

Molecular Structure of Complexes with Bifurcated Hydrogen Bond: II.* Theoretical Study of Solvate H-Complexes Formed by the Cyclic Dimer of *N*-Methyltrifluoromethanesulfonamide

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Abstract—According to the DFT calculations (B3LYP/6-31G*), the structure of solvate complexes formed by *N*-methyltrifluoromethanesulfonamide with phosgene, formaldehyde, and DMSO and the mode of hydrogen bonding therein (two-center or bifurcate three-center) depend on the proton affinity of the onium base and composition of the complex. The 1:1 cyclic dimer–phosgene complex and 1:2 cyclic dimer–formaldehyde complex are stabilized by one or two bifurcated hydrogen bonds, respectively.

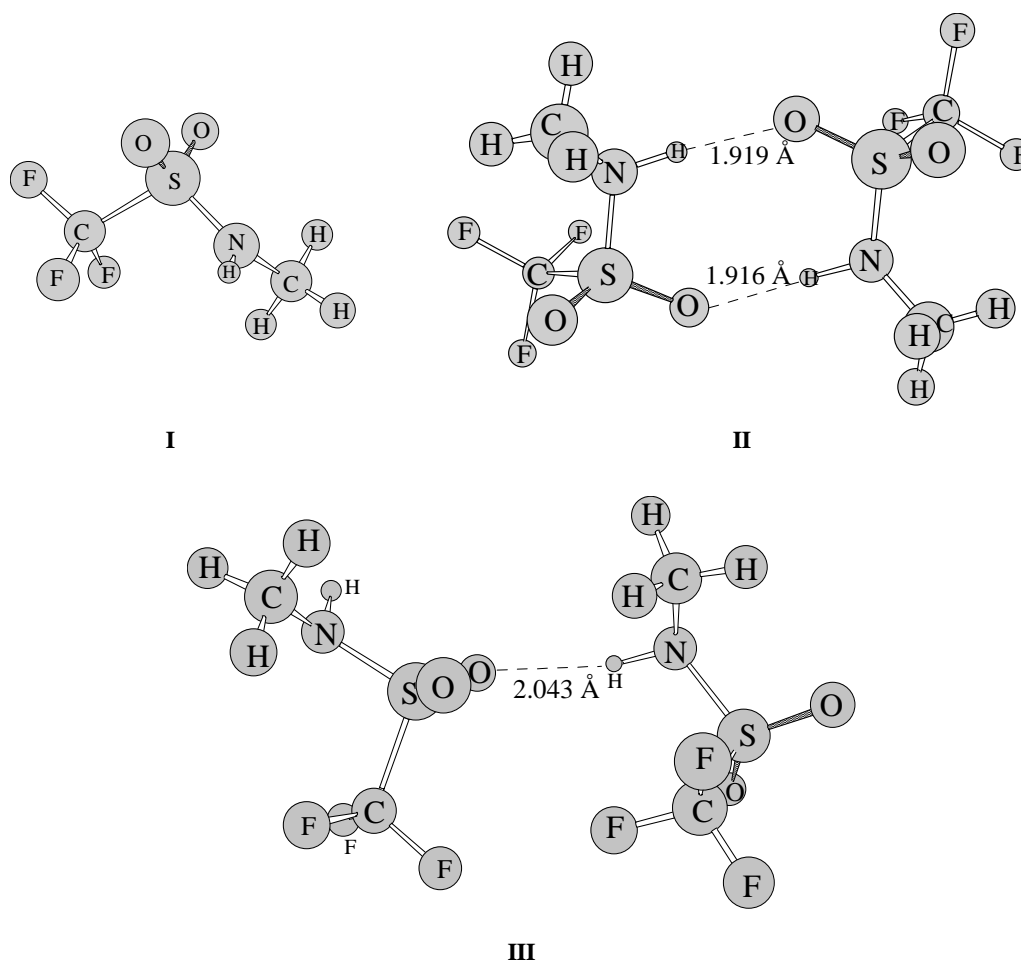
Cyclic dimers constitute an element of the supermolecular structure of carboxylic acids and trifluoromethanesulfonamides in the gas phase and in inert media [2–7]. With benzoic acid as an example it was shown that decomposition of such dimers into monomers is promoted by strong hydrogen bond acceptors, e.g., by tertiary amines [8]. This process includes two steps, the first of which leads to formation of a 1:1 intermolecular complex between the amine and chain dimer; provided that the amine is present in excess, it then gives rise to 1:1 complex with the monomer [8]. Experimental and theoretical studies of compounds with H-chelate rings showed that their interaction with proton acceptors involves formation of a bifurcate (three-center) hydrogen bond (BHB) and that strengthening of the intermolecular component of BHB could lead to rupture of the H-chelate ring and formation of a 1:1 two-center solvate complex [1, 9]. The state of equilibrium between the two- and three-center solvate complexes depends on both the strength of intramolecular hydrogen bond and protophilicity of the solvent. Analysis of hydrogen bonding (including formation of bifurcate hydrogen bonds) with solvent molecules is necessary to predict the structure of OH and NH acids in various media (whether they exist as dimers,

