Molecular Structure of Complexes with Bifurcated Hydrogen Bond: III.* Solvate H-Complexes Formed by Trifluoromethanesulfonamide and Its Cyclic Dimer

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Abstract—According to the data of IR spectroscopy, dielcometry, and B3LYP/6-31G* quantum-chemical calculations, trifluoromethanesulfonamide homoassociates in weakly basic protophilic media are converted into 2:1 solvate H-complexes. Cyclic trifluoromethanesulfonamide dimer decomposes in heteroassociate with dioxane with a composition of 1:3. Cyclic trifluoromethanesulfonamide dimer with dioxane forms a 1:4 H-complex with bifurcated (three-center) hydrogen bond involving the bridging hydrogen atom of the NH group (NH···O).

Perfluoroalkanesulfonamides like $CF_3SO_2NH_2$, $C_2F_5SO_2NH_2$, and $CF_3SO_2NHCH_3$ are NH acids with $pK_a(H_2O)$ values ranging from 6 to 8 [2, 3], which are capable of undergoing self-association. Their supramolecular structure directly depends on the solvent properties. These compounds in inert medium exist as equilibrium mixtures of monomeric species and homoassociates whose structure is determined by the solvent polarity [4–6]. Such homoassociates include chain and cyclic dimers, as well as cyclic trimers and tetramers. We previously performed a theoretical study of the effect of protophilic solvents on the structure of cyclic homoassociates formed by perfluoroalkanesulfonamides using solvate H-complexes of *N*-methyltrifluoromethanesulfonamide cyclic dimer as an example [1]. The structure of H-complexes and the mode of intermolecular hydrogen bonding (formation of two- or three-center hydrogen bonds) depend on the solvent properties and composition of the complex. In 1:1 heteroassociates formed by *N*-methyltrifluoromethanesulfonamide cyclic dimer and various solvent molecules, one of the endocyclic hydrogen bonds sharply weakens, and, at a certain strength of the hydrogen

bond with the solvent, the cyclic dimer decomposes to give solvate complex of chain dimer. This process involves formation of bifurcated (three-centered) hydrogen bond (BHB) with participation of the bridging hydrogen atom in the dimer. Cyclic self-associates derived from trifluoromethanesulfonamide $CF_3SO_2NH_2$ (**I**), in particular cyclic dimer **II**, are capable of interacting with protophilic solvents (Solv) to give three types of heteroassociates, complexes with two- or three-centered hydrogen bond and those containing both these (Scheme 1).

Scheme 1.
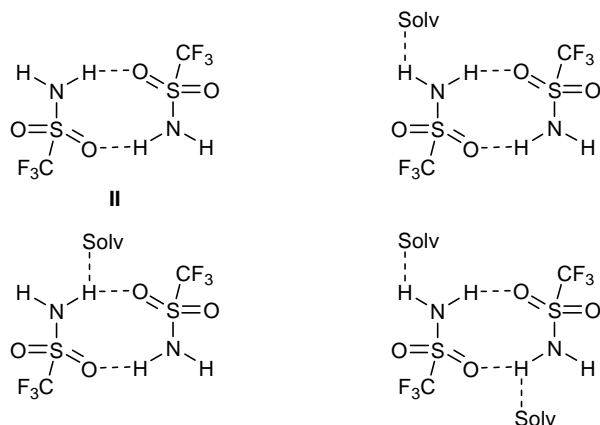
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* For communication II, see [1].

In the present work we examined the structure of such complexes and their relative stability by experimental and theoretical methods, namely by IR spectroscopy, dielcometry, and quantum chemical calculations in terms of the density functional theory (B3LYP/6-31G*). As shown previously, this calculation procedure quite satisfactorily reproduces the energy of formation of cyclic homoassociates of trifluoroacetic acid and *N*-methylacetamide [7] and geometric parameters of the trifluoromethanesulfonic acid molecule, as well as of some other compounds with intra- and intermolecular hydrogen bonds [8, 9].

