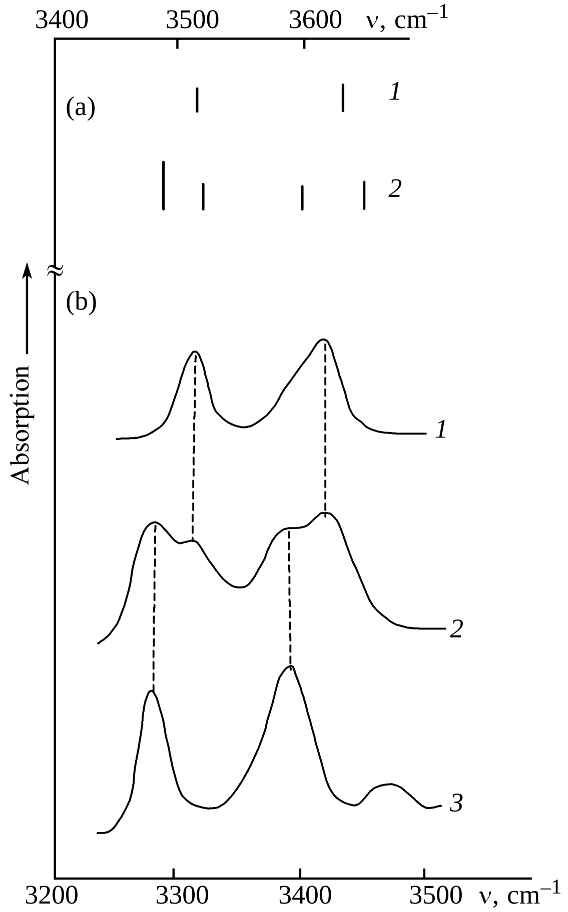


Fig. 3. IR spectra of amide **I**: (a) theoretical (B3LYP/6-31G*) spectra of (*1*) monomer **Ia** and (*2*) chain-like dimer **Ic**, upper frequency scale; (b) experimental spectra of **I**: (*1, 2*) in $C_2H_4Cl_2$, $[M]_0$ ~0.02 M, *T*, K: (*1*) 298 and (*2*) 237; (*3*) cyclic tetramer **If** in CCl_4, $[M]_0$ ~0.02 M, 298 K.

determined for solutions in C_2HCl_5 obey Eqs. (2) and (3). This may be due to a shift of the dynamic equilibrium at 298 K toward the monomer.

A different self-associate is stabilized in $CHCl_3$ (π^* 0.58), which is a proton-donor solvent. The high-frequency vibration band $\nu(NH_2)$ of the associate formed in $CHCl_3$ is shifted toward lower frequencies relative to the monomer by more than 30 cm^{-1} (Fig. 4, spectrum *3*). As a result, in this frequency range the maxima of the monomer and associate are observed separately. Furthermore, the $\nu_{as}(NH_2)$ frequency of the monomer in this solvent obeys Eq. (2). The band of NH_2 symmetric stretching vibrations of the monomer in $CHCl_3$ at 298 K is narrow and symmetrical, and the corresponding frequency $\nu_s(NH_2)$ strictly obeys Eq. (3). Inclusion of the $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ frequencies of the monomer measured in $CHCl_3$ and C_2HCl_5 into the statistical sample does not alter the parameters of solvatochromic equations (4) and (5) compared to (2) and (3):

$$\nu_{as}(NH_2) = (3475 \pm 2) - (23 \pm 3)\pi^*, \tag{4}$$

$$r\ 0.965,\ Sd\ 5,\ n\ 7.$$

$$\nu_{as}(NH_2) = (3367 \pm 2) - (29 \pm 3)\pi^*, \tag{5}$$

$$r\ 0.967,\ Sd\ 6,\ n\ 7.$$

If we assume that the band of NH_2 symmetric vibrations of the monomer fully overlaps with the low-frequency band of the self-associate, then the difference between the band frequencies of the self-associate cannot exceed 90 cm^{-1}. This value differs from that characteristic of **If** (Δν 107 cm^{-1} in CCl_4 and 110 cm^{-1} in C_2Cl_4).