trimers, polyassociates, solvate complexes, etc.) and the mechanism of interaction between the solute and the solvent. The goal of the present work was to elucidate the possibility for formation of solvate complexes between the cyclic dimer of *N*-methyltrifluoromethanesulfonamide (**I**), on the one hand, and phosgene, formaldehyde, and dimethyl sulfoxide, on the other, and examine their geometric structure, type of hydrogen bond stabilizing the complexes, and conditions ensuring transformation of the cyclic dimer into chain dimer or monomeric species.

Quantum-chemical calculations of the isolated molecule of *N*-methyltrifluoromethanesulfonamide (**I**), its cyclic dimer **II**, chain dimer **III**, and solvate H-complexes were performed in terms of the density functional theory (DFT B3LYP) using the 6-31G* basis set with full geometry optimization with the aid of GAUSSIAN-98 software package [10]. The suitability of the above method for our purposes was confirmed by the calculation of trifluoromethanesulfonic acid with the 6-31G** basis set, which was characterized by a good agreement between the calculated geometric parameters and those determined by the gas-phase electron diffraction method [11]. Schemes 1–4 show the structures of the most energetically favorable monomeric and dimeric species and the corresponding H-complexes. The calculated energies of formation of the dimers and 1:1 solvates

* For communication I, see [1].

Scheme 1.



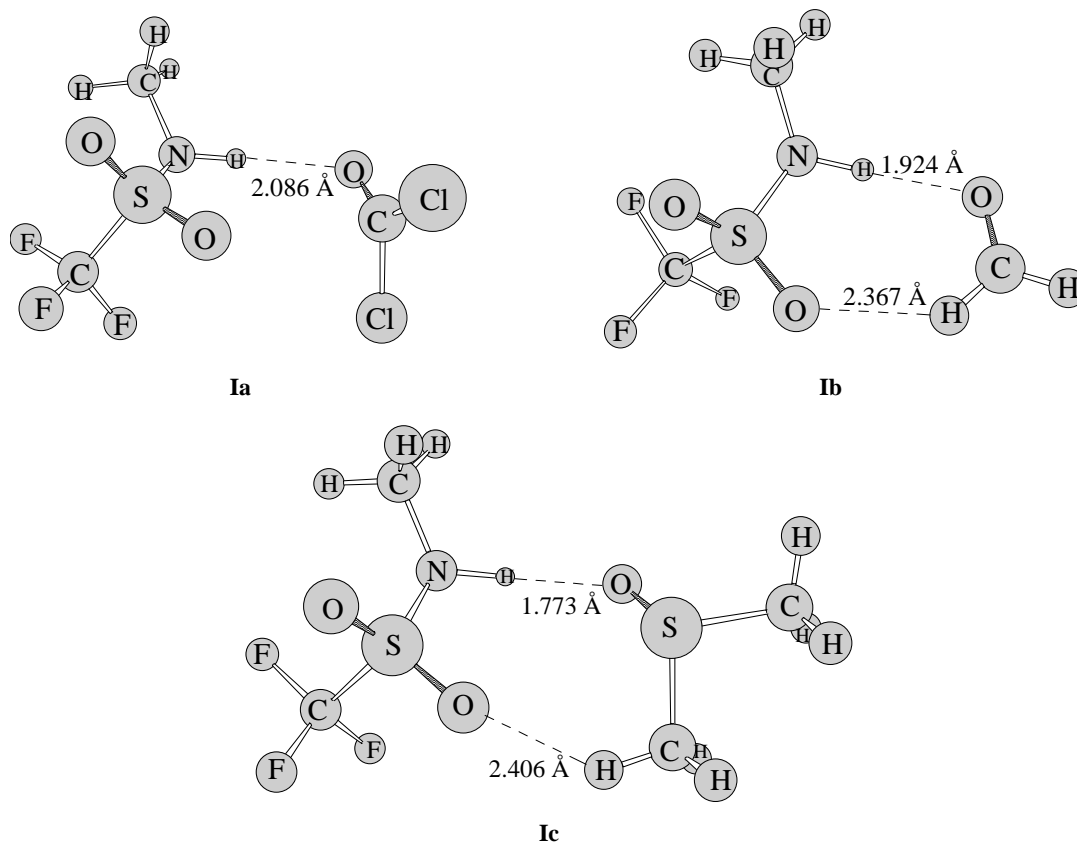
($-\Delta E_H$), N–H...O bond angles, NH...O hydrogen bond lengths ($l_{N...O}$), and nonvalence distances ($l_{H...O}$) are given in table. As in the previous communication [1], $l_{N...O}$ is the length of the hydrogen bond, and $l_{H...O}$ is the nonvalence distance in that bond. The calculations of amide **I** and its cyclic dimer **II** by the B3LYP method with the split basis set with account taken of both polarizational and diffuse functions on heavy atoms and hydrogen atoms (6-311++G**) give fairly similar results: the distances characterizing the H-bond are slightly shorter, but the N–H...O bond angle and the energy of formation of dimer **II** remain almost unchanged (see table).