According to our data, trifluoromethanesulfonamide (**I**) gives rise to self-associates with different structures. In weakly polar inert solvents like carbon tetrachloride and tetrachloroethylene, cyclic tetramers are formed; the amino group therein is involved in two NH···O=S hydrogen bonds. Trifluoromethanesulfonamide self-associates in CHCl₃ (which is a medium-polarity solvent) are cyclic trimers with one free N–H bond, and highly polar pentachloroethane and dichloroethane stabilize chain dimers [6] due to their greater polarity as compared to cyclic homoassociates. The dipole moment of amide **I**, measured from a dilute solution in CH_2Cl_2, i.e., under the conditions ensuring its existence in the monomeric form (according to the IR data), is equal to 3.60 D [6]; this value approaches that calculated for monomeric species of **I** (see below). The dipole moment measured from a solution of **I** in benzene was 3.76 D. This result was surprising. Taking into account only the polarity and polarizability of benzene, cyclic homoassociates with a dipole moment μ of smaller than 0.3 D [6] might be expected to exist in benzene solution. However, the presence of monomer-

ic species of amide **I** in benzene solution also followed from the data of IR spectroscopy.

In the IR spectra of solutions of amide **I** in benzene, stretching vibrations of the N–H bonds appeared as a doublet at 3414/3306 cm⁻¹ (v_{as}/v_s). The corresponding bands in the spectra recorded from solutions in inert solvents are located at higher frequences: 3475/3366 (CCl₄) and 3449/3334 cm⁻¹ (CH₂Cl₂) (Table 1); these bands belong to monomeric species solvated in a nonspecific mode [6]. The low-frequency shift observed in protophilic medium is induced by specific interaction with the solvent; the ability of the latter to form hydrogen bonds is quantitatively characterized by the Kamlet–Taft solvatochromic parameter β [10] (Table 1). The distances between the components of the doublet are almost similar for inert and protophilic solvents (Δv = 110–120 cm⁻¹). Comparison of these experimental data with the results of quantum-chemical calculations prompted us to determine the structure of solvate complexes formed by amide **I** in protophilic media.

H-Complexes of trifluoromethanesulfonamide (I) with 1,4-dioxane. According to the calculations, amide **I** can exist as two invertomers **Ia** and **Ib**.
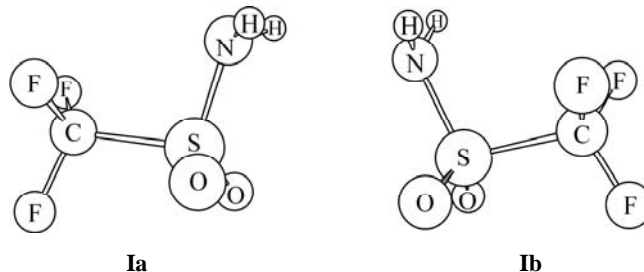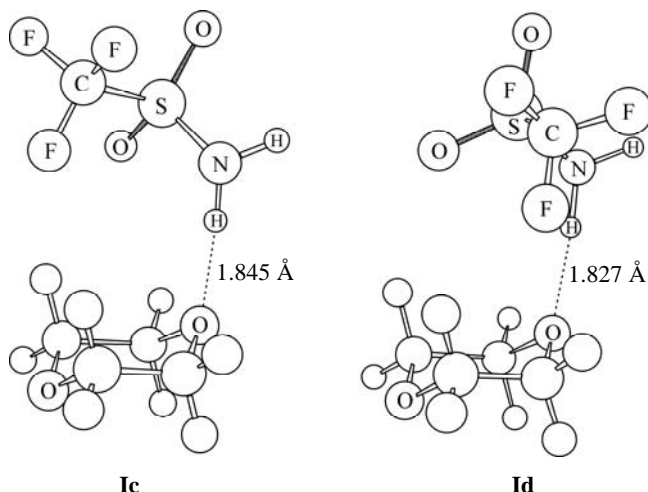

Ia   **Ib**

Invertomer **Ia** is energetically more favorable than **Ib** by 0.80 kcal/mol. Previous B3LYP/6-31G** calculations gave an analogous value (0.75 kcal/mol) [8]. The nonvalence distance $l_{H···O}$ in the complex of **Ia** with dioxane (**Ic**) is 1.845 Å, the corresponding distance in complex **Id** with invertomer **Ib** is 1.827 Å, and the N–H···O angles in **Ic** and **Id** are equal to 174°, i.e., the hydrogen bond is linear.