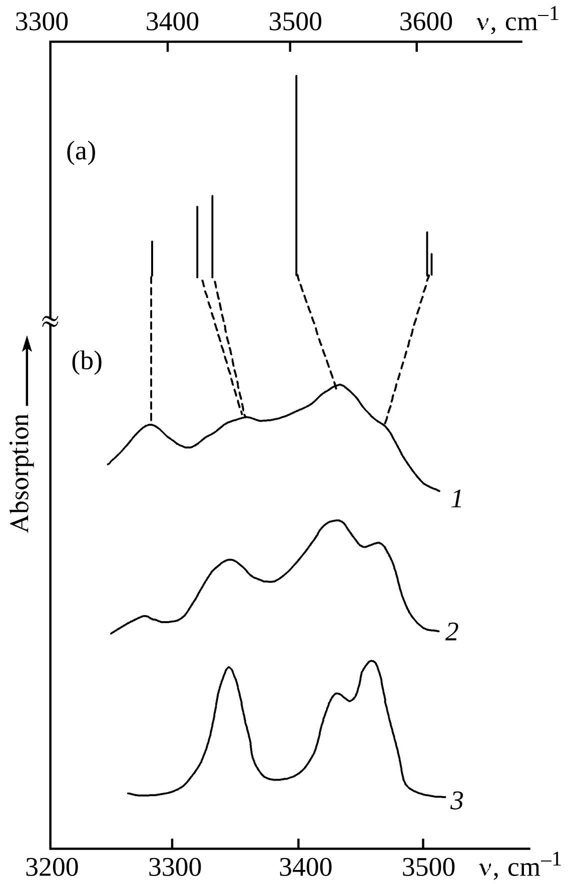


Fig. 4. IR spectra of amide **I**: (a) theoretical (B3LYP/6-31G*) spectrum of cyclic trimer **Id**, upper frequency scale; (b) spectra of **I** in $CHCl_3$, $[M]_0$ 0.02 M, *T*, K: (*1*) 255, (*2*) 263, and (*3*) 298.

As the temperature of a solution of **I** in $CHCl_3$ is decreased, the absorption peaks of the associate grow in intensity (Fig. 4). At 255 K, the frequencies and relative intensities of these bands reasonably agree with the calculation results for cyclic trimer **Id**. As expected, the frequencies of the free NH bonds in Id are shifted toward lower values relative to the monomer by only ~25 cm^{-1}. The calculated differences between the vibration frequencies of the associated NH groups in **Id** are 75 and 115 cm^{-1}, and the corresponding experimental values are 70 and 135 cm^{-1} (Fig. 4; see table).

The most complex spectral pattern was observed in solvents of intermediate polarity, *n*-C_4H_9Cl and *n*-C_4H_9Br ($0.3 < \pi^* < 0.5$). The ν(NH) values measured in these solvents do not obey regression equations (2) and (3). Both bands of amide **I** are strongly broadened, which suggests coexistence of several types of associates. We failed to elucidate their structure but revealed some analogies with solutions in CCl_4 and $CHCl_3$. These data suggest the occurrence of a complex equilibrium in intermediate-polarity solvents, involving at least three species: monomer, cyclic trimer **Id**, and cyclic tetramer **If**.

Mutual monomer–cyclic tetramer transformations were also revealed in solutions of amide **II** in low-polarity inert solvents. The intensity ratio of the corresponding IR bands of **II** shows that the relative content of its self-associates in CCl_4 is considerably lower compared to **I**. In highly polar solvents, the monomer of **II** is virtually the only species.

EXPERIMENTAL

The IR spectra of solutions were recorded on a Specord IR-75 spectrophotometer. The dielectric permittivities of solutions were measured on an Sh2-5 device (OKBA Joint-Stock Company, Angarsk, Russia) at 1 MHz and 25°C. The dipole moments were calculated by the Higasi formula [11]. Amides **I**–**III** were purified by double sublimation and recrystallization from benzene.

The quantum-chemical calculations were performed with the GAUSSIAN-98 program package [12].

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