According to the calculations, the hydrogen bonds in dimer **II** are almost linear: the N–H...O bond angles are 175 and 177°. The eight-membered ring thus formed has a nearly planar structure. In going to chain dimer **III**, the N–H...O angle decreases to 160°, approaching the lower limit estimated for two-center hydrogen bonds [12].

The nonvalence H...O distance (1.916 and 1.919 Å) in cyclic dimer **II** is considerably shorter than the sum of van der Waals radii of the hydrogen and oxygen atoms, and it is typical of intermolecular (1.90 Å) and intramolecular (1.89 Å) hydrogen bonds like N–H...O=C [12]. The calculated length of the NH...O hydrogen bond in **II** is 2.939 and 2.941 Å. These values coincide with the length of intermolecular hydrogen bond, which was found experimentally for crystalline carboxylic acid amides (the average value is 2.93 Å [7]), indicating their comparable strengths. It should be noted that the calculated H-bond lengths in cyclic trifluoromethanesulfonamide ($CF_3SO_2NH_2$) dimer are 2.932 and 2.934 Å.

The calculated energy of formation of cyclic dimer **II** per hydrogen bond (6.18 kcal/mol) differs only slightly from the energy of formation of chain dimer **III** (6.26 kcal/mol), but it exceeds values determined experimentally in solution for *N*-methylacetamide self-associates (3.6 kcal/mol in benzene) and cyclic dimer

Scheme 2.