The hydrogen bond H···O lies in the dioxane symmetry plane, and it forms an angle τ of 144° (**Ic**) or 147° (**Id**) with the COC plane in the dioxane molecule. The energy of H-complex **Ic** is slightly higher despite the distance NH···O therein is longer (Table 2). Therefore, the equilibrium between complexes **Ic** and **Id** is displaced toward the former to a greater extent (by ~1.1 kcal/mol), as compared to the shift of the

Table 1. Vibration frequencies of the N–H bonds in the IR spectra of solutions of trifluoromethanesulfonamide (**I**)

Solvent	β	π*[a]	v(NH), cm⁻¹		Δv(NH), cm⁻¹
Carbon tetrachloride	0	0.28	3475	3360	115
Methylene chloride	0	0.82	3449	3334	115
Chlorobenzene	0.07	0.71	3441	3324	117
Benzene	0.10	0.59	3414	3306	108
Toluene	0.11	0.54	3404	3293	111
m-Xylene	0.12	0.47	3392	3283	109
p-Xylene	0.12	0.43	3392	3286	106
Nitromethane	0.25	0.85	3398	3280	118
Nitrobenzene	0.30	1.01	3392	3268	124

[a] Solvent polarity/polarizability parameter [8].

Ic   **Id**

equilibrium between **Ia** and **Ib** toward **Ia**. The differences in the energy of formation and structure of complexes **Ic** and **Id** do not affect vibration frequencies of the NH_2 group (Table 2), and the complexes could not be distinguished by IR spectra. On the other hand, these complexes have different dipole moments μ. The calculated dipole moments of isolated invertomers **Ia** and **Ib** differ considerably and are 3.36 and 4.23 D, respectively. Upon formation of 1:1 H-complexes with dioxane, the dipole moments increase by ~0.6 (**Ic**) and ~0.3 D (**Id**) (Table 2).

Ie
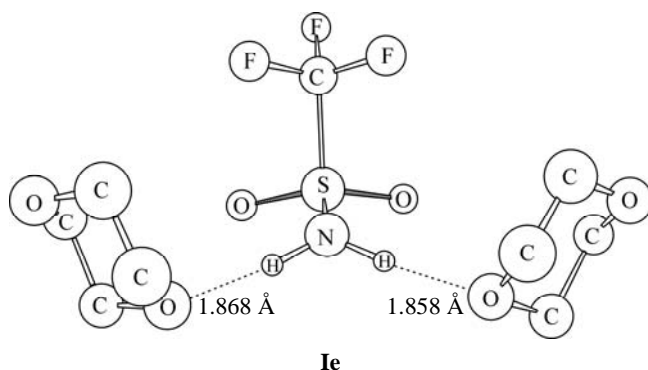
The formation of the second two-center hydrogen bond in 1:2 complexes of **I** with dioxane changes the geometric parameters of the H-bonded fragment in sulfonamide **I**. The distances $l_{H\cdots O}$ extend to 1.868 and 1.858 Å in complex **Ie** derived from invertomer **Ia** and to 1.857 and 1.853 Å in complex **If** derived from invertomer **Ib**. The N–H$\cdots$O angles in complexes **Ie** and **If** are 172 and 176°, respectively, i.e., the hydrogen bonds therein are almost linear, as in 1:1 complexes **Ic** and **Id**. The hydrogen bond lies in the symmetry plane of the dioxane molecule, and the angles τ are 143 and 145° in complexes **Ie** and **If**, respectively.