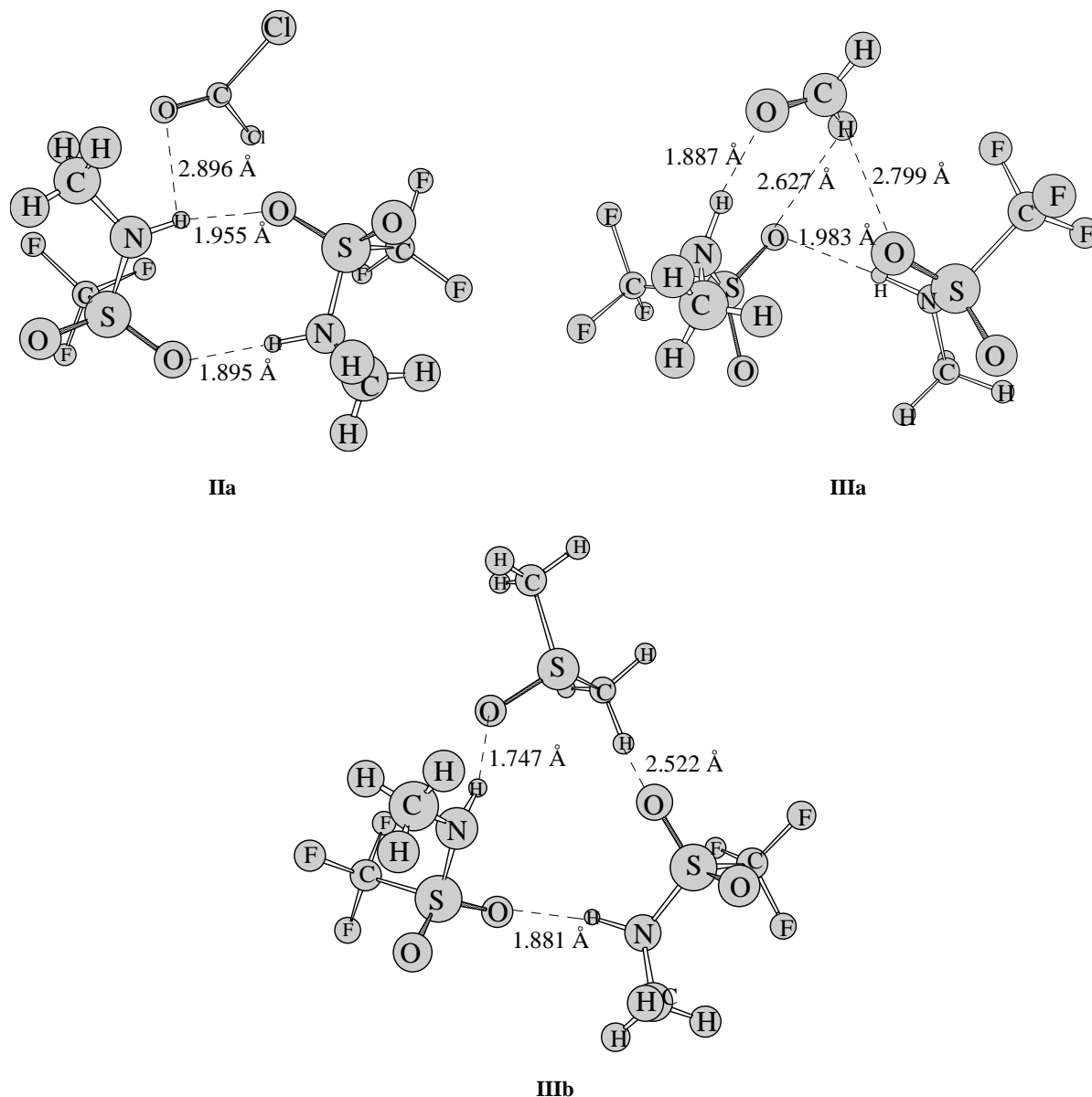
of trifluoroacetic acid (4.42 kcal/mol in CCl_4) [7]. A question arises so as to how much the theoretical energy of formation of self-associates is overestimated with respect to the experimental data and whether the hydrogen bonds in cyclic dimers of carboxylic acids and their amides and trifluoromethanesulfonamide are in fact equally strong. Therefore, we performed additional calculations of centrosymmetrical dimers of trifluoroacetic acid and *N*-methylacetamide. The energy of formation of the cyclic dimer (9.26 kcal/mol per hydrogen bond) was found to exceed that of amide **II**. The energy of hydrogen bond in trifluoroacetic acid self-associates in the gas phase (determined experimentally from the vapor density and by IR spectroscopy) is lower by approximately 2 kcal/mol than the theoretical value (7.75 and 6.85 kcal/mol, respectively [7]). According to the calculations, the hydrogen bond in *N*-methylacetamide cyclic dimer is also slightly stronger than in dimer **II**; its energy is equal to 8.76 kcal/mol. The above energies of formation of self-associates are consistent with variations in the $\text{XH}\cdots\text{O}$ hydrogen bond lengths. For example, $l_{\text{N}\cdots\text{O}}$ in *N*-methylacetamide dimer is 2.885 Å, and $l_{\text{O}\cdots\text{O}}$ in trifluoroacetic acid dimer is 2.696 Å.

The nonvalence distance $\text{H}\cdots\text{O}$ and the length of the two-center $\text{NH}\cdots\text{O}$ hydrogen bond in 1:1 H-complexes of monomeric amide **I** decrease in the series phosgene (**Ia**) > formaldehyde (**Ib**) > DMSO (**Ic**), in parallel with increase in the energies of formation of the solvates (Scheme 2, see table).