The energy parameters of hydrogen bonds in **Ie** and **If** change in parallel with the nonvalence $l_{H\cdots O}$ distances. The values of $-\Delta\Delta E$ per hydrogen bond are 9.61 (**Ie**) and 9.77 kcal/mol (**If**) (Table 2), i.e., each hydrogen bond is slightly weaker than in the 1:1 complex. The formation of 1:2 complexes almost does not affect the state of invertomer equilibrium relative to the equilibrium between the free invertomers (0.5 against 0.8 kcal/mol). The difference between the dipole moments of the 1:2 complexes is smaller ($\Delta\mu \approx 0.4$ D), and their N–H vibration frequencies are almost similar (tabl. 2). However, they sharply differ from the 1:1 complexes by the frequency gap between $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ (~110 against ~320 cm^{-1}).

Thus our theoretical and experimental data on stretching vibrations of the NH_2 group in amide **I** in protophilic media indicate formation of 1:2 solvate H-complexes with weak hydrogen bond acceptors.

Structure and energy of formation of cyclic trifluoromethanesulfonamide dimer (II). Transformations of cyclic homoassociates of amide **I** in protophilic medium were studied using cyclic dimer **II** as an example to enable comparison with the data obtained by us previously for cyclic *N*-methyltrifluoromethanesulfonamide dimer (**III**) [1]. Depending on mutual orientation of the CF_3 groups, dimer **II** may have C_i or C_{2v} symmetry. The calculated energy of the centrosymmetric structure is slightly greater [4]; therefore, further analysis was performed for structure **II** with a C_{2v} symmetry. On the whole, the parameters found for dimer **II** (Table 2) are similar to those typical of dimer **III**. Insofar as amide **I** is a stronger NH acid than its *N*-methyl derivative (pK_a 7.56 and 6.39, respectively [3]), the nonvalence distances $l_{H\cdots O}$ in **II** are slightly shorter (1.911 and 1.914 Å against 1.916 and 1.919 Å in **III**). The hydrogen bonds in dimer **II**, as in **III**, are close to linear: the NH$\cdots$O angles are 173 and 174°. Like the 1:1 complex of amide **I** with dioxane (**Ic**), dimer **II** is characterized by a large difference between the $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ frequencies [$\Delta\nu(NH) \approx 190$ cm^{-1}, Table 2], as compared to free invertomer **Ia** [$\Delta\nu(NH) \approx 120$ cm^{-1}, Table 2] which can be regarded as monomeric subunit of **II**. The calculated energy of formation of dimer **II** (6.21 kcal/mol) almost coincides with that found for analogous *N*-methyltrifluoromethanesulfonamide dimer **III** (6.18 kcal/mol [5]).

Complexes of cyclic trifluoromethanesulfonamide dimer with 1,4-dioxane. According to the calculations, the most energetically favorable complex of cyclic dimer **II** with dioxane (1:1 complex **IIa**) is

Table 2. Calculated (B3LYP/6-31G*) total energies (E), dipole moments (μ), vibration frequencies of the N–H bonds, energies of formation (ΔE_H) of H-complexes of trifluoromethanesulfonamide (**I**) and its cyclic dimer **II** with dioxane, and lengths of nonvalence H$\cdots$O bonds

| Structure	$-E$, a.u.	$-\Delta E_H$, kcal/mol	μ, D	$l_{H\cdots O}$, Å		$\nu(NH)$,[a] cm^{-1}
				endocyclic	H-bond with dioxane	
Ia	942.134374		3.36			3633 (61), 3516 (53)
Ib	942.133092		4.23			3648 (52), 3523 (43)
Ic	1249.808765	10.10	3.95		1.845	3602 (111), 3285 (772)
Id	1249.808262	9.79	4.54		1.827	3609 (100), 3288 (801)
Ie	1557.481588	19.22	4.17		1.868, 1.858	3401 (1239), 3289 (399)
If	1557.482093	19.54	4.56		1.852, 1.857	3399 (1282), 3286 (361)
II	1884.288537	12.42	0.36	1.914, 1.911		3609 (163), 3426 (1097), 3608 (156), 3405 (1.4)
IIa	2191.959640	8.04	1.65	1.888, 1.937[b]	1.849	3605 (144), 3387 (561), 3487 (902), 3318 (728)
IIb	2499.636614	19.76	2.22	1.956, 1.937	1.904, 1.840	3462 (722), 3446 (658)
IIc	2807.303726	25.30	1.49	1.955, 2.897[b]	1.898, 1.842, 1.888	
IId	3114.970197	30.43	1.58	2.815,[b] 2.086[b]	1.884, 2.614, 1.884, 1.858	