A characteristic feature of hydrogen bond formation and variation of its strength is increase of the positive charge on the hydrogen atom in the $\text{NH}\cdots\text{O}$ moiety; with respect to the isolated molecule, this gain is 0.031, 0.039, and 0.070 e for H-complexes **Ia**, **Ib**, and **Ic**, respectively.

Cyclic dimer **II** with "onium" bases gives rise to H-complexes of two types (Scheme 3). Being the weakest hydrogen bond acceptor, phosgene with cyclic dimer **II** forms three-center H-complex **IIa**. The nonvalence intermolecular $\text{NH}\cdots\text{O}$ (S) distance in this complex (2.896 Å) exceeds the sum of the respective van der Waals radii, indicating preferentially non-specific character of interaction between the components. However, the formation of BHB in complex **IIa**, as well as in compounds with intramolecular hydrogen bond [12], follows from the sharp weakening of the

Scheme 3.



nonvalence H...O bond (1.955 Å), which is contiguous to the intermolecular hydrogen bond NH...O (S), from considerable strengthening of the second hydrogen bond in the cyclic dimer (1.895 Å) (Schemes 1, 3), and from the outer bond angle N–H...O (109°), which is typical of bifurcated hydrogen bond. Interaction of the cyclic dimer with stronger proton acceptors leads to rupture of one of the ring hydrogen bonds and formation of two-center intermolecular H-complexes **IIIa** and **IIIb** with chain dimer **III**. It should be emphasized that these complexes are energetically more favorable than those derived from the monomeric species (see table).

As already noted, the two-center H-bond in complex **IIa** is stronger than in isolated cyclic dimer **II**. It is shorter by ~0.02 Å, whereas the inner NH...O bond angle changes insignificantly (by 2°; see table). Weakening of the second H-bond in dimer **II** (in the solvate complex with phosgene, this bond is an intramolecular component of BHB) corresponds to decrease of the angle between the valence N–H bond and nonvalence H...O bond by 7°, increase of the NH...O hydrogen bond length by ~0.02 Å, and increase of the nonvalence H...O distance by ~0.04 Å. This structural reorganization is analogous to that observed for H-chelate rings upon formation of

Calculated (B3LYP/6-31G*) parameters of H-complexes formed by *N*-methyltrifluoromethanesulfonamide (**I**) and its dimers **II** and **III** with solvents (S)

Comp. no.	$-\Delta E_{\text{H}}$, ^a kcal/mol	$l_{\text{H}\cdots\text{O}}$, Å	$l_{\text{N}\cdots\text{O}}$, Å	$l_{\text{H}\cdots\text{O}(\text{S})}$, Å	$l_{\text{N}\cdots\text{O}(\text{S})}$, Å	$\angle\text{NH}\cdots\text{O}$, deg	$\angle\text{NH}\cdots\text{O}(\text{S})$, deg
I	0						
Ia	4.32			2.086	3.078		164
Ib	9.16			1.924	2.951		177
Ic	13.64			1.773	2.811		178
II	0 (6.18) ^b (6.11) ^c	1.916 (1.900) ^c 1.919 (1.907) ^c	2.939 (2.921) ^c 2.941 (2.925) ^c			175 (174) ^c 177 (176) ^c	
IIa	3.65		2.920 ^d 2.965 ^e	2.896	3.372	177 ^d 168 ^e	109
IIb	11.03	2.013 ^e 2.081 ^e	2.985 ^e 3.019 ^e	2.621 2.436	3.158 3.075	157 151	113 120
III	0 (6.26) ^b	2.043	3.023			160	
IIIa	12.01	1.982	3.000	1.887	2.909	172	171
IIIb	16.68	1.881	2.890	1.746	2.765	167	165

^a Energy of formation of H-complexes.

^b In parentheses is given the energy of formation per hydrogen bond.

^c Data of B3LYP/6-311++G** calculations.

^d Two-center hydrogen bond.

^e Three-center hydrogen bond.