[a] In parentheses are given the relative intensities.
[b] The length of the endocyclic hydrogen bond contiguous to the hydrogen bond with dioxane.

formed with participation of the free N–H bond which is involved in a strong two-center hydrogen bond NH$\cdots$O, the $l_{H\cdots O}$ distance being 1.849 Å. The angles characterizing orientation of the NH$\cdots$O bond differ insignificantly from the corresponding angles in the 1:1 complex of monomeric amide **I** with dioxane. The hydrogen bond in complex **IIa** deviates from the symmetry plane of the dioxane molecule by an angle of
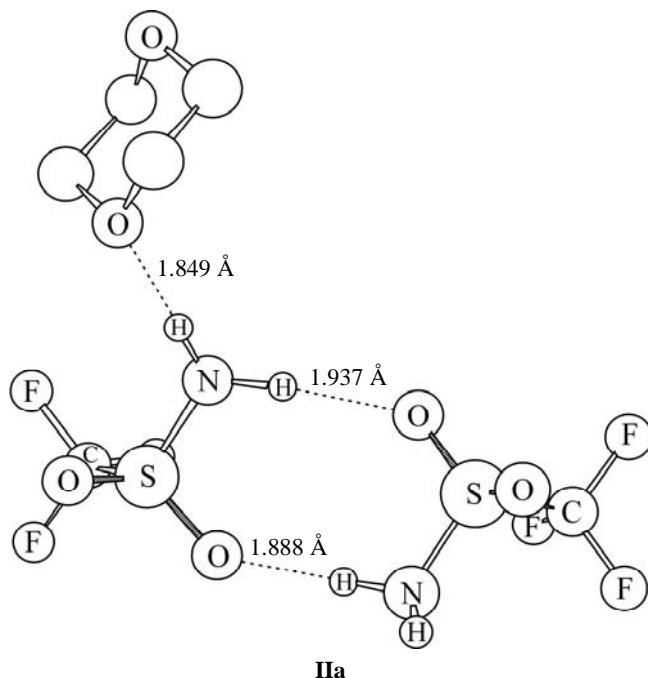
17°, the angle τ is 150°, and the bond angle N–H$\cdots$O decreases to 168°. The endocyclic hydrogen bond contiguous to that formed with dioxane is weakened to approximately the same extent as in going from 1:1 H-complexes of amide **I** to 1:2 complexes (Table 2, cf. complexes **Ic** and **Ie**). Thus, there exists an analogy in the structure of the coordination entity of 1:2 complexes of monomeric amide **I** and complexes formed by cyclic dimer **II** with one intermolecular hydrogen bond. By contrast, the second hydrogen bond, which closes the H-ring in dimer **IIa**, becomes stronger: the $l_{H\cdots O}$ distance shortens by about 0.025 Å. We can