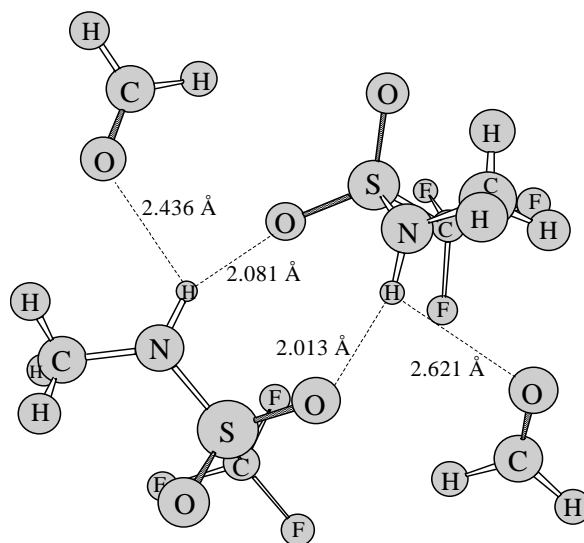
H-complexes with BHB [1, 9, 12]. It is interesting that, unlike two-center hydrogen bond, the positive charge on the bridging hydrogen atom involved in BHB decreases by 0.005 *e* relative to isolated cyclic dimer **II** (see table). This indicates electron density redistribution over the entire H-bond chain. The energy of formation of three-center complex **IIa** is smaller than the energy of formation of 1:1 two-center complex **Ia** between the monomeric species and the same proton acceptor. This means that the proton-donor power of amide **I** decreases upon formation of cyclic dimer. By contrast, the energies of formation of complexes **IIIa** and **IIIb** exceed those found for associates **Ib** and **Ic** by 2.85 and 3.04 kcal/mol, respectively (see above). Increase of the strength of intermolecular H-bonds with the chain dimer is reflected in their lengths. The N...O (S) distances in H-complexes **IIIa** and **IIIb** are shorter by 0.042 and 0.046 Å, respectively, than the corresponding distances in complexes **Ib** and **Ic** with the monomeric species.

The complexes with formaldehyde and DMSO, apart from NH...O hydrogen bonds, are characterized by the existence of fairly short CH...O distances (2.4–2.8 Å) which can also contribute to stabilization of these systems. The parameters of hydrogen bonds in the chain dimer involved in complexes **IIIa** and **IIIb**

strongly depend on the strength of the intermolecular hydrogen bond with the base (see table). The NH...O hydrogen bond in complex **IIIa** (with formaldehyde) is shorter by 0.061 Å than in isolated dimer **III**; the corresponding difference for the strong complex with DMSO (**IIIb**) is as large as 0.162 Å.

Thus, our theoretical data suggest that complex formation of *N*-methyl-trifluoromethanesulfonamide

Scheme 4.



cyclic dimers with the examined proton acceptors leads to strengthening of the H...O bond between the monomeric species. An analogous conclusion was drawn previously on the basis of the experimental heats of formation of H-complexes between benzoic acid and tertiary amines [8]. In the complex with DMSO (**IIIb**), the H...O bond is so strong that addition of a weak base like formaldehyde to the bridging hydrogen atom is impossible. According to the calculations, in this case the oxygen atom of formaldehyde moves away from the NH hydrogen atom in the dimer to a distance much exceeding the sum of the corresponding van der Waals radii.

By contrast, calculation of a system consisting of dimer **II** and two formaldehyde molecules showed that formation of two bifurcated hydrogen bonds with bridging hydrogen atoms stabilizes 1:2 H-complex **IIIb** (Scheme 4). The energy of formation of complex **IIIb** is 11.03 kcal/mol, and the intermolecular H...O bond is longer than in H-complexes **Ib** and **IIIa** by ~0.6 Å, while the intramolecular H...O bonds in the dimer become weaker (their length increases by ~0.13 Å). The bond angles in such complex (113 and 120°) are typical of bifurcated (three-center) hydrogen bond [12].

The results of theoretical calculations led us to conclude that the structure of H-complexes derived from *N*-methyltrifluoromethanesulfonamide cyclic dimer in solution and the mode of hydrogen bonding therein are governed by both proton-acceptor power of the solvent and ratio of the components. Even such a weak base as formaldehyde behaves in an unusual way with respect to the cyclic dimer: one hydrogen bond in the dimer is cleaved upon formation of the 1:1 complex, while the H-ring is stabilized again in the 1:2 complex. The reaction of dimer **II** with two molecules of a strong base (DMSO) leads to rupture of both hydrogen bonds in the dimer and formation of 1:1 solvate complex **Ic**. Therefore, decomposition of *N*-methyltrifluoromethanesulfonamide cyclic dimer by the action of onium bases involves intermediate formation of complexes with bifurcated hydrogen bond.

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