IIa

IIb

IIc
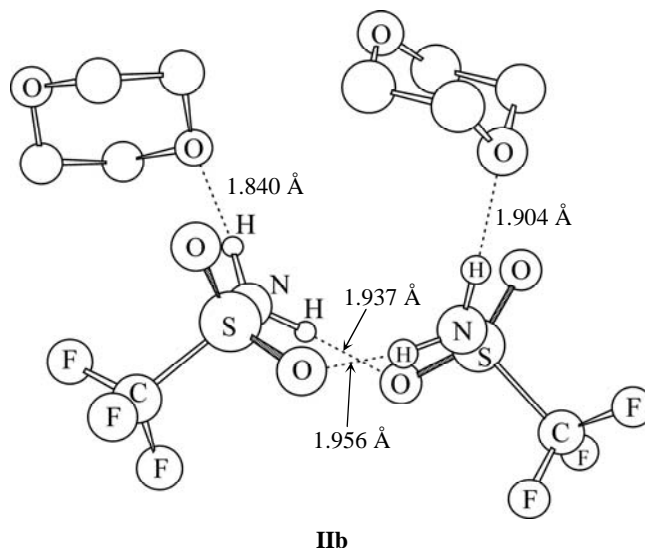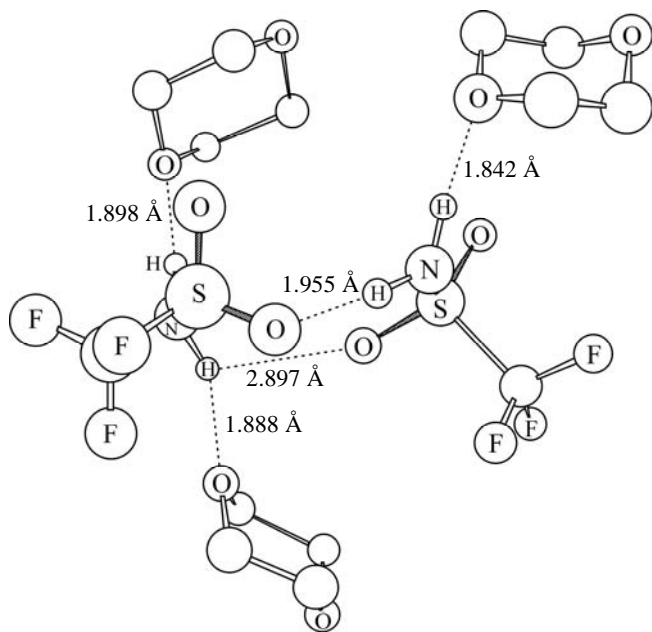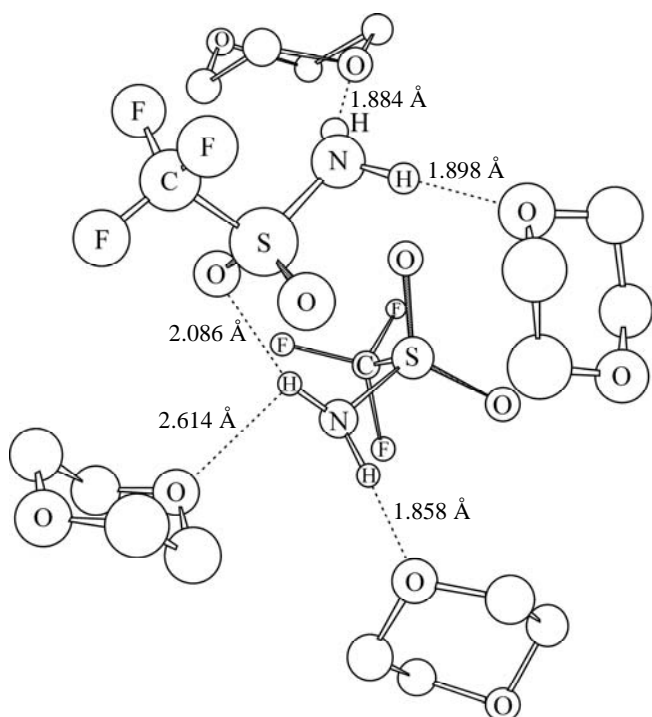
IId

conclude that the formation of 1:1 complex **IIa** from cyclic dimer **II** and dioxane is accompanied by weakening of one endocyclic hydrogen bond and strengthening (approximately to the same extent) of the other. Taking into account almost similar lengths of the nonvalence hydrogen bonds in complexes **Ic** and **IIa** (Table 2), the ability of the monomeric subunit of dimer **IIa** to act as hydrogen bond donor is similar to

that of free invertomer **Ia**. The energy of stabilization of complex **IIa** is 8 kcal/mol; this value is lower by 2 kcal/mol than the energy of stabilization of complex **Ic** (Table 2). We failed to identify a 1:1 complex with bifurcated hydrogen bond, where dioxane molecule would be coordinated only to the bridging hydrogen atom in dimer **II**: in the course of geometry optimization this structure was transformed into structure **IIa** with two-center hydrogen bond.

The above noted tendency for the endocyclic hydrogen bond to weaken upon formation of intermolecular hydrogen bond with the solvent is also typical of the 1:2 complex of dimer **II** with dioxane (structure **IIb**). The two-center hydrogen bonds with dioxane molecules in **IIb** become shorter ($l_{H\cdots O}$ 1.840 and 1.904 Å), while the endocyclic hydrogen bonds extend to 1.937 and 1.956 Å. Correspondingly, the energy of formation of complex **IIb** is higher: the energy per hydrogen bond (9.88 kcal/mol) is almost equal to the energy of formation of monomeric H-complexes. In other words, the endocyclic hydrogen bonds in 1:2 complex **IIb** are so weak that they only slightly affect the hydrogen bonds with the solvent.

A qualitatively different pattern is observed in the complex formed by dimer **II** with three dioxane molecules. The third molecule of dioxane is coordinated to the bridging hydrogen atom of cyclic dimer **IIb**, and the H-bonded ring is opened. As a result, complex **IIc** with three two-center hydrogen bonds is obtained, the $l_{H\cdots O}$ distances therein being equal to 1.842, 1.888, and 1.898 Å.

The new hydrogen bond ($l_{H\cdots O} = 1.842$ Å) is linear, while the adjacent ring NH$\cdots$O bond is broken (the distance $l_{H\cdots O} = 2.897$ Å exceeds the sum of the van der Waals radii of hydrogen and oxygen atoms). The second endocyclic hydrogen bond NH$\cdots$O in the dimer also extends but only by 0.016 Å. As noted above, endocyclic hydrogen bonds in 1:2 complex **IIb** become weaker, which favors opening of the H-bonded ring upon coordination of the third dioxane molecule. Complex with bifurcated hydrogen bond, which could mediate opening of the cyclic dimer, turned out to be unstable: during optimization process it was transformed into complex **IIc** with three two-center hydrogen bonds.

In the preceding communication [1] we showed by theoretical methods that the formation of 1:1 H-complexes by cyclic *N*-methyltrifluoromethanesulfonamide dimer **III** and such strong bases as formaldehyde and DMSO is also accompanied by decomposition of the

cyclic structure to give open-chain dimer linked to the base by two-center hydrogen bond. However, three-center H-complexes with less basic phosgene (1:1) and formaldehyde (1:2) were stable. The cyclic dimer structure was retained, and one or two bifurcated hydrogen bonds were formed, respectively.

The calculations showed that only addition of the forth dioxane molecule afforded stable complex **IId** of cyclic dimer **II** with bifurcated hydrogen bond. The distance between the H-bonded dioxane oxygen atom and the ring hydrogen atom is 2.614 Å. The external bond angle N–H⋯O (104°) is typical of BHB [11]. The endocyclic NH⋯O bond contiguous to the intermolecular hydrogen bond with dioxane is longer by 0.131 Å than the corresponding bond in the 1:3 complex. This is also characteristic of bifurcated hydrogen bond in compounds with intramolecular hydrogen bond [11, 12]. The second endocyclic hydrogen bond shortens by 0.082 Å. The energy of stabilization of **IId** is 5.13 kcal/mol (cf. 5.54 kcal/mol for **IIc**).

Thus the energy of stabilization was the highest (11.72 kcal/mol) for the 1:2 complex with two-center hydrogen bonds. The endocyclic hydrogen bonds in the cyclic dimer become weaker as a result of complex formation, and coordination of the third dioxane molecule favors opening of the H-bonded ring.

EXPERIMENTAL

The IR spectra were recorded on a Specord 75IR spectrometer. The dielectric permittivities of solutions were measured on an Sh2-5 instrument (Angarsk, *OKBA* joint-stock company) at a frequency of 1 MHz at 25°C. The dipole moments were calculated by the Higasi formula [13]. Trifluoromethanesulfonamide (**I**) was purified by double sublimation, followed by re-crystallization from benzene and drying under reduced pressure.

Quantum-chemical calculations were performed using GAUSSIAN-98 software package [14].

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